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A method for determining the thickness of tribological performing thin layers formed by selective transfer

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Abstract. A new stage in the research of the unconventional friction couples (alloys or pseudo-alloys in thin layers) to implement them in the designing and execution of machines is represented by the modern friction couples which are based on selective transfer (transfer of a material from one element of the friction couple to the other in the presence of a lubricant forming a superficial layer, antifriction, very thin, the order of several microns, which behaves very well to friction and wear). A selective transfer can be achieved with certainty in a friction couple, lubricated with glycerine or with a special lubricant, if in the friction area there is a material from alloys on based copper. The thin superficial layer formed through selective transfer in the friction process of a friction couple is made of the elements of the alloy based on copper, where the copper is predominant. Hence results the practical necessity to determine the thickness of superficial thin layers (0.1 - 4 µm) obtained in the friction couples, by selective transfer (mass selective transfer through diffusion from one element of the friction couple to another, in conditions of local energies favourable to the transfer process and in the presence of relative motion). The aim of this paper is presenting and explaining a methodology for determining the thickness of layers formed by selective transfer, in the friction process, on the surfaces of elements friction couples.

1. Introduction

By bombarding a thin object with a focused beam of electrons, a part of the electrons passes through the object or disperses without loss of energy. The other part of the electrons lose partially or wholly the energy and afterwards are either leaving from the object, or are absorbed by the material of the object.

Electrons beam energy is consumed at the ionisation or the excitation of the atoms and molecules of the object material.

Since the early 20th century, the braking law of the electrons was known, and described through a simple exponent known under the name Lenard's law [1].

For the analysis of the thin layers, it is required to take into consideration this law, in order to present as accurately as possible the processing mechanism of the electrons interaction with the thin layers. Viatskin showed in [1] through an experiment as the absorption curve of electrons with an

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energy of 0.4 to 500 keV has a character, not of simple exponent, but much more complex, mathematically expressed by the following relationship:

$$I = I_0 e^{\mu x q(z)}, \quad (1)$$

where: I - is the intensity of X-rays generated by the substrate, in the pulses per sec; I_0 - intensity of X-rays generated by the base material, in the pulses per sec; μ - linear absorption coefficient in m^{-1}; x - thickness of the object after the direction of dispersion radiation, in m; $q(z)$ - coefficient that depends on the order number of the elements composing the object, with values between $5 < q < 30$ (for beryllium $q = 5$, and $q = 27$ for gold).

The relation (1) allows to specify the average route of electrons in the substance of the object and therefore, we can get closer to the excitation area of X-rays in the object [1-5] with greater accuracy. Therefore this paper presents a practical method for determining the thickness of superficial thin layers (0.1-4 μm) obtained in the friction couples and which is functioning with selective transfer [6-12].

A practical possibility for measuring the thickness of thin layers consists in the focusing of the incident radiation of electrons beam in the thickest area, respectively thinnest area of the selective layer, its penetration and reading the number of pulses per second, i.e. I for each case, and I_0 for basic material - steel [13-15]. The penetration depth, x_m of the electrons beam is the dependence upon the atomic mass, A of the element, the order number z of the elements composing the object, the density, ρ of the sample, the tension of acceleration U, according to of the relationship [6, 8]:

$$x_m = 1.1 \cdot 10^{-13} \frac{A \cdot U^2}{z \cdot \rho} \text{ [mm]}, \quad (2)$$

and x - the thickness of the object after the direction of dispersed radiation, results from relation (1).

The moment in which the electrons had penetrated in the layer is determined by the apparition of the dispersed radiation, as the answer of the substrate.

The principal inconveniences of this method are:

- there is the possibility that the thickness of the layer could be so small, that the tension for which the penetration occurs may be of the critical potential for the excitation of the substrate;
- there is the possibility that the absorption in the layer may be very high, for the wavelength of the X-radiation, in order for the substrate to answer, and the radiation can't penetrate the layer;
- the precision of the measurement of the acceleration tension is pretty diminished.

