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SURFACE FREE ENERGY OF THIN-LAYER COATINGS DEPOSITED BY MEANS OF THE ARC-VACUUM METHOD

Keywords

Thin-layer coatings, arc-vacuum method, contact angle, Wilhelm's method, surface free energy.

Abstract

The aim of this research was to determine the surface free energy (SFE) of executed solids as a quantity characterizing surface properties. The most frequent method used for determining surface free energy of solids is a method based on the measurement of dynamic contact angle and advancing angle. Advancing angle can be measured by means of sessile-drop method or the Wilhelmy method. In this work the contact angle was measured with the use of the Wilhelmy's method. The liquids selected for the investigation were α -bromonaphthalene, diiodomethane, formamide, ethylene glycol, glycerin and water. These liquids are characterized by well known physicochemical properties. SFE was determined by means of the following methods: Wu, Owens-Wendt-Rabel-Kaelbl, Van Oss and Fowkes methods. Investigated thin-layer coatings turned out to be solids with medium surface free energy.

Introduction

SFE is a difference between the total energy of all atoms or surface molecules and between the energy they would have if they were situated inside the body. The measure of SFE is a work that has to be done in order to transfer atoms or molecules from the inside of the body to the surface. SFE in the critical state (i.e. in a critical temperature and pressure) equals zero, because then the differences between the phases disappear and thus the surface also vanishes [1].

1. Calculation of free surface energy of solids

The calculation of free surface energy from the measurement on the contact angle is based on Young's equation. Young's equation is a basic connection between contact angle and the surface tension of liquids, solids and interfacial tension of solid-liquid. The solution of Young's equation in relation to free surface energy of solids is possible only in the situation when we can determine the surface interfacial free energy of solid-liquid as a function of a solid and a liquid [2, 3].

The conditions of equilibrium are described by Young's equation:

$$\sigma_L \cos \theta + \sigma_{SL} = \sigma_S \quad (1)$$

where: σ_L – denotes surface tension of liquid (free surface energy of liquids)
 σ_S – denotes surface tension of solids (free surface energy of solids)
 σ_{SL} – denotes interfacial tension between liquid and solid (free interfacial energy).

The equation has two measurable values – surface tension of liquids and the contact angle. The equation has also two immeasurable values σ_S σ_{SL} . In thermodynamic categories the adhesion energy W_a (2) equals the work needed to divide the surface solid-liquid.

$$W_a = \sigma_L + \sigma_S - \sigma_{SL} \quad (2)$$

After substitution into Young's equation we obtain Young-Dupre equation

$$W_a = \sigma_L(1 + \cos \theta) \quad (3)$$

2. Experimental section

2.1. Samples for investigation

Samples for investigation were made of 1H18N9 steel. Their measurements were: 20x20x0.5mm. The shape and measurement of samples was according to the method of calculation of the contact angle of Wilhelm's method. Samples were subjected to electro polishing in a technology elaborated in the Surface Engineering Department in 3% ammonium-sulphate solution bath. On the polished samples, coatings from TiN, CrN, (Ti,Cr)N, TiN/TiC₁₀N₉₀, TiN/TiC₂₀N₈₀, the roughness and the thickness of which were presented in Table 1 were deposited by means of the arc-vacuum method.

Table 1. Parameters of roughness and thickness of the investigated coatings

Symbol of coating	Parameters of roughness			Thickness [μm]
	R _a [μm]	R _t [μm]	R _z [μm]	
(Ti,Cr)N	0.140	3.000	1.370	1.5
CrN	0.060	1.153	0.533	1.45
TiN	0.097	2.300	0.853	1.8
TiN/TiC ₁₀ N ₉₀	0.063	1.837	0.460	1.5
TiN/TiC ₂₀ N ₈₀	0.180	4.343	1.783	1.57
Steel 1H18N9	0.040	0.890	0.237	-

Standard liquids are liquids that have a well-known value of surface tension and fraction of dispersion and polar interaction. Below, the values of physicochemical properties of selected standard liquids are presented. Values presented in Table 2 are used in the calculation of SFE by methods of Wu, Owens-Wendt-Rabel-Kaelbl, and Fowkes. Values presented in Table 3 are used in the calculation of SFE by Van Oss method.

