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METHOD OF DETERMINING THE SURFACE TENSION AND SURFACE ENERGY OF TRIBOLOGICAL WEAR PARTICLES

METODA WYZNACZANIA NAPIĘCIA POWIERZCHNIOWEGO I ENERGII POWIERZCHNIOWEJ CZĄSTEK ZUŻYCIA TRIBOLOGICZNEGO

Key words:	surface tension, surface energy, thermodynamic system, friction, wear, energy dissipation, work of dissipation, heat of friction.
Abstract:	Surface tension of friction wear product material is linked with unit mechanical work of newly-formed surfaces of solids. A definition of surface energy also addresses the thermal effect, which is indirectly connected with wear. Physical differences between the development of liquids and solids surfaces are discussed. Both of the quantities defined are described in analytical terms and their value is determined for a selected example of experimental testing. The discussion is based on the first law of thermodynamics using the concept of specific enthalpy of wear products. Boundaries of an area in space where mechanical energy is dissipated and dimensions of a wear particle being formed are taken into account. Mechanical and thermal parts of the energy balance are differentiated.
Słowa kluczowe:	napięcie powierzchniowe, energia powierzchniowa, system termodynamiczny, tarcie, zużycie, rozpraszanie energii, praca dyssypacji, ciepło tarcia.
Streszczenie:	Napięcie powierzchniowe materiału produktów zużycia tarciowego zostało powiązane z jednostkową pracą mechaniczną nowo utworzonej powierzchni ciał stałych. W definicji energii powierzchniowej uwzględniono również efekt cieplny, który jest pośrednio związany ze zużyciem. Podkreślono różnice o charakterze fizycznym między rozwojem powierzchni cieczy i ciał stałych. Obie zdefiniowane wielkości zostały opisane analitycznie, a ich wartości określono dla wybranego przykładu badań eksperymentalnych. Rozważania oparto na pierwszej zasadzie termodynamiki, w której wykorzystano koncepcję entalpii właściwej produktów zużycia. Uwzględniono granice obszaru przestrzennego, w którym energia mechaniczna jest rozpraszana, oraz wymiary powstałej cząstki zużycia. W bilansie energetycznym rozdzielono część mechaniczną i termiczną.

INTRODUCTION

Surface energy and surface tension, to a large extent, determine the tensile strength of elastic solids, the shape of liquid surfaces, substance humidification, the application of adhesives, and a number of capillary and interphase phenomena. These physical quantities are important to tribology, particularly in case of problems with lubrication and tribological wear. Forces of atoms or particles active on a surface are sources of surface phenomena. They are only partly saturated, which determines levels of surface energy and releases surface phenomena. As a rule, three types of forces can obtain between particles or atoms of a solid or liquid and their environment. These are electrostatic, magnetic, and dispersion forces (the latter are results of atom element motion). Their reach is limited. They generate the field of surface attractive forces over a distance of merely several 10^{-10} m. Interpretation and definition of surface energy and surface tension of liquids are not difficult in general. Surface energy and surface tension of liquids are numerically and dimensionally identical. As distinct to liquids, surface tension and surface energy of solids are not the same. When a new liquid surface arises, its particles adopt their final equilibrium positions in a short time as they are highly mobile. After a new solid surface

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is formed, the process of shifting surface atoms to their equilibrium position can only be slow as their mobility is low. Such a surface is not in equilibrium long after a solid surface is formed, and sometimes permanently. There are a number of theoretical and experimental methods of defining surface tension and surface energy of solids. However, data produced by their testing when melted have been the most reliable till now. Surface energy of a solid is assumed to be approximately 20–30% greater than of its corresponding liquid [L. 1]. Some authors [L. 2] state surface energy values for selected metals. For instance, lead – 0.9 Jm^{-2}, aluminum – 1.8 Jm^{-2}, copper – 2 Jm^{-2}, and tool steel – 3 Jm^{-2}. However, test methods of surface tension and surface energy apply to solids 'without a past', that is, newly formed surfaces, e.g., arising from brittle fracture. Treatment of a new surface, for example, by grinding and especially polishing, substantially changes all of its original properties. The running-in process causes even greater changes of initial surface properties.

This paper continues to present fundamental notions and definitions of surface energy and surface tension, especially of liquids. A new method is then proposed of defining surface tension of solids subject to tribological wear. Separation of the mechanical part of friction work and its linking to the surface of tribological wear particles being generated is the core of this approach. An original interpretation of the formation mechanism of a new surface during tribological wear of a solid is presented, distinct from the surface development mechanism in liquids. The discussion is aimed at addressing dependences between surface tension, the intensity of wear, the friction coefficient, certain properties of the friction material, its mechanical loading, and selected geometrical properties of a friction couple. The resultant analytical description is illustrated quantitatively for selected examples of metal friction.

SURFACE ENERGY AND SURFACE TENSION

Definitions of surface tension and surface energy find their most convenient interpretation for a dual phase gas-liquid system. The physical surface of a liquid consists of a particle layer with non-equilibrium intermolecular forces. Intermolecular forces arising from this very thin superficial layer are oriented in the direction of the liquid phase. These forces tend to reduce the liquid's surface and thereby reduce the energy of the system. Tension in the superficial layer of a liquid, that is, the ratio of forces tangential to the liquid surface to a unit of its cross-section length is known as surface tension γ [L. 1]. γ is illustrated in the example of a soap membrane stretched over a wire frame – Fig. 1. One edge of the frame, with a length of b, is mobile. Moving it by dx requires work dA_F to counter the surface tension:

