



PHYSICAL ASPECTS OF WEAR OF THE PISTON-RING-CYLINDER UNIT

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Abstract

The research in presented paper has shown that the physical aspects of interfacial phenomena, described by the total value of surface free energy and the values of its components, make it possible to select more suitable materials for sliding pairs. The total value of surface free energy depends on the molecular structure and the bonds characteristic of a given material and determines its hardness. In order to reduce friction losses in a sliding pair which is being designed, it is proposed to match such materials for the pair that the surface of one of them has a high sum of surface free energy components originating from van der Waals interactions while the other material's surface has a possibly low value of the sum. Furthermore, proper values of the components of surface free energy ensure proper wettability with lubricating oil. Pursuing the practical goal of this research, a new piston packing ring/combustion engine PRC unit cylinder liner sliding pair was designed and made.

Keywords: Surface Energy, Wear, Coatings, Nitriding, Diesel Engines

1. Introduction

Interfacial forces produced by intermolecular interactions occur on the surfaces of sliding pair components in both rotary motion and to-and-fro motion. In solid/liquid and liquid/gas interfacial regions atoms belonging to each of the phases are subject to a different system of forces than atoms located within the phases [1]. Atoms at an interface are attracted by both their own phase atoms and the adjoining phase atoms whereby they are located in an asymmetric field of forces. When the forces of attraction towards one of the phases are greater, the atoms migrate into the phase until they reach an equilibrium through changes in the distances between the atoms located at the interface [5]. The differentiation of forces in the interfacial region is the cause of many phenomena such as: adsorption, wetting, adhesion and so on.

The state of phase boundaries can be described on the basis of thermodynamics [6]. Various thermodynamic functions such as: internal energy (U), free energy (F) and free enthalpy (G) (also called the Gibbs function) are used for this purpose. In diphasic systems one can distinguish a region of pure phases, referred to as α and β , and a region of transient surface phase σ between the boundary phases [7]. Therefore free enthalpy G (at a constant temperature and pressure) or free energy F (at a constant temperature and volume) is used describe surface properties. Hence interfacial tension γ is defined as:

$$\gamma = \left(\frac{dF^s}{dA} \right)_{T,V} \quad \text{and} \quad \gamma = \left(\frac{dG^s}{dA} \right)_{T,p}, \quad (1)$$

were:

γ – surface free energy,
 F – free energy,
 A – surface,
 G – free enthalpy.

Interfacial tension γ is also referred to as interfacial free energy or in short, interfacial energy (especially in the case of solids). When air is one of the phases or the considered phase adjoins a vacuum, then instead of the attribute ‘interfacial’, the attribute ‘surface’ is used. In his latest comprehensive study [18] H. Lyklema recommends to use the term interfacial (surface) tension for both liquids and solids. Sometimes instead of γ , symbol F_A^S , referred to as excess surface free energy, is used. In the present work, surface free energy γ and surface tension are used for respectively solids and liquids.

2. Calculation of surface free energy from surface tension of molten solid body

It is difficult to determine surface free energy for solids. According to many researchers, it is possible to calculate surface free energy from measurements of the free surface of melted solids [18]. Such problems feature prominently in metallurgy where the surface tension of fused metals is of major importance [3]. Allen [2] compared surface tension values for metals at their melting points and found a clear relationship between fusion temperature and surface tension for different metals. [5]. The relationship between surface tension and temperature is expressed by the Gibbs-Helmholtz equation:

$$\gamma_s = \gamma_m + \frac{d\gamma}{dt}(T - T_m), \quad (2)$$

where:

γ_s – surface tension of molten metal at temperature T ,
 γ_m – surface tension of molten metal at fusion temperature T_m ,
 T_m – the fusion temperature of the metal,
 $\frac{d\gamma}{dT}$ – Temperature coefficient, whose value is always negative for metals, was introduced [1].

3. Calculation of surface free energy from Young’s modulus and other parameters

R.J. Good [10] proposed a relationship between surface free energy and Young’s modulus, assuming that the value of Young’s modulus E is a consequence of intermolecular force F_r :

$$E = r_0 \left(\frac{dF_r}{dr} \right), \quad (3)$$

where:

E – Young’s modulus,
 r_0 – a distance between the centres of molecules being in equilibrium between attractive and repulsive forces,

F_r – the force of intermolecular interactions at distance r .

