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Ferrocene derivatives in boundary lubrication

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1. Introduction

Most of the publications dealing with organometallic additives discuss metal dialkyldithiophosphates [1, 2]. The exceptions are organometallic tin and iron compounds used in laboratory and model investigations as friction modifiers and kinematics' pair surface modifiers [3, 4]. The investigation results of the interaction of carboxylic acids with the surface during friction seem to be quite interesting. This kind of study has rarely been reported in tribological literature within the last 15 years [5].The results of the latest investigation of materials of peculiar future usage, as well as limiting energy losses caused by friction and wear lay foundation of the present progress in machine building. Already in 1966, it was estimated that approximately 30 % of raw materials used in the process were lost due to wear [6]. The loss of materials and energy may be considerably limited when the materials and lubricants are appropriately chosen. Attempts to achieve the best effect made it possible to find many, but not all, solutions of the problem [7]. The reason is that mechanical, physical and chemical processes which take place in a friction pair have not been examined and exhaustively described yet. The development and application of new researches concerning kinetics, as well as friction and wear mechanisms, have great impact on surface durability of machine elements. Therefore, it is important to precisely examine mechanisms which govern the behaviour of lubricants and additives in boundary friction conditions. Our researches aim at presenting relationships between various media in friction processes in order to characterise those processes. It is known that lubricant oils without additives are insufficient because they do not minimalise friction and wear of working elements [8]. In modern constructions, friction pairs that resist extreme loads are applied. Thus, the demand of new, synthetic additives still increases, since the additives complement basic lubricants [9-11]. Scientific literature proves that the creation of the surface layer has crucial impact on the friction and wear processes [12]. Among numerous additives undergoing examination, ferrocene derivatives evoke the greatest interest as the potential modifiers, although their properties, as well as probable possibility to create protective layers on friction surfaces have not been exhaustively discussed so far. Relatively high thermal stability, the presence of metal in the 'sandwich' structure, and first and foremost possibility of numerous ferrocene modifications let us expect to obtain some interesting and profitable phenomena on the friction surface. This is the reason why ferrocene derivatives are the objective of this paper.

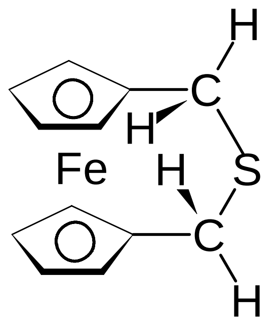
Project aim and subject. The subject of this paper is the selected results from the studies on the evaluation of the effect of some paraffin oil based liquid lubricants modified with ferrocene derivatives upon friction surface modification.

The effect of lubrication on wear. Senatorski's studies have shown that there is an important influence of oil viscosity on wear rate in the conditions of analysis of wear resistance of carburized, nitrided and chromium-plated layers [13]. One should also keep in mind adsorption – the first initial stage of lubricant - surface interaction which often determines both the type and course of friction and the character of wear changes. Both the above considerations and mathematical models are developed with the aim of underlining the effect of lubricant – friction pair surface interaction on the performance of friction pairs during operation.

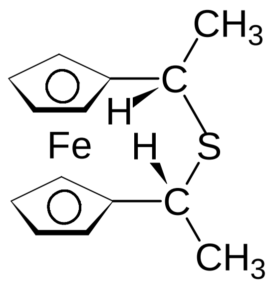
2. Experimental

2.1. Ferrocene derivatives. Wear tests

From among interesting and effective compounds, the following compounds have been chosen: 1,1'dialkyl-2thia [3] ferrocenophane 1SJ -4SJ, see Fig. 1.



1S



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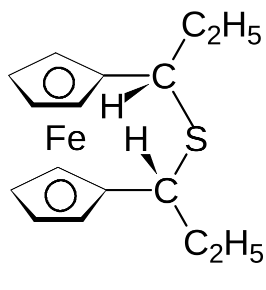

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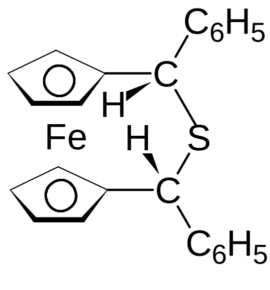


4S

Fig. 1 Structure of searched 1,1'dialkyl-2thia [3] ferrocenophane

In order to find the most appropriate work conditions, the influence of concentration onto the wear scar diameter was investigated on the basis of unsubsidized ferrocene = FcH and 3SJ compound see Fig. 2.