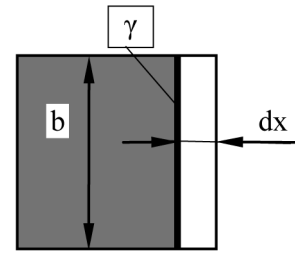$$dA_F = \gamma b dx. \qquad (1)$$

Fig. 1.   Diagram of liquid layer area expansion dF = bdx in effect of surface tension
Rys. 1.   Schemat przyrostu powierzchni dF = bdx warstwy cieczy pod wpływem napięcia powierzchniowego

This work is associated with a membrane surface expanding by dF = bdx. Thus, work dA_F also expresses surface dF times surface energy e_F for a unit of the surface:

$$dA_F = e_F dF. \qquad (2)$$

(1) and (2) imply, for liquids, surface tension is equal to surface energy, provided γ is constant:

$$\gamma = e_F. \qquad (3)$$

The unit of surface tension is Nm^{-1} and of surface energy Jm^{-2}. Surface tension cannot be seen as a stretching force between liquid particles. In the case shown in Fig. 1, a new surface is formed by pulling internal particles on top. A numerical growth of superficial particle is the source of tension that counters this pulling. Contrary to tensile strength, surface tension of a liquid membrane does not change when the membrane is elongated. As surface tension depends on intermolecular forces, each liquid has its own surface tension. A.H. Cottrell [L. 3] claims there is an approximate dependence between surface energy e_F and heat of vaporisation for a unit of volume e_D, namely:

$$e_F \approx 3^{-1} r e_D, \qquad (4)$$

where r – radius of a particle.

This interpretation of surface tension and surface energy and their interdependence only have mechanical reasons. From the thermodynamic point of view, work forming a surface causes a homogenous growth of the "thermodynamic surface potential" and its corresponding thermal effects. In line with the definition of free energy, surface tension γ may be interpreted as free energy for a unit of surface [L. 3]. To arrive at an analytical dependence between γ and e_F, A. H. Cottrell [L. 3] treated the liquid surface phase as a heat engine and subjected it to the thermodynamic cycle. His analysis produced the following dependence:

$$\gamma = e_F + \Theta \frac{d\gamma}{d\Theta}, \tag{5}$$

where Θ – liquid temperature. Only if $\Theta = 0K$, γ and e_F are equal. At greater temperatures, $d\gamma/d\Theta$ is negative and $\gamma < e_F$. Since $-d\gamma/d\Theta$ is entropy S_F of a surface for a unit of area, (5) can become:

$$\gamma = e_F - \Theta S_F = e_F - Q_F, \tag{6}$$

where Q_F – latent heat for a unit of surface. Equation (6) describes an isothermal, reversible thermodynamic process. The system (associated with a new surface of atoms or particles) absorbs heat Q_F from its environment and assures its isothermal nature. The system's temperature would decline otherwise. The model of generating a new surface of the liquid membrane as illustrated in **Fig. 1** has allowed for expressing the dependences (1–6) and a physical interpretation of surface tension as a unit free energy of a surface. As distinct from the mechanism described above, the process of forming a new solid surface is more complicated. In particular, the thermodynamic cycle mentioned above is impossible where an object is a solid.

In tribological wear, particles are separated from a solid surface as fine material fragments of indefinite shape and varied dimensions. The size of a newly-formed surface of wear products depends not only on physical properties of a solid in friction but also on a wear mechanism, parameters of a friction process, interactions of the environment, the tribological system, and the structure of such a system. The following discussion of a method of evaluating surface tension of solids in the process of tribological wear, the law of mass and energy conservation, and the first law of thermodynamics for open systems are utilised. The interpretation of surface tension as energy with reference to a unit of surface is taken advantage of as well. This corresponds to mechanical work required to increase a surface by a single unit in isothermal conditions.

UNIT WORK OF DISSIPATION

A quantitative evaluation of surface tension and surface energy based on analysis of processes in a system of solids in friction is proposed here. This analysis employs concepts and principles of phenomenological thermodynamics. A friction pair is treated as an open thermodynamic system. Processes in such a system are described by the equation for the first law of thermodynamics, namely **[L. 4, 5]**:

$$\Delta U = -\Delta I - Q_{1-2} + A_{t1-2} = -i\Delta m - Q_{1-2} + A_{t1-2}, \tag{7}$$

where ΔU – increment of the system's internal energy, ΔI – increment of enthalpy, Q_{1-2} – heat, A_{t1-2} – technical

work equal to work of friction A_t, i – average specific enthalpy characterising the wear mechanism, Δm – mass wear.

Separation of wear product particles from the material of solids in friction depends on mechanical work A_{dyss} and wear mechanism, quantitatively defined by specific enthalpy i. Work of friction A_t is a sum total of friction (dissipation) heat Q_{dyss} and work of mechanical dissipation A_{dyss}:

$$A_t = Q_{dyss} + A_{dyss}. \tag{8}$$

Specific enthalpy of wear products, i, is the sum total of the following components **[L. 5, 6]**:

$$i = u_c + a_{dyss}, \tag{9}$$

where u_c – internal energy of the wear product material caused by heating; a_{dyss} – specific work of mechanical dissipation – this refers to the process of wear product generation; the unit of u_c and a_{dyss} is $J \cdot kg^{-1}$. The physical quantity a_{dyss} is directly related to the work of mechanical dissipation A_{dyss}.

