A B S T R A C T

Tribology, as the scientific and professional discipline within the mechanical engineering, studies phenomena and processes on the interacting surfaces, in direct and indirect contact and in relative motion. It includes the study and application of the principles of friction, wear and lubrication, as well as phenomena connected with these processes. Given that a process involving friction is always accompanied by transformation of energy, more precisely an energy dissipation process which generates entropy, the concept of thermodynamic entropy production analysis represents one of appropriate tools for studying and analysing the behaviour of complex friction and wear processes. This paper presents a review of published works in which the thermodynamic approach was used in analysing the friction and wear processes in tribosystems.

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performed also from the aspect of the law of conservation of energy, i.e. from the aspect of the First law of thermodynamics.

Besides their energy-related character, these processes occur with a prominent dissipation of energy, as well as in the temperature and chemical non equilibrium, often with the occurrence of chemical reactions. That is why these processes must unavoidably be also classified in the group of irreversible thermodynamic processes. Hence, it is clear that in order to obtain a complete picture of these processes, their analysis should be made through the Second law of thermodynamics, i.e. through the balance of entropy (property of state that describes the degree of irreversibility of all physical processes).

Due to all above mentioned, this paper presents an attempt to describe the friction and wear processes through a typical thermodynamic approach. Because of their nature and the need to include in the description processes of exchange of material between the contact surfaces, that is the loss of material in the form of wear products, a tribological system that includes the two contacting bodies with their contact surfaces, was treated as an open thermodynamic system. That is why it is described through three basic laws defined for open thermodynamic systems: the law of conservation of mass (continuity equation) and the First and Second law of thermodynamics. Unlike the approach used so far [4-8], defining these balances based on the Prigogine theory of irreversible processes and the Gibbs Entropy Formula [9,10], which combines the first and Second law of thermodynamics, this paper uses the forms of these three laws which are used in the conventional technical thermodynamics. This was done primarily because of identified shortcomings of the Prigogine theory of irreversible processes in defining balances. Namely, the balances defined in this way either do not recognize energy and entropy effects of the exchange of material between contact surfaces or include them in a too complicated way.

2. MODEL

2.1 The physical model

Wear has been defined as "the progressive loss of substance from the operating surface of a body occurring as a result of relative motion at the surface", while friction has been defined as "the resisting force tangential to the common boundary between two bodies when, under the action of an external force, one body moves or tends to move relative to the surface of the other" [22]. This definition of friction refers mostly to the external friction and do not specifically include the internal friction (viscosity). External friction, and wear occurring in this case, will be the subject of this analysis.

Thus, a considered physical model is made up of two solid bodies in direct or indirect contact which are in relative motion against each other. Each body, viewed from a thermodynamic point of view, is a thermodynamically open system (subsystem), where the boundaries of each of the subsystems include the outer contours of the corresponding body and pass through their contact surface. Exchange of material between these bodies through this contact surface is exactly the reason that these systems have to be treated as open (Fig. 1).

![Fig. 1. Physical model of the tribological system and the areas of mechanical action (F_1 - friction force; F_n - normal force; \( \mu \) - coefficient of friction).](image)

2.2 The thermodynamical model

Thermodynamics is based on two fundamental laws; the first law implies conservation of energy and the second implies that, for any process to take place, the change in entropy has to be zero or positive. Entropy therefore can only be created, never destroyed. The first law is independent of the type of the process [21].

With the previously defined conditions, the mass balance of the subsystem which makes the body I (Fig. 2a), i.e. overall change in mass of the first body can be defined by the equation:

$$dm_{in} = d(m_1)_{cv} + dm_{out},$$

(1)
where: \( d(m)_\text{cv} \) is change of mass of the body I (body into control volume) in a differentially small moment of time \( dt \), \( dm_\text{in} \) is the mass of material of the body II, which is to be transferred to the body I in a differentially small moment of time \( dt \), \( dm_\text{out} \) is the mass of material of the body I which is separated by wear from the body I in a differentially small moment of time, and \( cv \) is the control volume.