Table 2. Data of physicochemical liquids used in determination of contact angle at a temperature of 20°C [7]

Liquid	Surface tension [mN/m]			Density of liquid [g/cm ³]	Viscosity [mPa·s]
	Complete	Dispersion part	Polar part		
Water (Rabel)	72.3	18.7	53.6	0.998	1.002
Formamide (Fowkes)	58.2	39.4	19.6	1.133	3.607
Diiodomethane (Buscher)	50.0	47.4	2.6	3.325	2.762
Ethylene glycol (Rabel)	47.5	29.3	18.2	1.109	20.01
α-bromonaphthalene (Buscher)	44.4	44.4	0	1.483	5.107
Glycerol (Buscher)	62.7	21.2	41.5	1.263	924.7

Table 3. Values of the total free surface energy and its components as a result of interaction of LW and AB used in the investigation of contact angle of liquids at a temperature of 20°C [mJ/m²] [7]

Liquid	σ	σ^{LW}	σ^{AB}	σ^+	σ^-
Polar:					
Water (Ström)	72.8	21.8	51.0	25.5	25.5
Formamide (A–B)	58.0	39.0	19.0	2.28	39.6
Ethylene glycol (A–B)	48.0	29.0	19.0	1.92	47.0
Non-polar:					
Diiodomethane	50.8	50.8	0	≈0	0
(Ström)	44.4	44.4	≈0	≈0	≈0
α -bromonaphthalene (Buscher)					

Prior to contact angle measurement, samples were ultrasonically cleaned in acetone, ethanol and deionised water in sequence. Next, the samples were dried. Advancing and receding contact angles were measured by means of Wilhelm's method in Krüss K12 Tensiometer. The temperature of the contact angle was 20°C. Every angle was measured twenty times. For calculation of SFE, the values of advancing contact angle were used.



Fig. 1. Tensiometer K12 made by KRÜSS GmbH

Table 4. The average values of contact angle for the examined coatings

Coating	α -bromo- naphthalene [°]	Diiodomethane [°]	Ethylene glycol [°]	formamide [°]	water [°]
(Ti,Cr)N	25.0	36.1	44.0	51.0	76.1
CrN	29.5	43.6	45.8	53.7	77.5
TiN	23.2	40.5	44.2	47.5	65.4
TiN/TiC ₁₀ N ₉₀	24.3	35.8	39.9	45.9	61.3
TiN/TiC ₂₀ N ₈₀	25.0	40.8	45.5	55.6	71.7
Steel 1H18N9	32.1	48.5	57.5	61.5	85.0

2.2. The calculation of surface free energy of investigated coatings

2.2.1. The calculation of surface free energy by Wu's method

According to Wu surface interfacial free energy is a sum of harmonic the mean of dispersion and polar interaction multiplied by 4. Complete SFE of solids and liquids is defined as a sum of dispersion and polar interaction [4].

$$\sigma_l = \sigma_l^d + \sigma_l^p \quad (4)$$

$$\sigma_s = \sigma_s^d + \sigma_s^p \quad (5)$$

$$\sigma_{ls} = \sigma_l + \sigma_s - 4 \left(\frac{\sigma_l^d \sigma_s^d}{\sigma_l^d + \sigma_s^d} \right) - 4 \left(\frac{\sigma_l^p \sigma_s^p}{\sigma_l^p + \sigma_s^p} \right) \quad (6)$$

where: σ_l – SFE liquid,

σ_s – SFE solid,

σ_l^d – a part of SFE contributed by dispersion interaction (the dispersion component),

σ_l^p – a part of SFE contributed by polar interaction (the polar component),

σ_{ls} – interfacial SFE

The indexes denote: *l*-liquid; *s* – solids; *p* – polar interactions; *d* – dispersion interactions.

Wu has defined the adhesion work as follows

$$W_a = \sigma_l (1 + \cos \theta) = 4 \frac{\sigma_s^d \times \sigma_l^d}{\sigma_s^d + \sigma_l^d} + 4 \frac{\sigma_s^p \times \sigma_l^p}{\sigma_s^p + \sigma_l^p} \quad (7)$$

This method can be used when the measured contact angle of two liquids have the following values: σ_l , σ_l^p , σ_l^d , ($\sigma_l^p \neq 0$).

The surface free energy of examined coatings was calculated for diiomethane-water model liquid system. According to computations, the highest value of SFE was obtained for TiN/TiC₁₀N₉₀ coatings and the lowest for CrN. The value of SFE for individual coatings differs especially in polar contribution. The magnitude of value of SFE of tested coatings is limited by the following boundaries: 46.2÷56.2 mN/m.