In the next tests the following 1,1'diethyl-2thia [3] ferrocenophane 3SJ and wear tests have been chosen for the further study, see Fig. 3.

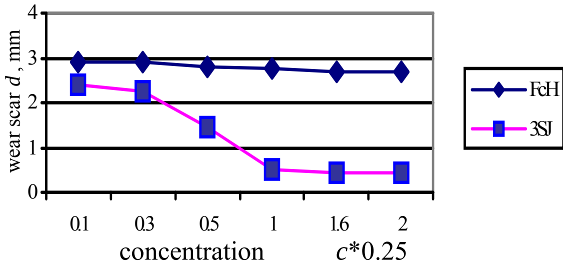
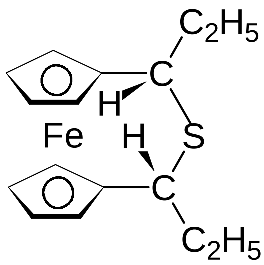


Fig. 2 Influence of concentration onto the wear FbA - test, solutions in white oil



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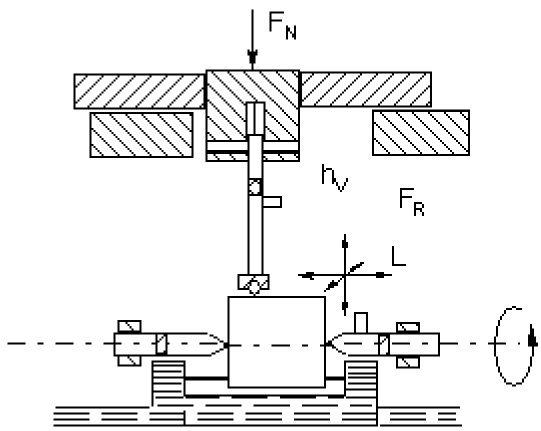


b

Fig. 3 Tested model systems: a - molecular structure of tested 1,1'diethyl-2thia [3] ferrocenophane; b - ZA – 2 Ball on cylinder configuration

2.2. Model wear tests - Test ZA-2

The tests were performed using Tribometer ZA-2 designed by Drechsler et al. specifically for the study of additives and lubricants [14]. Additionally, a friction pair of similar dimensions made of bearing bronze B1010 was designed. The lubricating agent was a solution of 1,1'-diethyl-2-thia [3] ferrocenophane sulphide (3SJ) of 0.025 mole/dm^3 concentration in paraffin oil. The 3SJ sulphide exhibited the highest reactivity towards the surface tested [4]. After the tests had been completed, the surfaces of the balls were analysed using an optical microscope. A wear scar of $a*b$ 2.57 * 2.38 mm with wear volume $VV = 0.7 * 10^{-3} mm^3$ was recorded for the steel 100Cr6 kinematic pair at the load of 31 N. The initial traces of reaction layers formed were observed in the polarized light under the microscope at the load of 50 N. Selected measurement results obtained for a solution of 3SJ sulphide are given in Table 1.

Keeping in mind the division of friction conditions depending on the friction coefficient determined [15], it becomes clear that the experiments were carried out under boundary friction conditions. Thus, operating conditions of tribometer ZA-2 are suitable for our observation purposes and for the evaluation of the effect of liquid lubricants on friction surface modification. The formation of reaction layers and their influence on friction coefficient reduction were observed throughout the investigations. The third column in Table 2, which illustrates the change in friction coefficient within the first second of tribometer ZA-2 operation, seems to be interesting in the light of theoretical considerations. It should be noted that starting from a load of 50 N the system moves within the first second of operation beyond the boundary friction area towards dry friction *> 0.15, but within the third second it returns to the boundary friction area. And so we are back with the motto of this project "the first seconds and minutes of the friction pair's motion are the most important ones". Figs. 4-5 show pictures of the surfaces examined, Fig. 7 gives the analysis results. Reaction layers can be clearly seen non-uniformly arranged on the surfaces of the balls tested.