The second main balance equation for the control volume of the body I represents the balance of energy or the First law of thermodynamics. For the so defined control volume (Fig. 2b) this balance in differential form, i.e. for a differentially small moment of time \( dt \), is as follows:

\[
\delta Q + \sum_{j=1}^{m} \delta W_j + u_\text{in}\, dm_\text{in} = d(U)_\text{cv} - \\
- \sum_{k=1}^{p} \mu_k \, dm_k - \sum_{l=1}^{n} \mu_l \, dm_l + \sum_{i=1}^{r} dE_i + u_\text{out} \, dm_\text{out},
\]

where: \( \delta Q \) is the elementary quantity of heat transferred to the body I in a differentially small moment of time, \( \delta W_j \) is the different type of elementary work done on the body I (work for overcoming adhesion forces, work for creating plastic deformation, etc.), \( d(U)_\text{cv} \) is the differential change of internal (thermal) energy of the body I (body into control volume), \( u_\text{in} \) is the specific internal (thermal) energy of the mass \( dm_\text{in} \), \( u_\text{out} \) is the specific internal (thermal) energy of the mass \( dm_\text{out} \), \( \mu_k \) and \( \mu_l \) are the elementary chemical work or elementary energy of chemical reaction of the \( k \)-th and \( l \)-th component, \( \mu_k \) and \( \mu_l \) are the chemical potentials of chemical reaction of the \( k \)-th and \( l \)-th component, \( dm_k \) and \( dm_l \) are the moles of substance “\( k \)” and “\( l \)” with the chemical potential \( \mu_k \) and \( \mu_l \) transported from the system to its surroundings, \( dE_i \) is the change of other forms of its internal energy, e.g. electrochemical, photochemical, etc.

Opposite to the aforementioned approach based on Prigogine theory of irreversible processes and Gibbons relation, two new terms \( u_\text{in}\, dm_\text{in} \) and \( u_\text{out}\, dm_\text{out} \) appear in the equation (2), and represent the energy transferred into the control volume of body I with mass transfer \( dm_\text{in} \) and out of the control volume of body I by wear \( dm_\text{out} \), respectively. The \( u_\text{in} \) and \( u_\text{out} \) denote specific internal energy of supplied and specific internal energy of removed material.

Finally, the third main balance equation for the control volume of the body I is the balance of entropy equation or the Second law of thermodynamics (Fig. 2c). This law in differential form, i.e. for a differentially small moment of time \( dt \) is:

\[
dS_{\text{gen}} + \int \frac{q\,dA}{T_\text{cs}} + s_\text{in} \, dm_\text{in} = d(S)_\text{cv} + s_\text{out} \, dm_\text{out},
\]

where: \( dS_{\text{gen}} \) is the entropy generation that occurs in the control volume of the body I caused by irreversible processes within the control volume (processes of dissipation of mechanical work, chemical reactions, nonequilibrium processes of heat and mass transfer, etc.); \( \int q\,dA/T_\text{cs} \) is an increment of entropy originating from the transfer of heat to the body I (where \( q \) is the specific heat flow, \( dA \) is the elementary surface of the control surface and \( T_\text{cs} \) is the temperature of that elementary surface), \( d(S)_\text{cv} \) is the differential change of entropy of the body I and \( s_\text{in} \) and \( s_\text{out} \) are the specific entropy of mass \( dm_\text{in} \) and \( dm_\text{out} \) respectively.
3. CAUSES OF ENTROPY GENERATION

Unfortunately, balances written in this way are too general and have no practical use regardless of their universality. Just because of that, all attempts in defining the models of tribological systems with laws of thermodynamics, defined in this and similar way, had a very limited success [5,6,11-14]. In addition, all attempts of theoretical elaboration of particular terms made so far, because of the extreme complexity of the derived equations and the accompanying inability of their solution, did not lead to the desired result.