The discussion of surface tension and surface energy of tribological wear particles concerns the structure of the energy balance for the friction process. This structure is characterised by the ratio η of work of mechanical dissipation and work of friction – A_{dyss}/A_t. Work of mechanical dissipation A_{dyss} can be determined by means of calorimetric testing as the difference between work of friction and friction heat **[L. 5, 6]**. This is a highly complicated method, limited to laboratory testing **[L. 7, 8]**. This author proposes an alternative method of determining η **[L. 9]**. The starting point for the method is the fact the real surface A_r is a sum total of individual microsurfaces A_{ri} of irregularity contacts and normally constitutes 10^{-5} to 10^{-2} of the nominal surface A_n. It is well known the ratio of nominal to real structure is equal to the ratio of unit surface pressures corresponding to hardness H and nominal unit pressure $p = N/A_n$, where N – normal force. Thus:

$$\frac{A_n}{A_r} = \frac{H}{p} = n_o, \tag{10}$$

where n_o – number of real direct roughness contacts on a nominal surface, assuming each elementary contact surface is identical. Equation (10) implies the nominal contact surface of solids in friction, assuming plastic contact of their irregularities, is n_o times greater than real surface.

Figure 2 illustrates the nominal surface A_n uniformly divided into n_o^2 identical surfaces A_{ri} **[L. 10]**. The fields inside bold lines are real contacts of
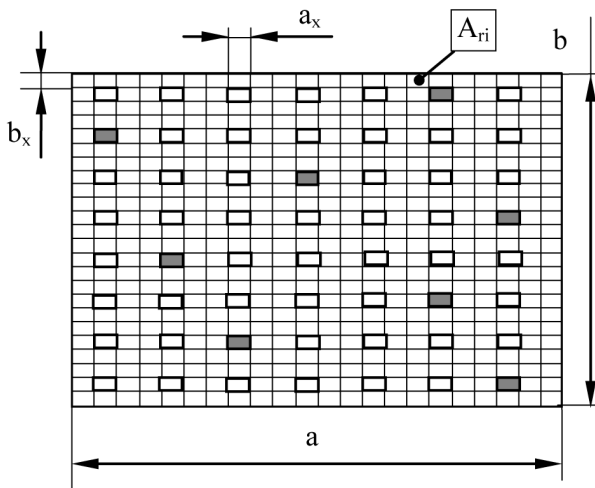
Fig. 2.   Nominal surface A_n divided into n^2 equal parts A_{ri}; the rectangles delineated in bold number n_o; the rectangles shaded and delineated in bold number n_V [L. 9], [10]
Rys. 2.   Powierzchnia nominalna A_n podzielona na n^2 równe części A_{ri}; liczba prostokątów zaznaczonych grubymi liniami wynosi n_o; liczba prostokątów zaciemnionych i narysowanych grubymi liniami wynosi n_V **[L. 9, 10]**

irregularity surfaces. They number n_o. Some of them are coloured. Wear particles arise there, numbering n_V. Where the friction path equals a, A_n is moved deeper inside a solid by the value of linear wear h_0.

The next step to determining η is to formulate the dependence according to which shear stress $\mu \cdot H = n_o \cdot \mu \cdot p$ prevails in each surface element A_{ri}. After introducing η, **[L. 9]** is expressed:

$$\mu H = n_o \mu p = n_k(\eta \mu p), \qquad (11)$$

where n_k – number of repeated contacts before a wear particle is separated. The wear coefficient k is the reverse of this number. η results:

$$\eta = \frac{n_o}{n_k} = \frac{H}{p} k. \qquad (12)$$

Work of mechanical dissipation A_{dyss} is part of friction work, hence:

$$A_{dyss} = k \frac{H}{p} A_t. \qquad (13)$$

According to J.F. Archard **[L. 11, 12]**, volumetric wear caused by friction V is described by:

$$V = k \frac{1N}{H}, \qquad (14)$$

where l – path of friction. On introducing the energetic measure of wear resistance, specific work of tribological wear is:

$$e_R^x = \frac{A_t}{\Delta m}, \qquad (15)$$

the wear coefficient is described by:

$$k = \frac{\mu H}{\rho e_R^x}. \qquad (16)$$

Specific work of dissipation $a_{dyss} = A_{dyss}/\Delta m$ is a fraction of the specific work of wear:

$$a_{dyss} = \eta e_R^x. \qquad (17)$$

Considering (13) and (15), a dependence is produced for the specific work of mechanical dissipation:

$$a_{dyss} = k \frac{H}{p} = e_R^x \frac{\mu H^2}{\rho p}. \qquad (18)$$

This is, therefore, a function of certain physical properties of the material (H, ρ), unit pressure (p), and coefficient of friction (μ). Specific work of dissipation a_{dyss} is related to mass wear, and it must be appropriately transformed to define surface tension and surface energy and relate the work to the surface of wear product particles being formed. To this end, the volume where energy is dissipated in friction and average volume of a generated wear particle must be defined.

ENERGY DISSIPATION IN A FRICTION VOLUME

The discussion in the foregoing sections applies to the macroscopic, phenomenological analysis of thermodynamic processes in an entire friction pair. They are general yet insufficient to assess surface tension of separated fragments of solids in friction. Both the quantities described in the preceding section, e_R^x and a_{dyss}, express the dependence between a certain expense of energy and a mass of material consumed by friction. Their values are very high, greater than vapourisation heat of a material. No physical reasons for this can be provided; therefore, they only have technical significance as measures of wear resistance. Real energy density is arrived at by referring the energy expenditure to the "friction volume." To make some progress towards the goal set in this study, a space needs to be separated from a friction pair where actual dissipation of mechanical energy takes place. Secondary processes associated with friction are ignored in this way. This space was first defined in 1980 by G. Fleischer **[L. 13]** and termed the "friction volume." G. Fleischer also introduced the notion of wear ratio ν of wear volume to friction volume or of linear wear to the "friction height." This author determined dimensions of wear zone in 2007 **[L. 14]**