2. Description of the method

An alternative method to determine the thickness of thin superficial layers was using an own method for assessing the thickness, by quantitative investigations. By this method, the investigations have been performed using an electron microprobe (type JXA – 5A JEOL), a device capable of such investigations. Electronic microprobe it can also use for analysis the composition of the superficial thin layers which are obtained in conditions of a selective transfer and can detect elements that are in concentrations of 10^{-3} % [8]. With the help of electron microprobe, steel samples (OL37 which is similar to the european/international steel, S235JR) on which there is transferred a thin superficial layer in the conditions of selective transfer, in the areas of contact with the samples of brass (based on aluminium), were bombarded with an electrons beam.

The layer thickness has been measured with a proper precision (± 10 Å) using the special device of the installation.

The microprobe is able to read the number of pulses per sec through the electronic display. Thus, it recorded the number of pulses for the K_α radiation of iron emitted by a clean area (where there is no transferred layer), respectively the number of pulses in the same period of time, for the same radiation, emitted by an area on which there is transferred layer [8, 9]. Using, the absorption law of radiations K_α of iron, for a layer with complex composition (layer deposited by selective transfer), given by relation (1), we managed to assess the thickness of these layers [8, 9].

The incident radiation of the electron beam was focused in the thickest area, respectively the thinnest area of the selective layer, by reading the number of pulses/sec, i.e. I for each case, and I_0 for basic material from steel (figure 1). For each area there are three records in order to establish I and I_0, as an average value. Must be mentioned that the areas thickest and most thin of the transferred film are chosen by many measurements of the thickness in the same area, marked on the surface of the sample.

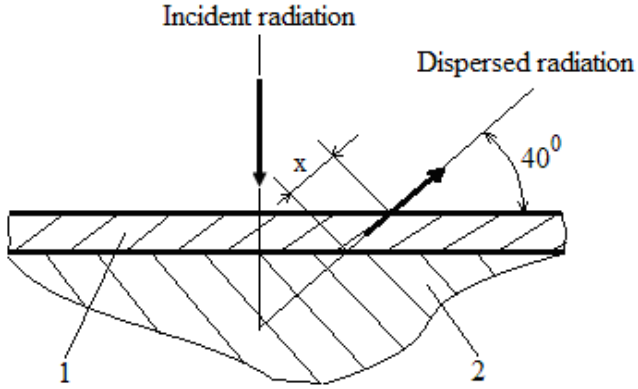


Figure 1. Schematic diagram for determining layer thickness formed by selective transfer with the help of microprobe electron: 1 - layer formed by selective transfer; 2 - base material.

3. Experimental results

For most samples (from aluminium bronze/S235JR; chemical composition of aluminium bronze is: about 83.5% Cu, 10% Al, 35% Zn, 2% Fe, 2% Mn, 0.3% Pb, 0.1% Sn, 0.05% As) tested on Timken tribometer to determine the thickness of selective layer after 2 hours of operation by friction at speeds and different loads, lubricated with glycerine and water, was followed and the time evolution of the selective layer thickness for different loads and the same speed, at different speeds and for the same load, is shown in figure 2 a, b.