For this reason, in order to make balance equations more applicable for practical use, the existing phenomenological (empirical) relationships that define specific processes which occur during wear and friction were used for defining the particular terms which exist in them. These processes are connected by the same causes of irreversibility. Since Klamecki [5] and then also Bryant [8] proposed their classification, some of the mathematical relations already proposed by these authors will be used.

As identified causes of irreversibility the authors specify: the dissipation of work for overcoming the adhesion forces, the dissipation of work for abrasion (plastic deformation) process, the dissipation of work for fracture (creating cracks and fissures), the processes of change in state of material, chemical reactions, heat conduction and diffusion processes. Each of these causes of entropy increase will be explained in detail.

3.1 Dissipation of mechanical work used for overcoming the adhesion forces

Dissipation of mechanical work used for overcoming the forces of adhesion is the work that is being spent for overcoming the electromagnetic intermolecular forces of attraction of solids at small distances. These small distances occur between the contact surfaces of the tribological system elements in the process of friction and wear. During these processes work dissipates and turns into other forms of energy, first heat and then into the internal (thermal) energy.

Since this work is defined as the product of the interface surface energy $\gamma$ (the surface tension of fluids in the case of fluids) and the newly created surface area $dA_s$, its energy value can be defined as:

$$\delta W_{ad} = \gamma dA_s.$$  (4)

Using the general expression that correlates the transferred amount of heat $\delta Q$, the change of entropy substance $dS$ and its temperature $T$

$$dS = \frac{\delta Q}{T},$$  (5)

under the assumption of complete dissipation of mechanical work into heat when mastering the adhesion forces, entropy change caused by this irreversible process can be written as:

$$dS_{gen,ad} = \frac{\delta W_{ad}}{T_m} = \frac{\gamma}{T_m}dA_s,$$  (6)

where $T_m$ is the local temperature of the body I.

It is important to note that under the influence of these types of electromagnetic intermolecular forces the adhesive wear of materials occurs. This type of wear is manifested by the transfer of material between the two contact surfaces, as well as by creation of wear products. The parts of energy and the parts of entropy, exchanged in that way between the control volumes are covered by the appropriate terms in equations (2) and (3) i.e. $u_{in}dm_{in}$ and $u_{out}dm_{out}$ and $s_{in}dm_{in}$ and $s_{out}dm_{out}$, respectively. Therefore, the terms $s_{in}dm_{in}$ and $s_{out}dm_{out}$ do not belong to the part of generated entropy, but to the part of entropy exchanged along with the exchange of substances.

3.2 Dissipation of mechanical work used for abrasion (plastic deformation) process

The process of abrasion, which is happening during the mutual movement of contact surfaces, as a result of penetration of asperities of harder material into the surface layers of softer material is accompanied by ploughing and/or cutting (plastic deformation) of both contact surfaces. Thus, the work used for abrasion of the surface could be defined as the product of the work for abrasion reduced to unit volume (work per volume) $w_{pl}$ and elementary change of the body volume $dV$:

$$\delta W_{ab} = w_{ab}dV.$$  (7)

Extensive studies on the relationship between abrasion, i.e. plastic deformation of the surface,
and dissipation of energy were conducted by Fouvry at all. [15-17]. They found that there is a linear function between the volume of the worn material and dissipation of the energy used during this process. They have presented this linear relationship by defining the appropriate coefficients for a large number of tested materials. One of the analysed cases, with a well defined linear dependence, is shown in Fig. 3.

![Fig. 3. Linear relationship between the dissipated energy during the process of fretting wear and worn material volume [4].](image)

3.3 Dissipation of mechanical work used for creating cracks and fissures

Work that is used for creating of cracks or fissures on the surface, as well as for the processes associated with the surface fatigue wear, i.e. pitting and to some extent erosive wear, is defined by the empirical expression:

\[ \delta W_{cr}^{ab} = (G - 2\gamma) dA_{cr}, \]  
where \( G \) is the energy release rate during the process of creating cracks, reduced to a unit crack area, \( \gamma \) is the surface energy, and \( A_{cr} \) is the area of cracks surface. So, the energy release rate is defined as:

\[ G = -\frac{\partial U_{cr}}{\partial A_{cr}}, \]  
where \( U_{cr} \) is internal energy of crack growth.