and demonstrated v is equal to the wear coefficient k. Friction heat, material defects, and wear particles arise in the friction volume and chemical reactions occur, also involving the environment. Secondary processes take place outside this area, deep in the friction pair, in particular, heat exchange and changes of material structure. The complexity of friction phenomena in solids makes it difficult to define surface tension of wear particles and requires a special method. The method is centred on balancing various energy effects in a tribological system, this time limited to the volume friction, and on identification of mechanical interactions, since only mechanical work generates a new surface of wear products.
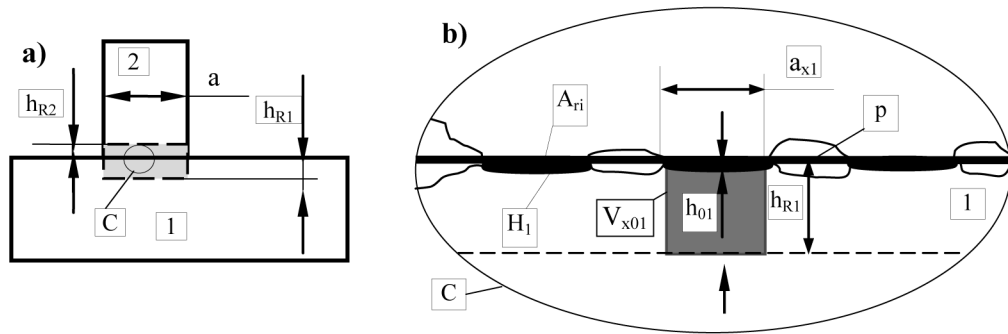

Fig. 3. **Boundary of the tribological system: a) where friction volume a·(h_{R1} + h_{R2}) as part of elements 1 and 2 forms a tribological system; width of the friction path b is perpendicular to the Figure's plane, b) geometrical properties of the friction volume around the element 1 [L. 9, 15]**

Rys. 3. Granica systemu tribologicznego. a) w przypadku, gdy objętość tarcia o wymiarach a·(h_{R1} + h_{R2}) jako część elementów 1 i 2 tworzy układ tribologiczny; szerokość ścieżki tarcia b jest prostopadła do płaszczyzny rysunku, b) właściwości geometryczne objętości tarcia wokół elementu 1 [L. 9, 15]

The volume of an item studied is determined by friction heights h_{R1}, h_{R2} and nominal surface of solids contact A_n with dimensions a·b, where a has the same sense as the vector of friction velocity v – **Fig. 3**. The friction heights are determined in **[L. 12, 14, 15]** and described as follows, with regard to friction pair elements 1 and 2, respectively:

$$h_{R1} = \frac{ap}{H_1} , \qquad (19)$$

$$h_{R2} = \frac{ap}{H_2} , \qquad (20)$$

where H_1, H_2 – hardness of the first and second friction element.

Figure 3b is a microscopic illustration of a wear particle separated from the material of element 1 with hardness H_1 and dimensions: a_{x1} b_{x1} h_{R1}, where: a_{x1} = a/n_{o1}, b_{x1} = b/n_{o1}. Elementary linear wear (height of wear) h_{01} in this model depends on height of the friction zone h_{R1}, that is, **[L. 14, 15]**:

$$h_{01} = k_1 h_{R1}. \qquad (21)$$

The ratio of linear wear h_{01} to elementary shift a_{x1} is defined by **[L. 2, 13]** as the specific intensity of linear wear i_{h1}. The above dependence and **Fig. 3a** imply: i_{h1} = h_{01}/a_{x1} = h_{01}/h_{R1}, since i_{h1} = k_1 **[L. 14, 15]**. Thus, h_{01} is equal to the elementary shift a_{x1} in this model of friction zone.

The wear coefficient k_1 is further assumed to be the reciprocal of the number of irregularity contacts n_{k1} necessary to produce a wear particle of element 1 of a friction pair with dimensions a_{x1} b_{x1} h_{R1}:

$$k_1 = \frac{1}{n_{k1}} . \qquad (22)$$

The friction zone volume of friction pair elements can be expressed on the basis of (19) and (20) as follows:

$$V_{R1} = A_n \frac{ap}{H_1} , \qquad (23)$$

$$V_{R2} = A_n \frac{ap}{H_2} . \qquad (24)$$

Volume and thus mass of material involved in friction is n_k times greater than its mass wear. Real maximum specific energies are lower as appropriate and the following is produced instead of e_R^x and a_{dyss1} after (12), (16), and (18) are taken into consideration:

$$e_R^x k_1 = e_R^x \frac{\mu H_1}{\rho_1 e_R^x} = \frac{\mu H_1}{\rho_1} , \qquad (25)$$

$$a_{dyss1}k_1 = \frac{\mu H_1^2}{\rho_1 p} \quad k_1 = \frac{\mu H_1 \eta_1}{\rho_1} \quad . \qquad (26)$$

Equation (25) describes total specific energy distributed across the friction zone. On the other hand, (26) describes only its part (less heat of friction) responsible for tribological wear. Volume, not mass involved in friction, should be taken into account when determining surface tension and surface energy. e_R^x and a_{dyss1} correspond to the densities e_{R1} and a^*_{dyss1} if material density ρ_1 is ignored in (25) and (26):

$$e_{R1} = \mu H_1, \qquad (27)$$

$$a^*_{dyss1} = \mu H_1 \eta_1. \qquad (28)$$

Similar dependences can be determined for element 2 of the friction pair. It should be noted, at this point, that specific work of wear is a system quantity that is the same for a friction pair and its particular elements [L. 5, 6, 10]. Therefore, the element is not indexed in the foregoing equations. Since η_1 is of the order of several per cent, the bulk of mechanical energy introduced to the friction zone is converted into heat of friction. The heat of friction is then discharged to the environment and does not contribute to tribological wear.