Table 5. The value of total surface free energy and its components for tested coatings at a temperature of 20°C [mN/m] calculated by means of Wu's method for the liquid system: diiodomethane–water

Coating	σ	σ^d	σ^p
(Ti,Cr)N	49.5	41.9	7.6
CrN	46.2	38.5	7.7
TiN	52.7	39.9	12.8
TiN/TiC ₁₀ N ₉₀	56.2	42.0	14.2
TiN/TiC ₂₀ N ₈₀	49.7	39.8	9.9
Stal 1H18N9	41.3	36.1	5.2

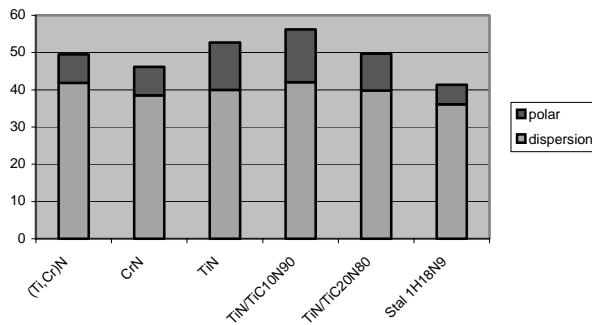


Fig. 2. The total surface free energy and its polar part and dispersion part for tested coatings by means of Wu's method

2.2.2. The determination of surface free energy by the Owens-Wendt-Rabel-Kaelble's method

Owens, Wendt, Rabel and Kaelble used the geometric mean approach to combine dispersion and polar components for the calculation of SFE [4]. In the model it is assumed that the total SFE of liquids and solids is merely a sum of both dispersion and polar components $\sigma = \sigma^d + \sigma^p$. The interfacial free energy σ_{ls} is a sum of geometric means of dispersion and polar contributions multiplied by 2.

$$\sigma_{sl} = \sigma_l + \sigma_s - 2 \left(\sigma_l^d \times \sigma_s^d \right)^{1/2} - 2 \left(\sigma_l^p \times \sigma_s^p \right)^{1/2} \quad (8)$$

Nevertheless, the work of adhesion is determined as follows:

$$W_a = \sigma_l (1 + \cos \theta) = 2 \left[\left(\sigma_l^d \times \sigma_s^d \right)^{1/2} + \left(\sigma_l^p \times \sigma_s^p \right)^{1/2} \right] \quad (9)$$

This method can be used to determine SFE of low-energy solids like polymers. The cosine of the contact angle is the function of four variables:

$$\cos \theta = f(\sigma_s, \sigma_s^d, \sigma_l, \sigma_l^d) \quad (10)$$

Table 6. The value of the total surface free energy and its components for tested coatings at a temperature of 20°C [mN/m] calculated by means of Owens-Wendt-Rabel-Kaelble's method for system water-formamide-ethylene-glycol-diiodomethane- α -bromonaphthalene

Coating	σ	σ^d	σ^p
(Ti,Cr)N	45.1	41.2	3.9
CrN	42.6	38.6	4.0
TiN	46.0	39.0	7.0
TiN/TiC ₁₀ N ₉₀	47.9	39.7	8.2
TiN/TiC ₂₀ N ₈₀	43.9	39.2	4.8
Stal 1H18N9	38.8	36.2	2.3

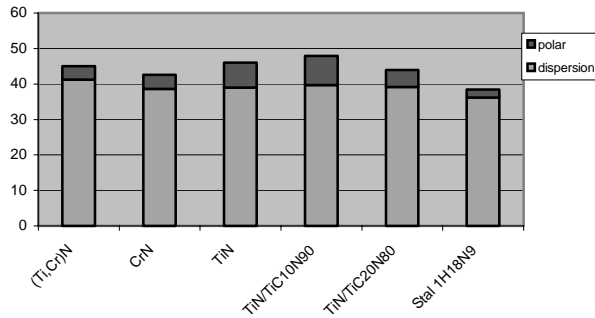


Fig. 3. The total surface free energy and its polar part and dispersion part for tested coatings by means of the Owens-Wendt-Rabel-Kaelble's method

The value of SFE of coatings tested by the Owens-Wendt-Rabel-Kaelble's method is included in the 43.9÷47.9mN/m range. The highest value of SFE was obtained for TiN/TiC₁₀N₉₀ coating and the lowest for CrN. The polar component amounts from 3.9 mN/m for (Ti,Cr)N coating to 8.2 mN/m for TiN/TiC₁₀N₉₀ coating.