Based on the foregoing and in accordance with the equation (5), the generation of entropy caused by this irreversible process can be determined as:

\[ dS_{gen,cr} = \frac{\delta W_{cr}}{T_{cr}} = \frac{(G - 2\gamma)}{T_{cr}} dA_{cr}, \]  
where \( T_{cr} \) is the local temperature of the cracked material at the crack tip.

3.4 Dissipation of energy used for phase transition process

The energy required for a phase transition, i.e. that is consumed during the process of melting and subsequent recrystallization of the metal surface can be determined as the product of the specific energy or latent heat absorbed or lost during the phase change from a liquid to a solid state \( r_{sol} \) and mass of molten metal \( m_{liq} \):

\[ dE_{phase} = r_{sol} d m_{liq}, \]  

According to equation (5) and in the case of complete dissipation of that energy, generation of entropy caused by this irreversible process can be determined as [8]:

\[ dS_{gen,phase} = \frac{dE_{sol}}{T_{phase}} = \frac{r_{sol}}{T_{phase}} d m_{liq}, \]  
where \( T_{phase} \) is the local temperature of the material in the place of phase change.

3.5 Change of entropy caused by the chemical reactions

Due to its special significance, the energy of chemical reactions, associated with corrosive and oxidative wear, was singled out from other energy influences in the equation of energy balance (2) and presented by the following expression:

\[ dE_{chem} = \sum_{k=1}^{p} \mu_k d n_k - \sum_{l=1}^{n} \mu_l d n_l, \]  

Appropriate change in entropy caused by different chemical reactions, in accordance with the expression (5) can be defined as:

\[ dS_{ch} = \sum_{k=1}^{p} \frac{\mu_k d n_k}{T_{ch,k}} - \sum_{l=1}^{n} \frac{\mu_l d n_l}{T_{ch,l}}, \]
where \( T_{ch,k} \) and \( T_{ch,l} \) are the local temperature at the place of chemical reaction for reactants and for products.

### 3.6 Change of entropy caused by the heat conduction process

The process of conduction of the heat throughout the body, released during friction \( \delta Q \) occurs in the temperature imbalance between the temperature at the boundary surface \( T_s \) and the temperature inside the body \( T_b \). Because of that temperature imbalance, this process inevitably causes an increase of entropy, which can be defined as [9]:

\[
dS_{gen,Q} = \left( \frac{1}{T_s} - \frac{1}{T_b} \right) \delta Q. \tag{16}
\]

In considering the amount of released heat \( \delta Q \), it should be noticed that it is only a part of the total dissipation of mechanical energy. As mentioned, a part of that energy is spent on the overcoming the adhesion, abrasive wear, formation of cracks and fissures, etc. The determination of allocation of mechanical energy and the share of its conversion into heat have studied by Chen and Li [18,19] and Elalem et al. [20]. Figure 4 shows the distribution of generated heat during sliding, for different loads, as a function of distance from the contact surface.

**Fig. 4.** Share of heat in the total dissipated energy depending on the distance from contact surface [4].

### 3.7 Generation of entropy due to diffusion processes

Although the assumed physical model does not anticipate a third body (lubricating fluid), in the case that it exists, generation of entropy caused by the process of diffusion of that fluid into structure of the body I or into the body II should be also taken into account.

### 4. CONCLUSION

Although the thermodynamic approach offers the possibility of a systematic analysis of behaviour of tribological systems, it is not yet sufficiently developed to have the practical use. For that approach to reach practical use, it should be improved and completed by the corresponding constitutive equations, which will connect the main physical processes with their energetic and entropic effects. Their creation will certainly require additional, dedicated experimental studies of individual processes. However, despite its shortcomings, this approach based on using main laws of physics: mass balance, energy balance and entropy balance, to reach a universal tribological model, still remains very promising, due to its methodical feature.

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