DETERMINATION OF WEAR PARTICLES' SURFACE TENSION AND SURFACE ENERGY

Surface tension and surface energy of tribological wear particles need to be defined prior to developing a method of their determination. Surface energy e_F^* describes the ratio of total energy expended in friction of a solid per unit of surface of a separated wear particle, whereas surface tension γ^* is but a mechanical component of e_F^*. Resolving the problem formulated in the title of

this section primarily requires the geometry of the part subject to wear to be considered. **Figures 2** and **3b** contain schematic representations of a particle with dimensions a_{x1} b_{x1} h_{R1} against the background of friction volume. Such a particle is generated after n_{k1} pulses of dissipated energy with density μH_1, whose component $\mu H_1 \eta_1$ directly contributes to formation of a new solid surface. Separation of a particle is schematically indicated with an arrow in **Fig. 3b** as an upward shift over the distance of h_{R1} material volume V_{x01}. Mechanical energy accumulated in the volume of a given particle is therefore described with:

$$A_{dyssx1} = \mu H_1 \eta_1 a_{x1} b_{x1} h_{R1} = \mu H_1 \eta_1 a_{x1}^2 b_{x1}. \qquad (29)$$

Since $a_{x1} = h_{R1}$, this energy component generates a new particle surface as it is separated from the superficial layer of a material. The process of surface development is characterised by surface energy e_{F1}^*, interpreted as energy density and expressed in Jm^{-2}. To determine surface energy, the surface area of a particle formed needs first to be determined. The discussion will continue to use the model of tribological wear based on **Fig. 3b**. The particle is a cuboid with a base $a_x b_x$ and height $h_{R1} = a_x$. Its surface F_{0x} is described as follows:

$$F_{0x} = a_{x1}b_{x1} + 2h_{R1}(a_{x1} + b_{x1}). \qquad (30)$$

A new surface formed in friction comprises a surface described with the above formula less the top particle surface, which already exists. Another surface is formed in the material of friction pair element. The newly formed surface on particle separation is

$$F_{0xx1} = 2[a_{x1}b_{x1} + 2h_{R1}(a_{x1} + b_{x1})]. \qquad (31)$$

Surface energy e_{F1}^* is defined as the energy dissipated across the volume of a future particle: $\mu H_1 a_{x1} b_{x1} h_{R1} = \mu H_1 a_{x1}^2 b_x$ divided by the F_{0xx1}:

$$e_{F1}^* = \frac{\mu H_1 a_{x1}^2 b_{x1}}{2[a_{x1}b_{1x} + 2a_{x1}(a_{x1} + b_{x1})]} = \frac{\mu H_1 a_{x1}b_{x1}}{2[b_{x1} + 2(a_{x1} + b_{x1})]} \qquad (32)$$

if $a_x = b_x$, then

$$e_{F1}^* = \frac{\mu H_1 a_{x1}}{10} = \frac{\mu H_1 ap}{10H_1} = \frac{\mu ap}{10} = \frac{\mu a^2 p}{10a} = \frac{\mu N}{10a} = \frac{T}{10a} . \qquad (33)$$

This dependence implies surface energy e_{F1}^* is a function of friction force T and dimension a of the nominal friction surface. e_{F1}^* should be expressed in $J \cdot m^{-2}$. Repeating the analysis for the second friction pair element will generate a parallel dependence, namely: $e_{F2}^* = \frac{T}{10a}$, which means surface energy of particles

formed from Elements 1 and 2 in tribological wear is the same, i.e. $e_{F1}^* = e_{F2}^*$. To describe surface tension γ_1^*, (32) needs to be modified considering the parameter η and thus ignoring the thermal effect of dissipation:

$$\gamma_1^* = \frac{\mu H_1 \eta_1 a_{x1}^2 b_{x1}}{2[a_{x1}b_{1x} + 2a_{x1}(a_{x1}+b_{x1})]} = \frac{\mu H_1 \eta_1 a_{x1} b_{x1}}{2[b_{x1} + 2(a_{x1}+b_{x1})]} \qquad (34)$$

if $a_x = b_x$, then:

$$\gamma_1^* = \frac{\mu H_1 \eta_1 a_{x1}}{10} = \frac{\mu H_1 \eta_1 ap}{10 H_1} = \frac{\mu \eta_1 ap}{10} = \frac{\mu N \eta_1}{10a} = \frac{T \eta_1}{10a} = \frac{T_{m1}}{10a}. \qquad (35)$$

Surface tension γ_1^* is, therefore, surface energy e_{F1}^* times η_1, expressed in $N \cdot m^{-1}$. $T_{m1} = T \cdot \eta$ is the mechanical component of friction force T responsible for friction wear [L. 5, 12]. Contrary to surface energy e_F^*, surface tension γ^* of particles of the material separated from each friction element is different: $\gamma_1^* \neq \gamma_2^*$. The foregoing discussion implies that the surface energy of solids (given identical units) is greater than surface tension. This is caused by heat of friction, which always indirectly associated with wear. In parallel with the dependence for liquid properties (6), the following can be written for solids:

$$\gamma_1^* = e_{F1}^* - Q_{F1}^*, \qquad (36)$$

where Q_{F1}^* is the thermal effect connected with formation of a new solid surface. As opposed to (6), (36) describes an irreversible process. In the event, surface tension is not interpreted as free energy as defined by (6). Since $e_{F1}^* \eta_1 = \gamma_1^*$ includes η_1, which rises as temperature grows ($d\eta_1/d\Theta > 0$), surface tension should be expected to be the rising function of temperature. This means heat Q_{F1}^* is a reducing function of temperature. The argument producing (32) – (36) can also be applied to the second friction pair element.