2.2.3. The calculation of surface free energy by Van Oss' method

Van Oss assumed that SFE liquid and solid is a sum of Lifschits-Van der Waals and Lewis acid-base components [3]. According to Van Oss' theory two equations have been originated:

$$\sigma = \sigma^{LW} + \sigma^{AB} \quad (11)$$

$$\sigma^{AB} = 2 (\sigma^+ \times \sigma^-)^{1/2} \tag{12}$$

the indexes denote:

LW – Lifschits-Van der Waals’ component,

AB – Lewis acid-base component.

Lewis acid-base component is a geometric mean of the electron-acceptor and electron-donor component. In this theory, the work of adhesion is expressed in form of the following equation:

$$W_a = \sigma_L (\cos\theta + 1) = 2(\sigma_s^{LW} \times \sigma_L^{LW})^{1/2} + 2(\sigma_s^+ \times \sigma_L^-)^{1/2} + 2(\sigma_s^- \times \sigma_L^+)^{1/2} - \Pi e \tag{13}$$

when $\Pi e = 0$.

The determination of SFE can be conducted by solving three equations with three unknowns.

Table 7. The total surface free energy and its components for tested coatings at a temperature of 20°C [mN/m] calculated by mean of Van Oss’ method (diiodomethane – formamide – water)

Coating	σ	σ^{LW}	σ^{AB}	σ^+	σ^-
(Ti,Cr)N	44.1	41.5	2.6	6.0	0.3
CrN	40.9	37.8	3.2	5.9	0.4
TiN	43.8	39.4	4.4	14.7	0.3
TiN/TiC ₁₀ N ₉₀	44.9	41.7	3.2	18.8	0.1
TiN/TiC ₂₀ N ₈₀	40.3	39.2	1.1	12.5	0.0
Stal 1H18N9	36.9	35.1	1.8	3.5	0.2

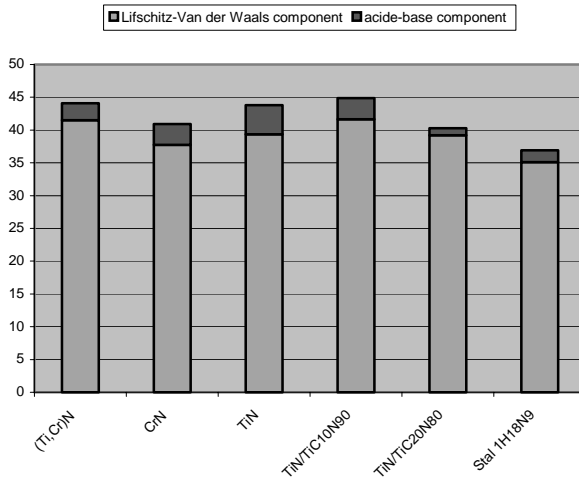


Fig. 4. The total surface free energy and its Lifschitz-Van der Waals component and the acid-base component for tested coatings by means of Van Oss’ method

The SFE of coatings for diiodometane – formamide - water liquid systems was evaluated by using Van Oss' approach. The highest value of SFE was obtained for TiN/TiC₁₀N₉₀ coatings and the lowest for CrN coatings. The differences in value of SFE of coatings are not considerable and hence up to 4 mN/m.

2.2.4. The determination of SFE by Fowkes' method

Fowkes assumed that SFE consists of two components: dispersion σ^d , which characterises London's interaction; and non-dispersion σ^{nd} which consists of remaining interactions. Fowkes established that, when using non-polar liquids, the work of adhesion can be expressed by the following equation:

$$W_a = \sigma_l(1 + \cos\theta) = 2(\sigma_s^d \times \sigma_l^d)^{1/2} \quad (14)$$

In the Fowkes' method the evaluation comprises 2 stages. In the initial stage, we have measured the contact angle for few non-polar liquids, and then we have solved the equation system by the graphic method in which we have approximated points by the polynomial of 1st order [2, 3]. In the next stage, we have determined the non-dispersion portion. The index *nd* denotes the non-dispersion portion (i.e. contributions to the σ^d resulting from other components than dispersion).