Table 1
Selected results of wear measurements carried out using Tribometer ZA-2

Load, N	Wear $V*10^{-3}$, mm^3	*m* (time 1s)	*m* (time 3s)
10	0.24	**0.2**	0.07
30	0.7	**0.20**	0.127
50	1.3	0.19	0.128
70	2.20	0.183	0.123
90	2.40	0.177	0.122
110	2.60	0.186	0.127

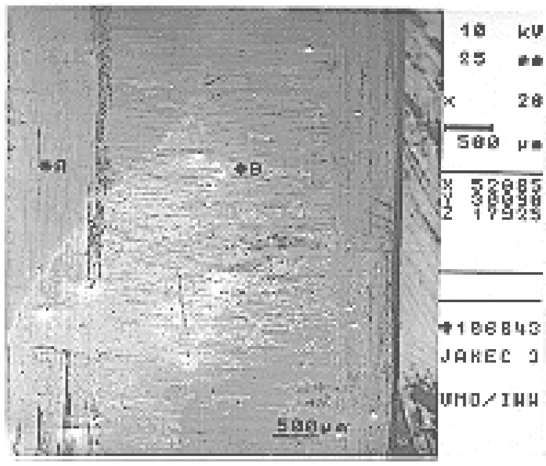


Fig. 4 Wear scar SEM image after ZA-2 test, $N = 50$ N, *= 0.096, $t = 3$ min

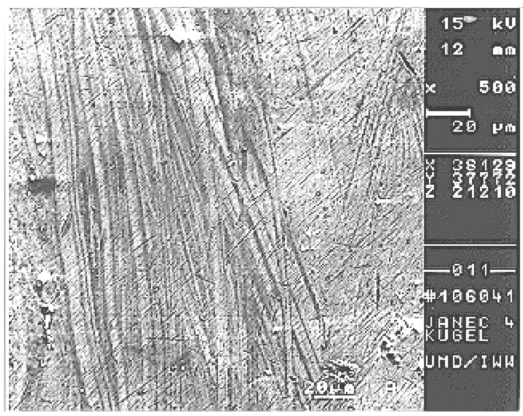


Fig. 5 Wear scar SEM image after ZA-2 test, $N = 50$ N, *= 0.096, $t = 3$ min, wear scar center

A skillful design of a system that will work properly since the startup guarantees continuous, and successful failure-free operation. To satisfy this condition it is important at the friction pair design stage to choose appropriate materials treating lubricant as a component of the same importance as the materials selected for the kinematic pairs being designed. Currently available results of investigations of sulphur ferrocene derivatives indicate a possibility to generate the mixed organic-inorganic layers on friction surfaces. Fig. 6 shows the enlarged image of a wear scar with the traces of reaction products on the surface.

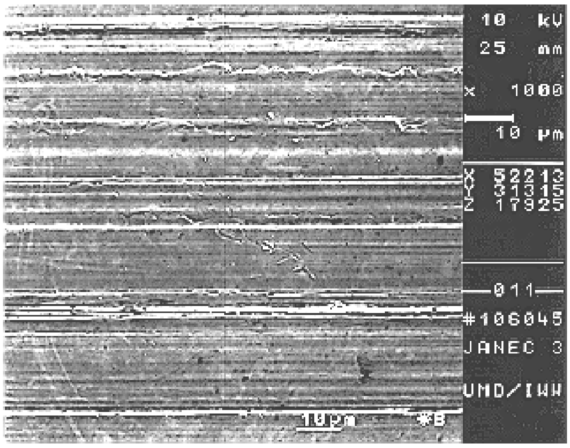


Fig. 6 Enlarged SEM image of wear scar after ZA-2 test, $N = 50$ N, *= 0.096, $t = 3$ min, reaction products are seen along friction path

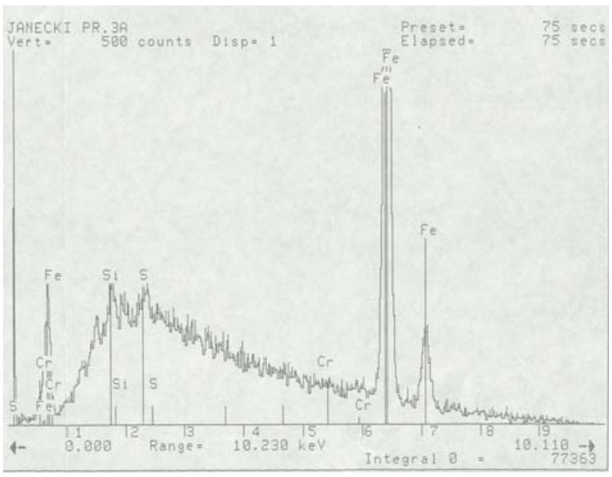


Fig. 7 SEM and Results of steel 100Cr6 surface analysis obtained using an EDS analyzer