This interpretation and description of surface energy and surface tension in line with (33) and (35) can be referred to (1), (2), and **Fig. 1**. Formation of a new solid surface in friction is obviously more complicated than for liquids, since wear product particles are generated in a range of locations, which means the new surface is not continuous. The situation can be shown schematically on the small scale of shear stress µH and, for practical reasons, on the scale of average shear stress µp and friction force T – **Fig. 4**.
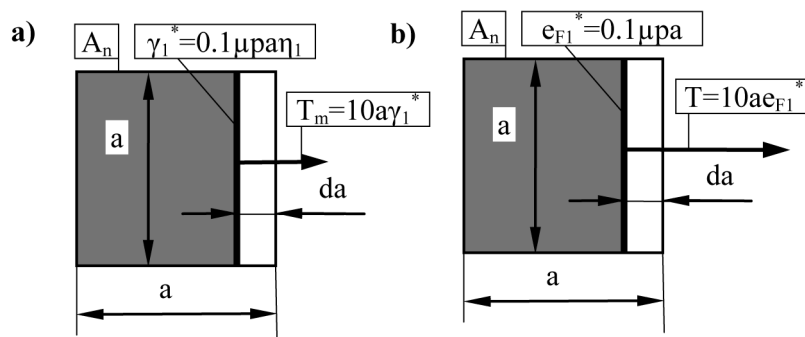

Fig. 4. Illustration of dependences between friction resistance and surface tension – a) and surface energy – b)
Rys. 4. Przedstawienie zależności między oporem tarcia a napięciem powierzchniowym – a) i energią powierzchniową – b)

For the purpose of the quantitative demonstration of the above discussion, test results for friction and wear of eight friction pairs and the required parameters are listed in **Table 1**. The methods and results are published in [L. 16]. This is pin-on-disk dry friction where temperature Θ can be measured 0.4–0.5 mm away from the friction surface. The friction velocity v is constant, 1 ms^{-1}, in every case. A 145Cr6 (tool steel containing: 1.4% C, 0.6% Mn, 0.2% Si, 1.5% Cr, 0.2% V) steel disk, hardness 60 HRC, worked with a 5x5x0.5 mm metal sample (nominal friction surface – 25 mm^2) made of a variety of materials: Armco iron (ferrite), C45 and C80U steels (0.8% C, pearlite), copper, aluminum, zinc, lead, and its LC60 alloy (60% tin) (**Table 1**), whose hardness is many times lower than of a steel disk. This allows for ignoring the wear of the disk in the model discussion. Mass wastage of the test sample was weighed on analytical scales. Friction coefficient µ, material density ρ, material hardness H, surface pressure p, three temperatures of the friction surface: Θ_1, Θ_2, Θ_3 and the corresponding specific work of wear (mean of 6 measurements) are provided in **Table 1 [L. 16]**.

Figure 5 shows a test stand diagram and 6 a copper grip with the attached sample which carries the load and provides for the necessary heat exchange and for the desired temperature Θ. **Table 2** lists values of η_1 computed for three temperatures Θ_1, Θ_2, Θ_3 according to (37), which results from (12) and (16):

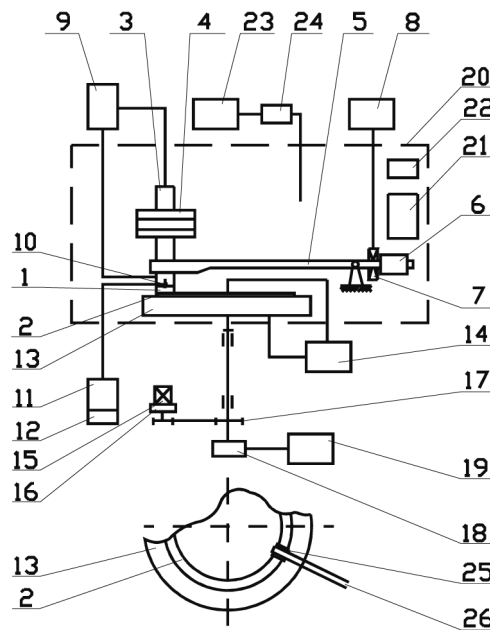$$\eta_1 = \frac{\mu H_1^2}{\rho_1 e_R^x p}. \qquad (37)$$

Fig. 5. **Schematic representation of the test stand: 1 – sample, 2 – countersample, 3 – clamping device, 4 – load, 5 – lever, 6 – counterweight, 7 – measurement bridge, 8 – friction force metre, 9 – thermostat, 10 – thermocouple, 11 – temperature metre, 12 – thermostat , 13 – disk, 14 – thermostat, 15 – electric motor, 16 – gear box, 17 – belt drive, 18 – speedometre, 19 – tachometre, 20 – climatic chamber, 21 – humidity metre, 22 – humidity sensor, 23 – air pump, 24 – air filter, 25 – cleaner, 26 – spring lever [L. 16]**

Rys. 5. Schematyczne przedstawienie stanowiska badawczego: 1 – próbka, 2 – przeciwpróbka, 3 – urządzenie zaciskowe, 4 – obciążenie, 5 – dźwignia, 6 – przeciwwaga, 7 – mostek pomiarowy, 8 – miernik siły tarcia, 9 – termostat, 10 – termopara, 11 – miernik temperatury, 12 – termostat , 13 – tarcza, 14 – termostat, 15 – silnik elektryczny, 16 – skrzynia biegów, 17 – napęd pasowy, 18 – prędkościomierz, 19 – obrotomierz, 20 – komora klimatyczna, 21 – wilgotnościomierz, 22 – czujnik wilgoci, 23 – pompa powietrza, 24 – filtr powietrza, 25 – czyścik, 26 – dźwignia sprężynowa **[L. 16]**
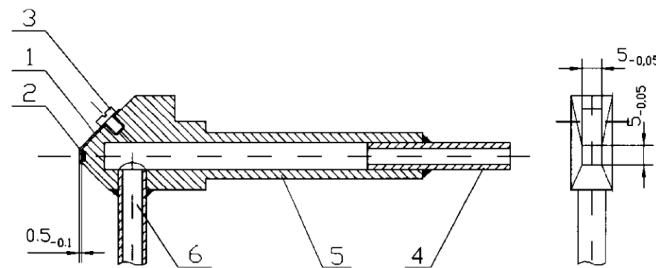