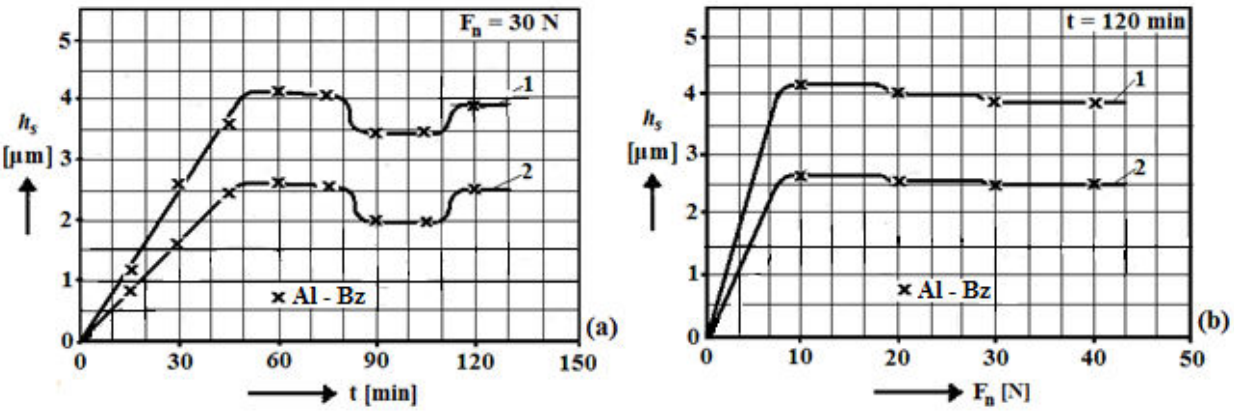
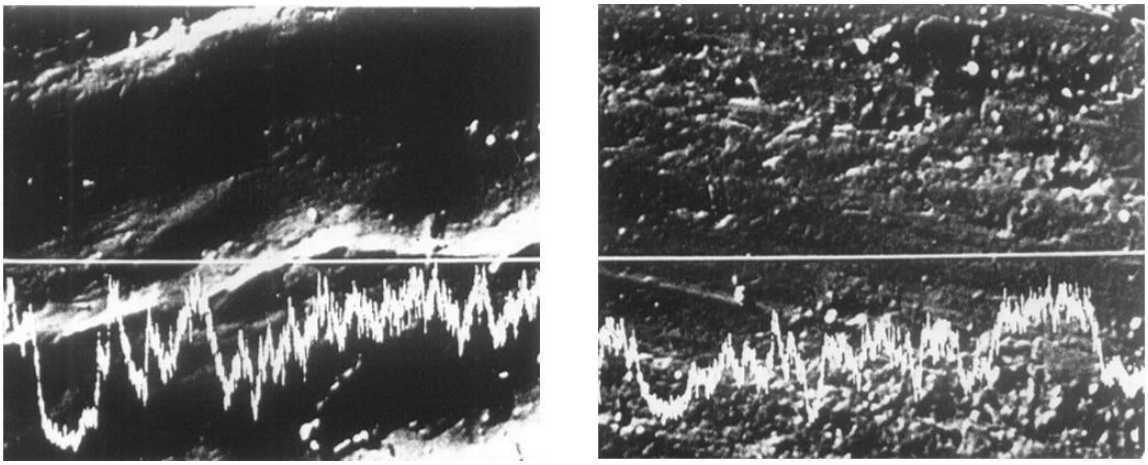


Figure 2. Variation of selective layer's thickness h_s function of the friction duration **t** at constant load (a); function of load F_n and constant friction time (b) of aluminium bronze at different sliding speeds (curves 1 to 0.93 m/s, curves 2 to 1.86 m/s).

It must be mentioned that the measurement was made after tribological tests and tribological conditions were used only to obtain the transfer films.

Images of the secondary electrons in figure 3 shows the topography of the surface of steel samples, on which was transferred a thin superficial layer of copper in the aluminium bronze in the conditions of selective transfer, based on which one can appreciate the uniformity of the layer. In figure 3 are showed the profiles of the variation of the concentration of copper (in the bronze aluminium composition) and iron (in the steel composition) on the surface areas that the film was transferred in the conditions of selective transfer after the direction marked with a white line.

The bottom half of the profiles shown in figure 3 represents the variation in the concentration of Fe in the base material (steel), in areas where the film was deposited by selective transfer in the friction process, and the upper part (of the profiles) represents the concentration variation Cu, in the film obtained by selective transfer.



(a) (b)

Figure 3. Images of the secondary electrons x 300 at the couple aluminium bronze/steel OL37 lubricated with glycerine: for v = 0.93 m/s (a), to v = 1.86 m/s (b).

If I and I_0 are read to determine the thickness transferred layer x (figure 3), we must know the value μ of the absorption coefficient, which is determined as follows: in the literature [16-22] is given the ratio μ/ρ [m^2/kg], called mass absorption coefficient (table 1).

Table 1. Parameter values needed to calculate the mass absorption coefficient.