Expression (3) holds for intermolecular distance r equal to r_0 and for constant temperature. From R.J. Good's considerations [10], based on the Lennard-Jones equation [17] for the energy of a system of molecules versus the distance between them, the following expression interrelating surface free energy with Young's modulus was derived [10]:

$$E = \frac{32\gamma_s}{r_0} \Rightarrow \gamma_s = \frac{Er_0}{32}, \quad (4)$$

where: Young's modulus E and distance r_0 are in respectively pascals (Pa) and meters (m) and calculated surface free energy γ_s of a solid is in joules per square meter (J/m^2) or newtons per meter (N/m).

Expression (4) allows one to estimate surface free energy on the basis of Young's modulus of a solid body and the intermolecular distance at which intermolecular interactions are at equilibrium. Since the material property resulting from intermolecular interactions is taken into account through expression (4) it is possible to calculate the total surface free energy if one knows the kind and number of bonds in a given solid. Since the surface free energy calculated on the basis of Young's modulus is for a material devoid of lattice defects, it may be considerably overestimated.

It follows from the above considerations that surface free energy is a result of interactions characteristic of the molecular structure of a given phase. Another material property is hardness and similarly as surface free energy it depends on a given material's structure. Material hardness is resistance to the forcing of elastic and plastic deformations. Therefore it is associated with volume elasticity modulus K which is a measurable and, as opposed to hardness [23], well defined quantity. The hardness of selected materials versus their volume elasticity modulus K is shown in fig. 1.

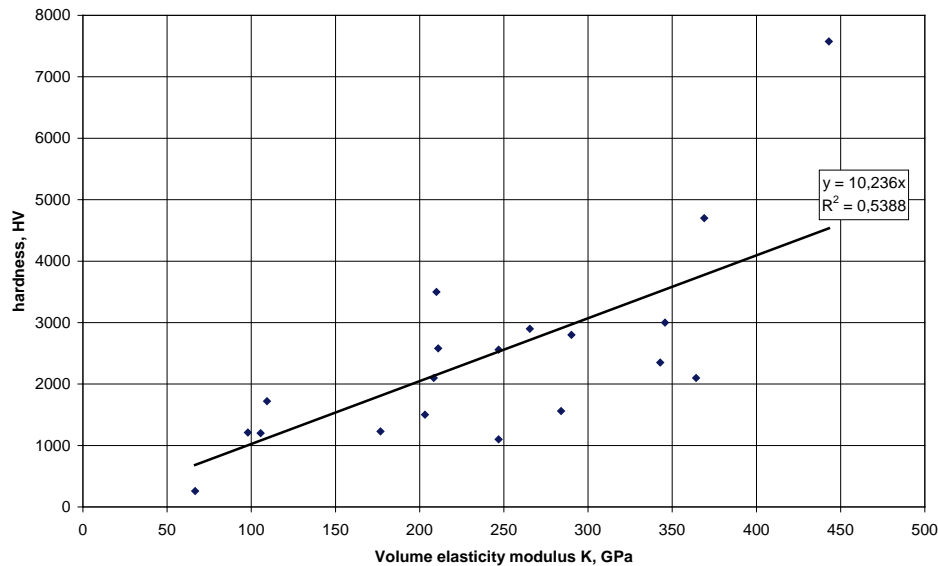


Fig.1. Hardness HV versus K for hard materials

By approximating the relation shown in fig. 1 with a linear function the following expression was obtained:

$$HV \cong a \cdot K \cong 10.236 \cdot K, \quad (16)$$

where:

HV – Vickers hardness, dimensionless quantity,

K – the modulus of volume elasticity of a perfect crystal [GPa],

a – a constant equal to 10.236 [1/GPa].

According to A. Witek [22], the value of the volume elasticity modulus is consistent with the Marvin Cohen (Berkeley University) theory proposed in 1985 and expanded in 1987. The theory allows one to calculate (with an error below 2%) the modulus of volume elasticity from this equation:

$$K = 1761 \cdot r_0^{-3.5}, \quad (6)$$

where:

K – the modulus of volume elasticity of a perfect crystal [GPa],

r_0 – an equilibrium distance between atoms or ions, i.e. the length of a chemical bond in the crystal lattice [angstroms].