Fig. 6. **Copper grip 5 and friction element: 1, 2 – thermocouple, 3 – sample fastening screw 1, 4 – supply of coolant, 6 – discharge of coolant [L. 16]**

Rys. 6. Miedziany uchwyt 5 z elementem ciernym: 1, 2 – termopara, 3 – wkręt mocujący próbkę 1, 4 – doprowadzenie czynnika chłodzącego, 6 – odprowadzenie czynnika chłodzącego **[L. 16]**

Surface energy for various materials is calculated according to (33) $e_{F1}^* = 0.1$ µap. Surface tension is expressed as $\gamma_1^* = e_{F1}^* \eta$, also for these temperatures.

Direct introduction of a thermodynamic interpretation of solid wear as per (6) is not reasonable, since it describes free energy for reversible, equilibrium, isochoric, and isothermal transformations. It characterises an item composed of atoms (particles) that moves from inside a liquid to its surface. This is accompanied by a certain thermal effect (ΘS_F). When wear particles are separated, however, the dissipated mechanical energy is distributed across a friction volume that is many micrometre deep. This is always an irreversible process. The friction heat generated is not the same as the heat associated with formation of a new solid surface. As part of the foregoing discussion, heat of friction is addressed separately from work of friction. The remaining work of friction is treated as the cause of formation of new solid surface particles.

Table 1. List of physical quantities required to determine surface tension of wear product material generated as part of a selected experiment [L. 16]

Tabela 1. Wykaz wielkości fizycznych, które są wymagane do określenia napięcia powierzchniowego materiału produktów zużycia, powstałych w warunkach wybranego eksperymentu [L. 16]

Sample material	μ	ρ_1	H_1	N	P	Θ_1	$(e_{R1}^x)_1$	Θ_2	$(e_{R1}^x)_2$	Θ_3	$(e_{R1}^x)_3$
	–	kg/m³	MPa	N	MPa	K	MJ/g	K	MJ/g	K	MJ/g
Fe	0.6	7860	1746.18	19.6	0.785	298	26.755	313	5.443	333	3.38
C45	0.6	7860	2158.2	29.43	1.177	298	62.409	313	15.692	333	9.083
C80U	0.6	7860	2687.94	29.43	1.177	298	6.743	313	3.095	333	1.244
Cu	0.51	9830	1236.06	9.81	0.392	293	14.509	313	11.840	333	6.61
Al	0.43	2700	794.61	9.81	0.392	293	19.263	313	11.108	333	8.437
Zn	0.5	7130	431.64	9.81	0.392	293	12.193	313	4.676	333	4.034
Pb	0.8	11340	58.86	0.49	0.020	293	0.785	303	0.635	313	0.429
LC60	0.5	8500	78.48	1.96	0.078	293	2.392	303	1.341	313	0.939

Table 2. Values of $(\eta_1)_1$, $(\eta_1)_2$, $(\eta_1)_3$, surface tension $(\gamma_1^*)_1$, $(\gamma_1^*)_2$, $(\gamma_1^*)_3$ for temperatures Θ_1, Θ_2, Θ_3 and surface energy e_{F1}^*

Tabela 2. Wartości parametrów $(\eta_1)_1$, $(\eta_1)_2$, $(\eta_1)_3$, napięcie powierzchniowe $(\gamma_1^*)_1$, $(\gamma_1^*)_2$, $(\gamma_1^*)_3$, wyznaczone dla temperatur Θ_1, Θ_2, Θ_3 i energia powierzchniowa e_{F1}^*

Sample material	$(\eta_1)_1$	$(\eta_1)_2$	$(\eta_1)_3$	$(\gamma_1^*)_1$	$(\gamma_1^*)_2$	$(\gamma_1^*)_3$	e_{F1}^*
	–	–	–	Nm⁻¹	Nm⁻¹	Nm⁻¹	Jm⁻²
Fe	0.011	0.054	0.088	0.261	1.283	2.066	23.550
C45	0.005	0.019	0.033	0.171	0.680	1.174	35.310
C80U	0.069	0.151	0.377	2.454	5.346	13.301	35.310
Cu	0.014	0.017	0.031	0.139	0.171	0.306	9.996
Al	0.013	0.023	0.030	0.112	0.195	0.256	8.428
Zn	0.003	0.007	0.008	0.027	0.070	0.081	9.800
Pb	0.016	0.019	0.028	0.012	0.015	0.023	0.800
LC60	0.002	0.003	0.005	0.004	0.007	0.010	1.950

The energetic condition of a newly uncovered surface, due for instance to fragile cracking of a metal, is substantially different from that of surfaces of tribological wear product particles produced from this metal. In the circumstances, values of e_{F1}^* and γ_1^* also differ from values given by the literature for metal elements. **Table 2** shows surface tension rises as friction contact temperature grows. This tendency is the reverse of what is expressed by (6) and (36). Equations (5) and (6) characterise the case of heat being supplied to a system from the environment in order to preserve the isothermal process of new surface formation. When friction arises, the dissipation heat is naturally discharged by the system to the environment as heat. In this example of tribological testing, the heat discharge from the friction zone is supported with a heat exchange. The required target temperature is guaranteed in this way.