It is assumed that a kinematic pair should be matched properly to ensure failure-free mating of its elements for as long as possible. EDS studies were carried out to analyse SEM recorded reaction layers being generated on the surface of a kinematic pair. The results are shown in Fig. 6. It is difficult to model and analyse the interactions of ferrocene iron and ferrocene sulphur with a steel friction surface. It is not possible to distinguish the coming from alloy iron signals from those coming from ferrocene iron without using the tracer method. The work [16] shows Auger spectroscopy analysis results of the surface of a steel ball tested by means of tribometer ZA-2. The steel surface analysis results do not contribute any essential new information that would help to develop a model. However, very large changes in the chemical composition of the steel surface analyzed were found. The changes appeared when the sample surface was etched with argon ions for 2 minutes. In comparison with the chemical composition of steel as given by Polish Standard, increased chromium and carbon contents were found after the signal coming from oxygen had faded. The model surface was changed to record the presence and to analyse the reaction products being generated on the surface in the presence of ferrocene derivatives. Bronze B1010 and copper surfaces were chosen for further investigations of ferrocene sulphides under boundary lubrication conditions.

2.3. Thermal studies in the presence of oil solutions

Earlier studies carried out using the "hot-wire" method indicated that 3SJ - 1,1'diethyl-2-thia [3] ferrocenophane was the most reactive compound in the conditions under which tribological experiments and model thermal tests were performed [17]. Thermal characteristic of 3SJ are presented in Table 2.

Table 2

Characteristic thermal properties determined using the derivatographic method (DTA)

t.t, K	Breakdown temp., K	Mass decrement at breakdown temp., %
325	411 – 553	43.5

The samples used were *1* a bronze B1010 plate and *2* a polished copper plate. They were dipped in an oil solution and heated in a drying chamber at 411 K for 3 hours. The surfaces of the samples after static-thermal tests were studied with the naked eye and with a magnifying glass. After thermal tests the sample surfaces did not change except sample *1* which was covered with a grey opalescent bloom of reaction products of the 3SJ solution. The samples were then analysed by SEM/EDS. Two parallel tests were made. Samples *1* and *2* were studied immediately after removal from oil solutions. The surfaces of samples *3* and *4* were washed with acetone and dried before analysis.

2.4. Instrumental analysis

Instrumental analysis was performed for the selected elements of kinematic pairs and representative samples. The samples analysed were: -*1*- polished copper plate surface, -*2*- polished bronze B1010 plate surface, -*3*- polished copper plate surface (washed with acetone), -*4*- polished bronze B1010 plate surface (washed with acetone).

Figs. 8 and 9 show surface analysis results obtained using SEM/EDS analysis methods. A review of the results points to the occurrence of interesting interactions between the surfaces of the samples tested and the solution of 3SJ in paraffin oil. This is particularly apparent in the case of sample 1. Sample 1 analysis results are given in Table 3.

Simultaneously, DTA analysis was performed for the samples of powdered iron and copper powder. DTA thermal effects and recorded TG mass variations observed in the case of the reaction of the 3SJ compound with the extended surface of iron powder "ferrum reductum" indicated that chemical changes were taking place between the

Table 3

EDS analysis results

Element	Percentage by *wt*	Percentage by atom	Accuracy 3 SIGMA	Constant *K*
S	9.21	16.73	0.10	0.0514
Fe	0.38	0.39	0.03	0.0046
Cu	90.41	82.88	0.35	0.8867

compounds analysed and the powder surface. The 3SJ compound - 1,1'diethyl-2-thia [3] ferrocenophane also reacts intensively with the surface of the copper sample. The shares of sulphur and iron in the grey opalescent reaction layer reach 9.21 % and 0.38 %, respectively. The image of a polished copper plate surface obtained using an electron microscope has been shown in Fig. 8.

