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# The polarity of metallic surfaces in the context of the corrosive and scuffing wear control



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## ABSTRACT

The concept of the metallic surfaces polarity in the context of scuffing performance is postulated and elucidated in the presented paper. The machining by grinding and surface treatment by burnishing is applied to control introducing changes in surface polarity and acid/base component of surface free energy is used for their quantitative determination. A clear relationship between the acid/base component of surface free energy and an activation of scuffing for the steel–cast iron friction pairs lubricated by oils with the surface-active sulphur-based additives is found. Obtained results are commented and clarified; thanks to the negative-ion concept of extreme pressure action of organo-sulphur compounds. Additionally, surface reactivity investigations are performed in order to determine the influence of acid/base component of surface free energy on the corrosion wear. It recognised a clear relationship between the acid/base component of surface free energy and the mass decrement of steel surfaces in the hydrochloric acid environment. On the basis of both parts of the investigations (scuffing and reactivity tests), an optimal surface polarity is determined for steel–cast iron friction pairs lubricated by lubricants with surface-active sulphur-based additives.

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## 1. Introduction

Current discussions of implications of tribological wear of adhesive etiology would be incomplete without an energetic foundation of this issue. First and foremost, it is connected with the very phenomenon of formation of adhesive tacking between solids, which in case of metals can result in development of adhesive wear, leading – in the worst case – to scuffing of the friction pair. The first hypothesis involving energetic causes of adhesive tacking is part of the theory published in 1961 by A.P. Semenov [1]. According to the theory, in order for adhesive tacking to form, apart from pure contact of two metals, their surfaces must reach the energetic threshold of tacking. In this manner, elements of electron structures of cooperating surface layers possess sufficient excitation, overcoming cohesive forces and entering mutual interrelations. This idea was mentioned in passing by other authors, for example H. Czichos et al. and their hypothesis that places the source of the scuffing process of metals in similarity to their electron structure and an achievement of critical level of interfacial energy (Czichos et al. [2]). This interfacial energy has been defined as a combination of thermal energy input and mechanical energy or mechanical stress. It was observed that at high thermal energy the endured mechanical stress is low while at low thermal energy it is

inverse. The modern science knows other theories concerning the initiation of scuffing. The most interesting of them connect the start of this process with

- an achievement of some critical temperatures initiating the instable wear (Blok [3], Lee and Cheng [4]);
- a size of debris (Rabinowicz [5]) or a speed of accumulation of the debris in the contact area (Enthoven and Spikes [6]);
- a plastic deformation of asperities (Jiajun et al. [7]);
- a critical friction power (Matveevsky [8]);
- formation and destruction of protective oxide films (Batchelor and Stachowiak [9]);
- desorption of polar constituents of lubricant from metallic surfaces (Spikes and Cameron [10], Bailey and Cameron [11]);
- a lubricant structure decomposition (Gates et al. [12], Hsu et al. [13]);
- an adiabatic shear instability (Hershberger et al. [14]).

The problem of precise identification of the scuffing initiation follows from the fact that none of the specific theories describe this process in the universal way. Apart from the reason making the adhesion possible, tacking formation has a direct connection with the electron structure of solids. Electron behaviour of metals can be characterised by the thermionic work function that is the minimum energy of electron necessary to escape from the Fermi level to the arbitrary point beyond this metal. There are works presenting the

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## Nomenclature

$\gamma_S$ (SFE)	Surface free energy [mJ/m <sup>2</sup> ]
$\gamma_S^{LW}$	Lifshitz-van der Waals component of surface free energy [mJ/m <sup>2</sup> ]
$\gamma_S^{+/-}$	Acid–base component of surface free energy [mJ/m <sup>2</sup> ]
$\gamma_S^+$	Acid component of surface free energy [mJ/m <sup>2</sup> ]

$\gamma_S^-$	Base component of surface free energy [mJ/m <sup>2</sup> ]
$\theta_W$	Contact angle for water [°]
$\theta_D$	Contact angle for diiodomethane [°]
$\theta_F$	Contact angle for formamide [°]
AW	Anti-wear
EP	Extreme pressure
AES	Auger electron spectroscopy

interdependence between the thermionic work function and adhesion in association of metal–ceramics (Li et al. [15,16]). It was found that the higher value of the thermionic work function corresponds to the lower value of adhesive force in the metal–ceramics contact. More complicated is the case of adhesion in the association of two metallic materials because thermionic work functions of both the metals play an essential role here. The analysis of adhesion in metals is often made on the basis of the surface free energy (SFE) which takes into account the molecular character of a surface layer. The formula developed by Mediema [17] can be recognised as an origin to this problem

$$\gamma_0^S = \frac{n_{ws}^{5/3}}{(\varphi^* - 0.6)^2} \quad (1)$$

where  $\gamma_0^S$  is the surface free energy of metal in the temperature of 0 K,  $\varphi^*$  is the parameter which approximately equals the thermionic work function of the metal and  $n_{ws}$  is the free electron density on the boundary of the Wigner–Seitz cell. These quantities are connected with the strength of metallic bonds and are typical for pure metals. In the case of physical pure metallic contact, it follows the electron flow from one metal to another with the lower Fermi level as a result of the double electric layer appearing in the interface. It disturbs the continuity of the Fermi surface between phases which can be reconstructed only when the free electron density on the boundaries of proper Wigner–Seitz cells will be continuous too.