At this stage measurements of contact angle are used, where $\sigma = \sigma_l^d + \sigma_l^{nd}$.

Table 8. The total surface free energy and its components for tested coating at a temperature of 20°C calculated by means of Fowkes' method for the liquid system: water, formamide, diiodomethane, ethylene glycol, α -bromonaphthalene

Coating	σ	σ^d	σ^{nd}
(Ti,Cr)N	44.9	40.9	4.0
CrN	42.5	38.3	4.1
TiN	46.8	40.2	6.6
TiN/TiC ₁₀ N ₉₀	48.7	41.1	7.6
TiN/TiC ₂₀ N ₈₀	44.4	39.8	4.6
Stal 1H18N9	39.1	36.7	2.5

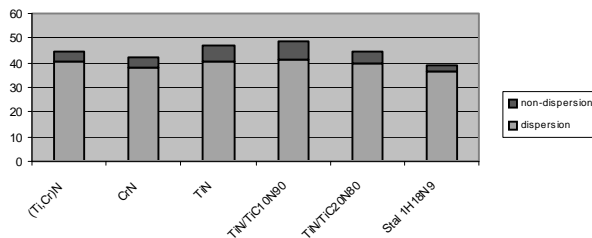


Fig. 5. The total surface free energy and its dispersion component and non-dispersion component for tested coatings by means of Fowkes' method

After analysing the results of determining the SFE by means of Fowkes' approach, it was established that the highest and the lowest value of SFE were obtained for TiN/TiC₁₀N₉₀ and CrN coatings, respectively. The difference of SFE for investigated coatings can be attributed to the variations of non-dispersion components. The value of SFE for individual coatings deposited by means of the arc-vacuum method varies between 42mN/m-48mN/m. All values of SFE for coatings are higher than the value of SFE for 1H18N9 steel.

Conclusions

From the results of conducted research, we can state that it is possible to determine the contact angle by means of Wilhelmy's method. The uncertainty of angle measurements in the Wilhelmy's approach for tested coating amounts 5°. The roughness coefficient R_a for coatings is at least ten times larger than the coefficient evaluated for polished 1H18N9 steel. The roughness of the sample's surface increases the uncertainty of contact angle measurements for samples covered by coatings. Using the determined contact angles, it is possible to calculate SFE of tested coatings. The differences in value of SFE for tested coatings are insignificant, only to 5 mN/m. The obtained results show that TiN/TiC₁₀N₉₀ and CrN coatings have respectively the highest and the lowest SFE. Obtained results show, that in the investigated coatings mainly dispersive interaction occur. Part of polar interaction is not large. According to our research, we are able to forecast that the coating with higher SFE will build the stronger adhesion junctions in friction nodes than the coatings with lower SFE. The research shows also that CrN coatings should be characterised by the lowest friction coefficient among 5 tested coatings. Due to analysing properties of coatings, it is possible to make a preliminary selection of coatings for specific utilitarian purposes.

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Swobodna energia powierzchniowa cienkowarstwowych powłok nakładanych metodą łukowo-próżniową

Słowa kluczowe

Powłoki cienkowarstwowe osadzone metodą łukowo-próżniową, kąt zwilżania, metoda Wilhelmięgo, napięcie powierzchniowe, swobodna energia powierzchniowa.

Streszczenie

Celem pracy było wyznaczenie swobodnej energii powierzchniowej (SFE) badanych ciał stałych jako wielkości charakteryzującej własności powierzchni. Najczęściej spotykaną metodą wyznaczania swobodnej energii powierzchniowej ciał stałych jest metoda oparta na pomiarze dynamicznego kąta zwilżania, kąta wstępującego. Kąt wstępujący może być mierzony metodą osadzonej kropli albo metodą Wilhelmięgo. W pracy mierzono kąt zwilżania metodą Wilhelmięgo. Jako cieczy modelowych użyto: α -bromonaftalenu, diiodometanu, formamidu, glikolu etylenowego, gliceryny oraz wody. Ciecze te charakteryzują się dobrze poznanymi własnościami fizykochemicznymi. SFE wyznaczono metodami: Wu, Owensa-Wendta-Rabela-Kaelble'a, Van Ossa oraz metodą Fowkesa. Badane powłoki cienkowarstwowe okazały się materiałami o średniej wartości swobodnej energii powierzchniowej.