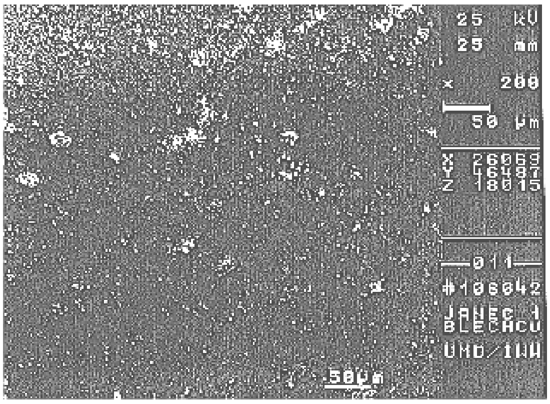


Fig. 8 SEM image of a copper surface tested in the solution of 3SJ sulphide in paraffin oil at 411 K for 3 hours

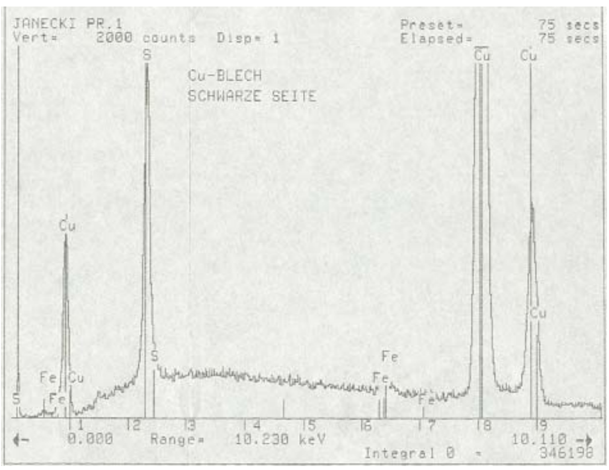
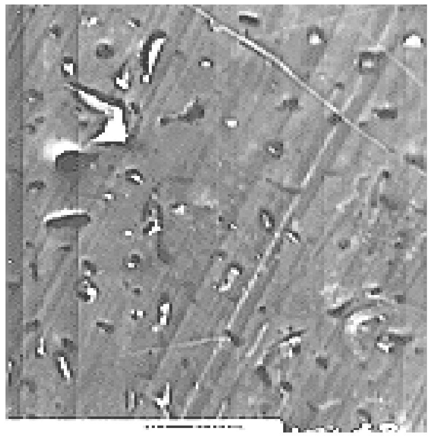


Fig. 9 Illustration of the results of EDS analysis of copper surface shown on Fig. 8

The bronze B1010 surface was studied after friction by means of scanning electron microscopy and Auger electron spectroscopy. The investigation results are shown in Fig. 10.

2.5. Four ball tests

The additional tests were performed using Four-ball Machine FbA designed specifically for the study of additives and lubricants. Exemplary results of friction surfaces examined in Ferrocene Sulphide solutions and tests conditions are given below in the following Figs. 11-18.



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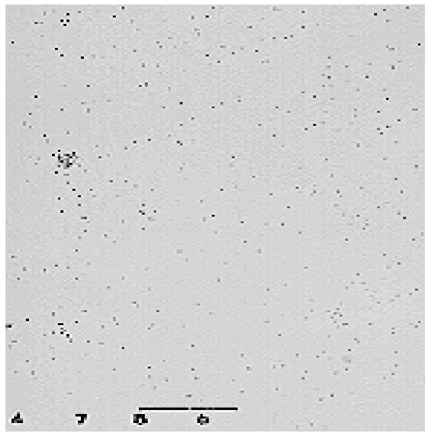

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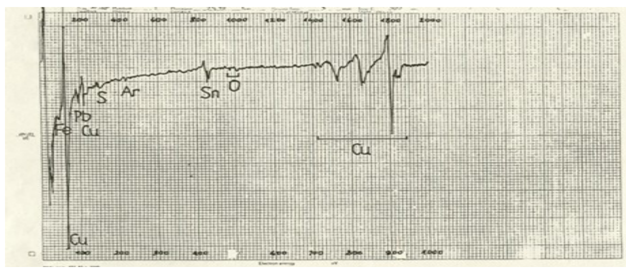

c

Fig. 10 SEM image of bronze B1010 surface tested in the solution of 3SJ sulphide in paraffin oil (a), distribution of ferrocene iron on the B1010 surface (b), AES Spectrum (c)