CONCLUSIONS

Formation of tribological wear particles is conditioned by development of new surfaces in solids. This study has demonstrated tribological wear is a result of mechanical energy dissipation across a friction volume. A considerable part of the dissipated energy is converted into heat of friction, subsequently transferred to the environment by means of the friction pair. Therefore, it plays no direct part in the process of wear. This implies some mechanical work needs to be performed in order to separate a material fragment from a superficial layer. Work of mechanical dissipation identified in the energy balance is referred to particle surfaces. Shape and dimensions of this particle are proposed assuming they are identical and evenly distributed across the nominal friction surface. Their number is defined by the ratio of unit pressures per real and nominal surface considering the coefficient of wear. Material differences in the development of the new surface in liquids and solids are analysed as well. Interpretations of surface tension γ

and surface energy e_F in mechanical and thermodynamic respects are discussed. From the mechanical point of view, both of the magnitudes are identical quantitatively yet they have different units and different physical meanings. Surface energy comprises both mechanical work of surface formation and the associated thermal effect. As far as liquids are concerned, surface energy is interpreted as thermodynamic potential and surface tension as free energy. This process of surface evolution is known as reversible thermodynamic transformation. On the other hand, the process of solid friction is irreversible. The equation for the first law of thermodynamics for open systems serves as the starting point for analytical description of friction and its impact in this paper. Specific enthalpy of wear products is used to describe surface tension and surface energy. The enthalpy has its thermal and mechanical components. A method of defining its mechanical portion, a_{dyss}, is proposed. Its value is then calculated with reference to a unit of surface of a wear particle generated. Surface tension is described on this basis. In parallel, surface energy is described in consideration of the specific work of wear. The discussion produces the dependence (36) between surface energy e_{F1}^* and surface tension γ_1^*. Tribological test results for samples made of eight different technical metals are utilised to determine these physical magnitudes in quantitative terms. The following conclusions can be drawn from this discussion and instances of experimentation:

– Surface energy is a systemic quantity that remains identical for each friction couple element: $e_{F1}^* = e_{F2}^*$.
– The above conclusion results from quality of specific works of wear: $e_{R1}^x = e_{R2}^x = e_R^x$.
– Surface tension γ^* varies for each friction couple element, and this is due to the fact specific work of mechanical dissipation a_{dyss} varies for each element.
– With regard to wear of solids, surface tension γ_1^* rises as temperature of friction surface increases. This is caused by the parameter η rising as temperature grows.
– Formation of a new liquid surface is described by the literature as a reversible isothermal process where heat is supplied from the environment to the system. In respect of tribological wear, heat is discharged to the environment at a set temperature of friction surface, and this determines the different dependences of surface tension on temperature for liquids and solids subject to wear.
– Coefficients and force of friction are in direct proportion to surface tension and surface energy.
– Values of surface tension and surface energy determined by the testing described here characterise fine metal oxide particles formed as part of running-in and do not apply to pure metals as a result.

NOMENCLATURE

a – length of the smaller friction element measured in the direction of friction velocity [m],

a_x – linear dimension of elementary contact surface of irregularities which is perpendicular to a_{dyss} – specific work of mechanical dissipation [J·kg^{-1}],

a_{dyss}^* – work of mechanical dissipation referred to volume [J·m^{-3}],

A_r – real contact surface of solids in friction [m^2],

A_{ri} – contact surface of surface irregularities [m^2],

A_n – nominal contact surface of solids in friction [m^2],

A_{1-2} – work [J],

A_{t1-2} – technical work (friction work) [J],

A_{dyss} – work of mechanical dissipation [J],

b – width of friction path [m],

b_x – dimension of elementary contact surface of irregularities which is perpendicular to a [m],

δA_F – elementary superficial work [J],

e_D – density of vapourisation heat [J·m^{-3}],

e_R – density of friction energy [J·m^{-3}],

e_R^x – specific work of wear [J·kg^{-1}],

e_F – surface energy [J·m^{-2}],

e_F^* – surface energy of solid [J·m^{-2}],

F – surface [m^2],

F_{0x} – surface of wear particle [m^2],

F_{0xx} – surface arising on formation of wear particle [m^2],

h – linear wear [m],

h_R – height of friction zone [m],

H – hardness of the softer friction couple material [MPa],

H_1, H_2 – material hardness of the first and second friction element [MPa],

i – specific enthalpy [J·kg^{-1}],

ΔI – enthalpy increment [J],

k – wear coefficient,

l – friction path [m],

m – mass [kg],

Δm – mass wear [kg],

n_k – critical number of contacts,

n_o – number of real irregularity contacts on the nominal contact surface,

n_V – number of friction particles generated on the nominal contact surface,

N – normal force [N],

Q_{1-2} – heat [J],

Q_{diss} – heat of dissipation [J],

δQ_F – elementary heat increment on the surface produced [J],

Q_F^* – heat of formation of a new solid surface unit

Q_F – unit latent heat [J·m^{-2}],

Q_F^* – heat discharged at formation of a new solid surface unit [J·m^{-2}],

p – nominal surface pressure [MPa],

S_F – entropy referred to a unit of surface [J·K^{-1}·m^{-2}],

dx – elementary shift [m],

dF – surface increment [m^2],

T – friction force [N],

T_m – T component responsible for triboogical wear [N],
u_c – internal energy of wear particle material [J·kg^{-1}],
ΔU – internal energy increment [J],
dU_F – superficial energy increment [J],
V – volume, volumetric wear [m^3],
v – friction velocity [m·s^{-1}],
γ – surface tension [N·m^{-1}],
γ^* – surface tension of solid [N·m^{-1}],
η – ratio A_{dyss}/A_{t1-2},
μ – friction coefficient,
ρ – density [kg·m^{-3}],
Θ – temperature [K],
1-2 – designation of thermodynamic transformation's
start and end,
1, 2 – index of friction couple element.

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