According to the Cohen theory, the modulus of volume elasticity can be calculated from the bond length. Volume elasticity coefficient K is related to Young's modulus E by the following formula [24]:

$$K = \frac{E}{3(1-2\nu)}, \quad (7)$$

where:

K – a modulus of volume elasticity [Pa],

E – Young's modulus [Pa],

ν – a Poisson fraction of 0-0.5.

Young's modulus in turn is related through relations defined by R.J. Good [10] (described by formula 15) to surface free energy. Hence total surface free energy and hardness are proportionally correlated through the modulus of volume elasticity and the Poisson fraction as follows:

$$\gamma_s = \frac{Er_0}{32} = 3Kr_0 \frac{1-2\nu}{32}, \quad (8)$$

where:

the meaning and the units of all the variables are consistent with the denotations in equations (4) and (7).

Using equations (5), (6) and (8) the following expression interrelating surface free energy γ_s , hardness HV , intermolecular distance r_0 and Poisson fraction ν was obtained:

$$\gamma_s \cong 307 \cdot HV \cdot r_0 \frac{1-2\nu}{32}, \quad (9)$$

where:

γ_s – surface free energy [mN/m],

HV – Vickers hardness, dimensionless quantity,

r_0 – a mean intermolecular distance [nm],

ν – a Poisson ratio of 0-0.5.

Equations (8) and (9) were formulated for a perfect crystal free of lattice defects. Their application is, however, limited since they yield, similarly as equation (23), overestimated surface free energy values.

3. Calculation of surface free energy from its components

F.M. Fowkes [8] proposed to divide surface free energy into the following components:

$$\gamma = \gamma^d + \gamma^m + \gamma^h + \gamma^o, \quad (10)$$

where:

γ^d – a dispersion component,

γ^m – a metallic bonds component,

γ^h – a hydrogen bonds component,

γ^o – other components, e.g. an ionic component, a covalent bonds component, etc.

In a simplified formulation, the surface free energy of liquids consists of a dispersion part and a polar part. For example, the surface free energy of water is 72.8 mN/m and it consists of dispersion part $\gamma^d = 21.8$ mN/m and polar part $\gamma^p = 51$ mN/m. Water has neither a metallic component nor a covalent component.

There are several methods of determining surface free energy components, based on solid body wetting phenomena. They employ two or three calibrating liquids with known surface free energy components and assume that surface free energy has only two components: a dispersion component and a polar component [13]. The latter is composed of Keesom (permanent dipoles) and Debye interactions (inductive dipoles) of the dipole-induced dipole type, of confirmative and multipole interactions and hydrogen bonds:

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad \text{and} \quad \gamma_S = \gamma_S^d + \gamma_S^p, \quad (11)$$

where:

γ_L – surface free energy as a sum of dispersion and polar interactions for the liquid,

γ_S – surface free energy as a sum of dispersion and polar interactions for the solid,

γ_L^d – the dispersion part of the liquid's surface free energy,

γ_L^p – the polar part of the liquid's surface free energy,

γ_S^d – the dispersion part of the solid's surface free energy,

γ_S^p – the polar part of the solid's surface free energy.

The above measuring methods are: the Fowkes method [8], the Owens-Wendt method [12] and the Wu method [24]. The Owens-Wendt and Wu methods are based on measurements by two calibrating liquids. The accuracy with which the methods identify dispersion and polar interactions considerably improves when a third calibrating liquid is employed. Currently the Owens-Wendt and Wu methods are being replaced with the van Oss-Good acid-base method with three calibrating liquids, which is based on the Lewis theory of acids and bases [11] and Fowkes's concept of components [9]. The method is still under development and requires further theoretical-experimental research [24].

4. Taking interfacial phenomena described by surface free energy into account when matching materials for sliding pairs

Considering the above, it is proposed to match materials for friction pairs also on the basis of a quantitative description of interfacial phenomena, using calculations and measurements of the surface free energy of solid bodies [16]. In order to reduce friction losses in a sliding pair which is being designed, it is proposed to match such materials for the pair that the surface of one of them has a high sum of surface free energy components originating from van der Waals interactions while the other material's surface has a possibly low value of the sum (fig. 3).