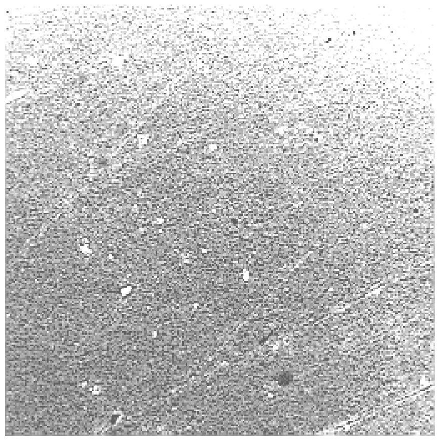

Fig. 11 An example of SEM picture of the pure surface of ŁH-15 Steel

The surface differentiation is immediately visible, although the surface was honed and washed with acetone. For the sake of comparison, the picture of wear scar surface after FbA test is presented in Fig. 12. In the middle of the wear scar (0.5 mm diameter), along the scan line, eminent traces of sulphur are visible. The changes of sulphur concentration are pictured by the white bend line across the wear tracks.

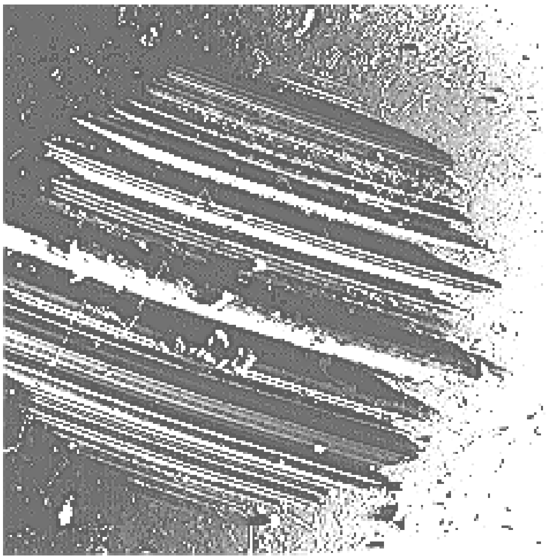

Fig. 12 Wear scar on the worn surface of the examined ball after FbA test; load 5 N; analysed solution of 3SJ in white oil; concentration 0.025 mol/dm^3

The SEM picture of changes on the upper layer of friction surface in the presence of ferrocene sulphide solutions with various wear scars is presented in Fig. 13.

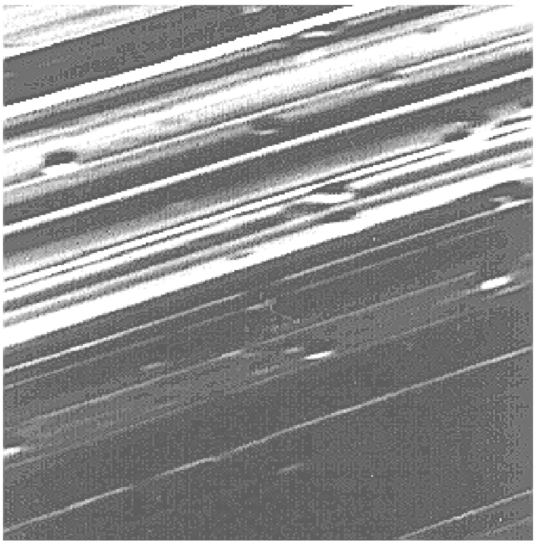

Fig. 13 An example of details of friction surface friction FbA test, load 10 N; lubricant: 3SJ solution in white oil, c = 0.025 mol/dm^3

More obvious instance of surface material after FbA test is presented in Fig. 14. Near the wear scar (in the middle), layers of the reaction products were shown on the right side of the photograph.

Zooming of the wear tracks on the friction surface is presented in the Fig. 15. The changes of chemical properties of analysed surfaces are illustrated by means of characteristic lines along the scan line. The routs of those lines delimit the changes of sulphur concentration in analysed materials.

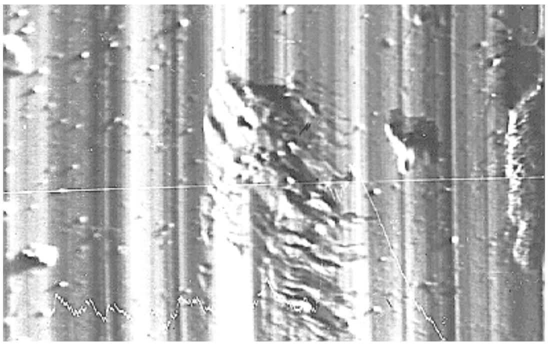

Fig. 14 SEM picture of wear scar FbA test, load 10 N; lubricant: 3SJ solution in white oil, c = 0.025 mol/dm^3