To sum up, the interaction between metals is connected with their thermionic work functions and free electron density. It was proved for vacuum conditions that the value of (SFE) is dependent only on these factors [17]. The simplest and most accessible method of determining free surface energy is its calculation on the basis of Young's equation. It requires however for the contact angle to be measured on the analysed surface using test liquids with known surface tension. In modern science, two methods are used to determine (SFE): polar/dispersion (Owens–Wendt method) and acid/base (van Oss method). The method devised by van Oss et al. [18] is considered more accurate and it better reflects the chemical aspect of the problem. They suggested that the characteristics of the polar part are best performed on the basis of Lewis theory of acid and base. The dispersive component is characterised on the basis of Lifshitz interactions, which are part of interparticle van der Waals forces. It has to be stressed at this point that establishing surface free energy using van Oss method, as well as other methods based on measurement of the contact angle, does not lead to the establishment of the total value of surface free energy of metals. These methods can be used, however, for estimating the polar and dispersive components, which allow for relatively detailed analysis of interfacial interactions and identification of changes which may take place in the surface layer at the technological and exploitation levels. The literature (e.g. Bargir et al. [19], Wojciechowski and Nosal [20]) contains examples of using such methods for estimating the value of (SFE) of metals.

From the thermodynamic point of view, the higher value of (SFE) responds to the higher reactivity of the solid surface. This fact may translate the implication or acceleration of processes proceeded within the surface layer. The example can be the adhesion phenomena and the (SFE) increasing which can lead to the quicker achievement of the

energetic threshold of tacking. As a consequence, wear processes based on the adhesion phenomena can be subject to intensification too. On the other hand, an energetic intensified activity of surface layer may be used to create the improved adhesive wear and scuffing resistance. If the friction pair is lubricated by oil with anti-wear (AW) and extreme pressure (EP) additives which chemically react with the metallic surface, scuffing resistance may significantly increase.

In order to verify foregoing statements the experiment was planned in which the interdependence between (SFE) and the surface concentration of elements used in AW and EP additives has been determined. The estimation of the concentration in atomic percentages was carried out by the Auger electron spectroscopy (AES). Additionally, the influence of surface free energy on the corrosive wear of metallic surfaces was investigated. The aim of this part of the experiment was the confirmation of relationship between energy state of metallic surface and its reactivity.

## 2. Experimental methodology

Specimens used in the experiment were made of AISI 4130 steel in the shape of rings of 45 mm external diameter and the width of 12 mm. The cylinders of all specimens were subject to grinding so that their surface roughness  $R_a$  was equal to approx. 0.5  $\mu\text{m}$ . The specimens were then divided into six batches, all of which were subject to burnishing with sixth values of pressure (thus creating different levels of energy introduced to the surface layer). Burnishing of cylinder was performed by two symmetrical spherical sector-shaped rolls of 50 mm in diameter. Real local contacting asperities pressure inducing elasto-plastic deformation is difficult to be established, therefore Hertz pressure as an indicator is mentioned. Estimated plasticity index following Greenwood–Williamson approach is 2.5 consequently; contact is suppose to be plastic [25]. Particular levels of burnishing pressures comply with the following pressures of burnishing tools on machining surfaces: 1st: 1.3 GPa, 2nd: 1.64 GPa, 3rd: 1.87 GPa, 4th: 2.06 GPa, 5th: 2.22 GPa, and 6th: 2.36 GPa. Kinematic conditions are burnishing speed—100 m/min, burnishing feed—0.08 mm/rev., number of tool pass—2, lubricated by a 1 to 1 mixture of mineral oil and kerosene.

Systematic areal morphological analyses were performed, thanks to optical interferometer on milimetric region relevant to contact surface during experimental tribological investigations. The area of 1.2 mm  $\times$  0.9 mm in five parts of cylindrical surfaces every 72° were performed. Metrological analyses have been done very carefully and consciously taking into consideration calibration as well as transfer function and measurement limitations of selected topometric device.

The (SFE) of rubbing bodies was established on the basis of the measurements of static contact angle on the surfaces of specimens, thanks to goniometer PG3 made by Fibro System AB after cleaning with propanone and then drying. On the surface of the prepared specimens, drops of special trapped, drop method with pure water, diiodomethane and formamide of 2  $\mu\text{l}$  was performed. It means that each drop is released from the applicator as soon as contact with the surface is made. The contact angle between the surface of the specimen and the tangent plane to the surface of the

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