The two surfaces should have high hardness, i.e. a high value of the total surface free energy. Thanks to the other surface's low sum of van der Waals interactions frictional resistance will be reduced due to a reduction in the work of adhesion to this surface, especially in mixed friction conditions.

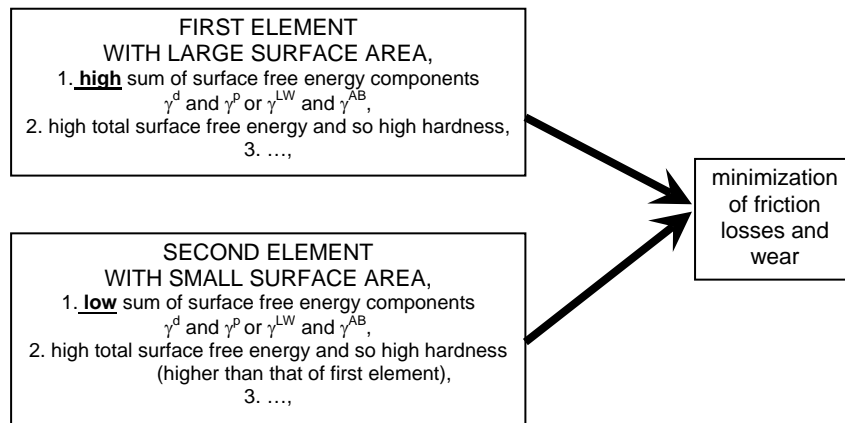


Fig.3. Scheme of matching sliding pair elements [16]

Moreover, the large difference between the sums of surface free energy components is due to the materials' insolubility in the solid state, which is pointed out by Bowle in his numerous papers. Thanks to the use of surface free energy and its components for matching sliding pair elements this process can be described quantitatively [15]. Especially in the case of the second element it is postulated that, except for the generally low value of the surface free energy component originating from dispersion forces, the dispersion component be dominant relative to the other components. If the elements are so matched, friction losses will be reduced. In mixed friction conditions, for which, in the author's opinion, the proposed solutions will be most beneficial, the features of the second element's surface will contribute to a reduction in friction losses thanks to their reduction in the boundary layer formed on the surface of this element.

5. Calculations of surface free energy of exemplary materials for sliding pairs

5.1. Calculations of surface free energy from Young's modulus and other parameters

Calculations based on Young's modulus give a full picture of surface free energy. As mentioned above, one can use equation (4) for this purpose. The calculated values of surface free energy γ for the particular materials, Young's modulus E , hardness HV , Poisson fraction ν and other are shown in table 1.

Tab. 1. Surface free energy values calculated from Young's modulus (γ_Y), hardness and Poisson fraction (γ_{HV}) and surface tension at melting point (γ_{Ti})

Material	Young's modulus E , GPa	Hardness HV	Poisson fraction Y	Melting point T_m , K	Temperature coefficient $d\gamma/dT$, mN/Km	γ_Y mN/m	γ_{HV} mN/m	γ_{Ti} mN/m
Cast iron EN-GJL-200	100 [20]	250**	0.25 [20]	1500 [3]	-0.49 [3]	875	342	2460
Nitrided cast iron EN-GJL-200	200 [20]	800**	0.25 [20]	1500 [3]	-0.49 [3]	1250	1093	2460
TiN	590 [4]	2100 [4] (1600)*	0.23 [20]	3223 [4]	-0.25 [3]	3503	2067 (1574)*	2734

* values for coating, ** measurement values

Similarly, surface free energy values were calculated from relation (9) for surface free energy γ_{HV} as a function of hardness HV and Poisson fraction ν . The values are presented in table 6 which also shows surface free energy values calculated on the basis of molten solid surface tension γ_{Ti} , using relation (2). Although the presented methods of estimating surface free energy yield different results, they are still useful considering that there are no other methods of estimating total surface free energy. In the author's opinion, the method based on hardness and the Poisson fraction is the most adequate, mainly because of the fact that hardness is resistance to the forcing of elastic and plastic deformations. The method's applicability is limited to very hard (above 200 HV) materials.