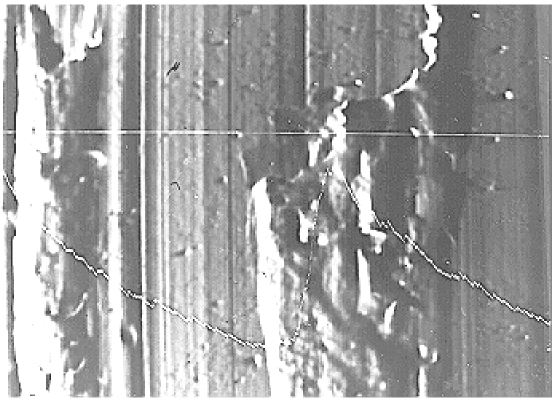

Fig. 15 SEM picture of a fragment of reaction layer wear scar in the middle FbA test 10 N; solution of 3SJ; c = 0.025 mol/dm^3 in white oil

In case of higher load, e.g. 20 N, a deformation of the upper layer is observed in the field of wear scar. By means of SEM, visible deformation of such type is detected on the surface. Figs. 16 and 17 present the chosen examples of surface materials.

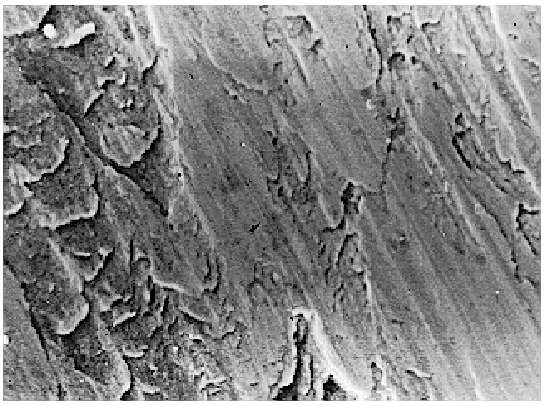

Fig. 16 SEM picture of wear scar; FbA test, load 20 N, steel £H-15, solution of 3SJ, c = 0.025 mol/dm^3 in white oil

In case of the examined solutions of the compound 3SJ (see Fig. 17) various wear scars were registered. The most interesting result is presented in Fig. 18. SEM picture reveals a wear scar as well as a transfer of the material after the tribological test. Reaction layers were observed which are connected with the friction surface. Bright layers containing the products of tribochemical reaction are also eminently visible in Fig. 18.

Fig. 17 SEM picture of wear scar; FbA test, load 20 N, steel £H-15, solution of 3SJ, $c = 0.025$ mol/dm^3 in white oil

Fig. 18 SEM picture of wear scar; FbA test, load 20 N, steel £H-15, solution of 3SJ, $c = 0,025$ mol/dm^3 in white oil

3. Results

The results of model friction and thermal tests lead to the conclusion that in the conditions studied there was a reaction between the sulphide tested and the surface. If there had been unreacted sulphide (C5H4)2Fe(CHC2H5)2S 1,1'diethyl-2-thia [3] ferrocenophane left on the surface, the share of sulphur and iron would have been 10.66 % and 18.66 %, respectively (see Table 4) because $C\%_S = 9.21\ \% < 10.66\ \%$ and $C\%_{Fe} = 0.38\ \% < 18.66\ \%$.

Table 4

Percent share of sulphur and iron in 3SJ sulphide and on the surface

In compound		On surface	
$C\%_S$	$C\%_{Fe}$	$C\%_S$	$C\%_{Fe}$
10.66	18.66	9.21	0.38