Alloy	Element	z	c_i	μ_i/ρ_i	ρ_i	μ/ρ	ρ	μ	$q(z)$
Aluminium bronze	Cu	29	85.00	7.98	8930	8.562	8360	$7.16 \cdot 10^4$	9.9
	Al	13	9.00	7.34	2710				
	Zn	30	2.00	8.85	7140				
	Fe	26	2.00	5.95	7870				
	Mn	25	1.60	43.1	8140				
	Pb	82	0.25	35.4	11340				
	Sn	50	0.10	38.2	7310				
	As	33	0.05	12.1	5700				

In the case alloys, μ/ρ is calculated with the relation:

$$\frac{\mu}{\rho} = \sum_{i=1}^{n} c_i \frac{\mu_i}{\rho_i}, \tag{3}$$

in which: c_i - is the concentration of the alloying element i, in %; μ_i - the coefficient of absorption of the element i, in m^{-1}; ρ_i - the density of the alloying element i, in kg/m^3.

From experimental results and from the picture above (figure 3) it can be observed the uniformity of the format layer through a selective transfer. Figure 3, respectively, represents the image of the

secondary electrons increase by 300, where it can be observed the profiles of variation of the Cu and Fe concentration from the surface of the zone where it had been realized the transfer of a thin superficial layer in condition of a selective transfer after a direction marked by the white line.

The image of secondary electrons presents the relief of steel sample on which it had been transferred a thin superficial layer of Cu from the bronze which had functioned in the condition of the selective transfer and it can appreciate the uniformity of the layer. The inferior part below the profiles reproduced in figure 3 represents the variation of the Fe concentration from the base material (steel) in the zone where it has been deposed the superficial layer through the selective transfer in the friction process, and the superior part of the profiles represents the variation of the Cu concentration from the obtained layer through the selective transfer.

The more luminous zones are details of the surface bulged out, and the darkness zones are depressions in the surface of the sample. The results obtained by this method (figure 2) are in agreement with those determined in the previous method.

A quantitative assessment of selective layer thickness shows the increase in time until it reaches a maximum (optimum), after that the transfer occurs in the reverse, remaining in function of the friction duration in the range of 0.1- 4 μm, but varies much more.

Layer thickness can be reduced 10-fold and to increase again. These changes in thickness correspond to observations at samples from steel OL37, which has worked together with the alloys on base copper at stress through friction, on which it is formed a layer of copper, which is related to the transfer of copper on the steel surface.

Figure 4 shows the transferred layer, in depth, with a porous structure, clearly delimiting the layer 1, interface 2 between layer 1 and the structure of the base material 3 (steel).

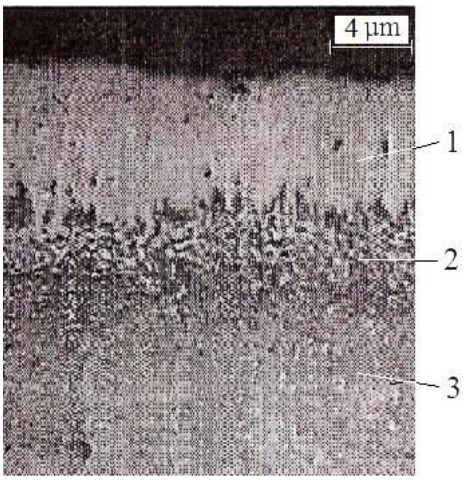


Figure 4. Selective layer structure in depth, (increased 12500:1): 1 - transferred layer, 2 - interface, 3 - base material.

4. Conclusions

The practical necessity to measure the thickness of the thin layers with a thickness of 0.1 - 4 μm obtained through different procedures, including the friction in the condition of a selective transfer, had imposed this method using the electronic microprobe.

Practically, this method can't be replaced in this particular case if it is necessary to determine the thickness of the thin layer of deficient and expensive materials like brass, bronze, copper (Cu), tin (Sn), zinc (Zn) and lead (Pb).

The reason that this method was selected from other methods of measurement, of the thickness of the thin layers, available (measurement on an optical microscope) is that the others do not enable the measurement of the layer with such a thickness.

The impossibility to measure layers so thin appears first of all because of the limited magnification of the optical microscope, and secondary because of the problems that occur at the samples preparations.

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The irregularity of the layer may be caused by the irregularity of the asperity of the steel probe's surface on which it had been transferred a thin superficial layer.

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