5.2. Measurements of surface free energy components from angle of wetting

The measurements were carried using a D2 Krüß goniometer with the DSA (Drop Shape Software). Three calibrating liquids with known surface free energy polar component γ^p and dispersion component γ^d for the Owens-Wendt, Fowkes and Kaelble methods and with known component γ^{LW} and component γ^{AB} for the van Oss-Good acidic-basic method were used for the measurements. The calibrating liquids were: water, formamide and diodomethane. The measurement results shown in table 3 confirm that after nitriding the dispersion component increases, which is accompanied by a slight increase in the sum of the components generated by van der Waals forces. Table 4 shows the results of surface free energy dispersion and polar component measurements for different coatings deposited using the PAPVD method.

Tab. 3. Measured surface free energy components of cast iron EN-GJL-200 before and after nitriding [16]

Material	Wetting angle Θ			Owen-Wendt method	Van Oss-Good acidic-basic method
	diodomethane	formamide	water		
EN-GJL-200	54.18	57.53	69.87	Sum of components: $\gamma = \mathbf{39.20}$	Sum of components $\gamma = \mathbf{36.07}$
				Dispersion component $\gamma^d = 29.06$	Component LW $\gamma^{LW} = 31.92$
				Polar component $\gamma^p = 10.14$	Component AB $\gamma^{AB} = 4.15$
					Acidic component = 0.28
Basic component = 15.51					
Nitrided EN-GJL-200 [14]	47.64	54.32	75.00	Sum of components $\gamma = \mathbf{40.41}$	Sum of components $\gamma = \mathbf{39.51}$
				Dispersion component $\gamma^d = 34.01$	Component LW $\gamma^{LW} = 35.58$
				Polar component $\gamma^p = 6.40$	Component AB $\gamma^{AB} = 3.93$
					Acidic component = 0.47
Basic component = 8.26					

Tab. 4. Sum of surface free energy components for TiN

Material	Wetting angle Θ			Surface free energy components	Calculation method	
	diodomethane	formamide	Water		Fowkes	Kaelbe
TiN [32, 33]	59.27	69.04	78.80	Sum of components γ	29.44	29.45
				Dispersion component γ^d	24.33	23.75
				Polar component γ^p	5.11	5.69

6. Experimental investigation of sliding pair and surface free energy of its elements

The influence of surface free energy and its components on tribological phenomena in a sliding pair was verified in a roll-block tester. Clinging to the counterface the specimen forms a distributed contact of 100 mm² with it. In accordance with the considerations presented in section 5, the counterspecimen was made from cast iron EN-GJL-200. Ten counterspecimens, of which five were subjected to vacuum nitriding, were prepared [19]. The specimens were made from cast iron designated in accordance with PN-EN 1560 as EN-GJL-350. As specified in section 5, their working surfaces were coated with titanium nitride, using the plasma-assisted physical vapour deposition (PAPVD) technique described in [21]. A linear speed of 1.25 m/s and a pressure of 5 MPa were used to create extremely difficult operating conditions for the sliding pairs, similar to the conditions prevailing in the first piston ring's inner dead centre area at the beginning of the internal-combustion engine's power stroke. As a result, mixed friction was obtained, as evidenced by the fact that the coefficient of friction was much above 0.01 – a value typical for fluid friction [15]. The range of tests carried out in the T05 microprocessor roller-block tribotester included measurements of friction forces and the wear and mass temperature of the specimen, which as time characteristics were archived in a computer system. After statistical handling the time characteristics were used to calculate the average friction coefficients for the sliding pairs (table 5). TiN coated specimen/cast iron counterspecimen pairs sliding in the presence of a lubricant – ELF SYNTHÈSE 5W50 synthetic oil (pairs: 12, 13, 15, 18). TiN coated specimen/nitrided cast iron counterspecimen pairs sliding in the presence of a lubricant – ELF SYNTHÈSE 5W50 synthetic oil ELF SYNTHÈSE 5W50 (pairs: 11, 14, 16, 17, 19).

Tab. 5. Plan of tests in tribotester T05

Specimen number	Counterspecimen	Load MPa	Speed m/s	Type of oil
11	nitrided cast iron	5	1.25	synthetic
12	cast iron	5	1.25	synthetic
13	cast iron	5	1.25	synthetic
14	nitrided cast iron	5	1.25	synthetic
15	cast iron	5	1.25	synthetic
16	nitrided cast iron	5	1.25	synthetic
17	nitrided cast iron	5	1.25	synthetic
18	cast iron	5	1.25	synthetic
19	nitrided cast iron	5	1.25	synthetic

The friction distance for one test run was set at 1350 m. The total friction distance was set at 20 runs. Once the sliding pair cooled down after each run, wear, being the sum of the wear of the specimen and that of the counterspecimen, was measured. The tests were conducted according to a static, determinate and complete test plan.