It can be concluded that a reaction layer containing less sulphur and iron than the 3SJ compound is formed on the surface of the plate tested. Under the experimental conditions no significant sulphur and ferrocene iron peaks have been observed on the surfaces of samples *3* and *4* washed thoroughly with acetone. Hence, the interactions observed under the experimental conditions do not lead to the formation of stable layers combined with the surface being studied. Additional friction tests on bronze B1010 samples were carried out using ZA-2 and their surfaces were analysed by AES. Some of the analysis results are been given in [18] and [20] (see also Fig. 4). The surface layer of the sample analysed was found to contain an increased content of sulphur and the presence of iron was increasing since the thirteenth minute of surface etching with a beam of argon ions. The above results confirm the previously observed tendency of ferrocene sulphur derivatives to form reaction layers on the surfaces of analysed samples. On the basis of tribological and chemical research the following mechanism of changes in ferrocene sulphur derivatives was proposed in [16], e.g. physical adsorption, reaction of sulphur with surface metal, also with iron from a ferrocene derivative, migration of reaction products on the surface (also into the layer). It follows from the percent share of sulphur and iron in ferrocene derivatives as well as from spectroscopic analysis of the derivatives that the reaction layer formed on the surface may be a mixture of copper sulphides, ferrocene iron and unreacted molecules of the compound studied. It follows from the basic analytical discussion with Prof. Ulrich Wendt from IWW Magdeburg that the surface layer being discussed and analysed may be described as shown in Table 5.

Table 5

Sequence of layers and their thickness

Type of layer	Thickness of layer, µm
External adsorptive	0.0003 – 0.0005
Oxide layer	0.01 – 0.1
Internal polished layer	0.1
Considerable deformations	up to 2
Average deformations	up to 10
Slight deformations	up to 50
Core of the analysed material sample	

Electrons with the energy of ~ 25 keV penetrate the surface to the depth of ~ 1 – 1.5 µm. The X-ray microanalysis helps to study the composition of surface layers; the data carrier is characteristic radiation of high-energy electrons. This method is suitable for the analysis of surface layers of about 1 µm in depth. The depth from which electrons (residing in the surface layer) can be knocked out is even smaller and equals 1nm which is equivalent to 2-3 atomic layers at the pressure of 10^{-6} - 10^{-11} hPa. Our experience in the study of the effetct of the environment on surface layer formation tells us that it is possible to obtain a maximum amount of data about the surface tested under boundary lubrication conditions by using a number of analytical methods. The methods of ion and electron spectrometry that are useful in this area are given in [18]. The compounds of interest – sulphur derivatives of ferrocene – interact with the surface of the tested metal samples at a certain defined depth. The reaction layer is non-measurable if its thickness is too small. The reaction layers generated on bronze B1010 and copper surfaces by a static thermal method exhibit poor adhesion to the surface and can readily be removed with polar solvents. The analysis of thin monomolecular layers should be carried out using Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (ESCA). Researches confirmed that ferrocene derivatives modify tribological properties of lubricants. Eminent relations between the structure and antifrictional behaviour were noted. 2-thia [3] ferrocenophanes show positive antifrictional behaviour in wide range of loads and temperatures. Antifrictional properties of those compounds improve proportionally to concentration. Introducing ferrocene derivatives into base oils results in a shift of maximal conditions of work to the areas of higher loads. This property distinctly depends on the structure of compounds being examined.

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FEROCENO DARINIAI ESANT RIBINIAM TEPIMO SLUOKSNIUI

R e z i u m ė

Nagrinėjant vieną iš reaktyviųjų – ferocenų 1,1 dietyl-2-triferocelofana buvo atlikti terminiai tyrimai ir trinties modeliavimas. Trinties modelio dėka gautų tyrimo rezultatų analizė parodo didelį sieros geležies ir feroceno geležies reaktyvumą, sąveikaujant su bandinių paviršiumi. Feroceno darinių reakcijos produktų buvimas metalinių bandinių paviršiuje patvirtintas instrumentiniais analitiniais metodais.

H. P. Janecki

FERROCENE DERIVATIVES IN BOUNDARY LUBRICATION

S u m m a r y

Model friction and thermal investigations have been carried out to study the most reactive of the ferrocene derivatives tested so far - 1,1' diethyl-2-thia ferrocenophane. The analysis of the results obtained from model friction investigations points to the reactive character of both sulphur and ferrocene iron in reactions with the surfaces of the samples tested. The presence of ferrocene derivative reaction products on the surface of the metal samples studied has been confirmed by means of instrumental analytical methods.

Г. П. Янецки

СТРОЕНИЯ ФЕРОЦЕНОВ ПРИ ГРАНИЧНОЙ СМАЗКЕ

Р е з ю м е

При исследовании одного из реактивных фероценов – 1,1 диетилтрифероцелофана были применены термические методы и фрикционная модель. Данные, полученные при исследовании, показывают реактивность железа серы и железа фероцена, при работе в паре с образцами. Наличие продуктов реакции строений фероцена на поверхности металлических образцов подтверждаются инструментально - аналитическими методами.

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