Tab. 6. Friction forces and friction and wear coefficients of sliding pairs tested for distance of 27000 m

SLIDING PAIR	Average tangent force N	Average friction coefficient	Average specimen temperature °C
TiN coated specimen Cast iron counterspecimen Synthetic oil Elf Synthese 5W50	28.1	0.044	54.5
TiN coated specimen Nitrided cast iron counterspecimen Synthetic oil Elf Synthese 5W50	8.0	0.015	40.5

Friction coefficients as a function of friction distance were calculated from friction force measurement results, as a quotient of the friction force and the pressure multiplied by the contact surface area. The graphs of the friction coefficients are shown in figs 5 and 6. Through regression analysis regression functions (in the polynomial form) were fitted to all the parameter values in the figures showing friction coefficient graphs. Through comparative studies the coefficients of friction of cast iron and nitrided cast iron counterspecimens sliding against TiN in the presence of synthetic oil were determined (tab. 6).

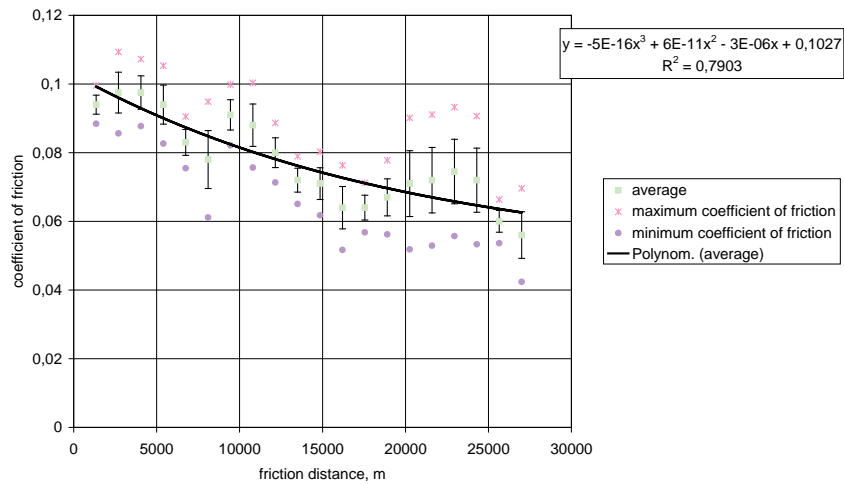


Fig.5. Coefficient of friction versus friction distance for cast iron counterface sliding against TiN coated specimen lubricated with synthetic oil

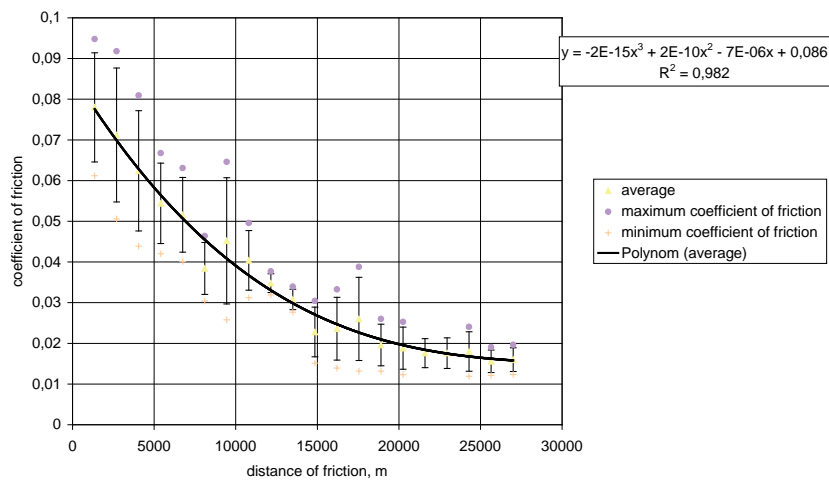


Fig. 6. Coefficient of friction versus friction distance for nitrided cast iron counterface sliding against TiN coated specimen lubricated with synthetic oil

The differences in surface free energy values between cast iron EN GJL 200 and nitrided cast iron EN GJL 200 resulted in considerable differences in the friction and wear coefficient values of the tested sliding pairs. Figures 9 show the average friction coefficients for the tested sliding pairs. The average surface free energy of the cast iron ($\gamma=1225$ mN/m) and the nitrided cast iron ($\gamma=1600$ mN/m) from which the tested counterspecimens were made, calculated from the data shown in table 4, are marked on the Y-axis. Nitriding of the cast iron resulted in an increase in total surface free energy (table 1) and consequently, in an increase in hardness. Also the dispersion component value (tables 2 and 3) of this energy increased as indicated by calculations using wetting angle measurements. High values of the surface free energy dispersion component are conducive to the formation of a uniform film of oil, which is well bounded with the base thanks to good wetting.

The causes of the lower friction coefficients are sought in the greatly reduced intensity of adhesion wear during mixed friction when microcontacts between surface irregularities occur as in the case of coatings with a lower sum of the dispersion component and the polar component of surface free energy, including the TiN coatings on the tested specimens (table 4). Also significant is the low value of the surface free energy polar component which for the TiN coating is several times lower than for the other coatings with a comparably low sum of the surface free energy dispersion and polar components (table 4). This is associated with a reduction in Keesom interactions at elevated temperatures [16].

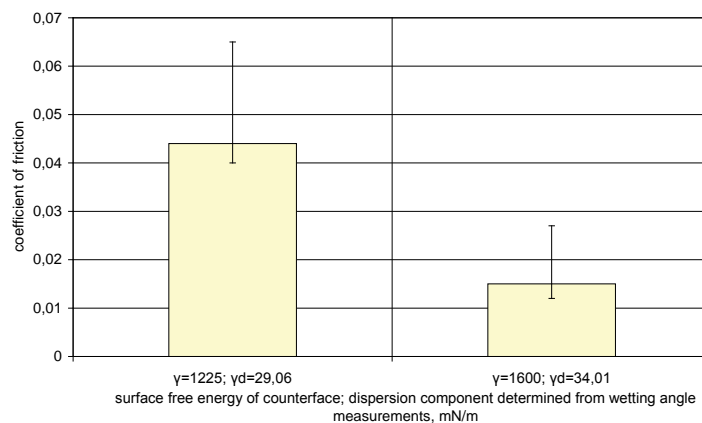


Fig. 9. Friction coefficient of sliding pair versus surface free energy of counterface

An additional factor which played a part in preventing adhesion wear was the use of synthetic oil as the lubricant. The low friction coefficients were obtained owing to the properties of the synthetic oil (mainly its ability to form an oil film already at the startup) combined with the property of the specimen's surface: low intensity of adhesion wear and the property of the counterspecimen: good durability of the lubricating film.

7. Conclusion

- Wear resistance (often identified with hardness) and wettability by a lubricant (usually lubricating oil) come to the fore among the well known material properties which should characterize sliding pair elements.
- Surface free energy estimates based on Young's modulus, hardness and surface tension at the fusion temperature allow one to assess general strength properties. For this only the main material properties are needed.
- By calculating surface free energy dispersion component γ_s^d from the Hamaker constant one can assess the wettability of a given body and consequently, the energy of adhesion to oil.

Then one can draw conclusions about the behaviour of the two interacting elements, especially in mix friction conditions.

- By calculating dispersion component γ_S^d or Lifshitz-van der Waals component γ_S^{LW} and polar component γ_S^p or acidic-basic component γ_S^{AB} of surface free energy on the basis of the angle of wetting by calibrating liquids one can gain insight into the components resulting from interfacial interactions. Using these methods one cannot calculate the total surface free energy of solid bodies characterized by metallic and covalent bonds. Nevertheless, measurements by calibrating liquids are important for the identification of the components playing a role in interfacial interactions, i.e. dispersion component γ_S^d or Lifshitz-van der Waals component γ_S^{LW} and polar component γ_S^p or acidic-basic component γ_S^{AB} .
- The estimations and calculations of surface free energy and its components done for the combustion engine's PRC unit made it possible to well match the materials for the sliding pair elements. The goodness of the match was confirmed by the results of tribological and combustion engine tests.

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