WELL DRILLING

Surface activity of fine heterogeneous fillers oxide nature during friction

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M.P. Tsapliy V.V. Yudina
cand. of Engineering sciences
A.P. **Pavlovskiy O.O. Mischuk**
cand.of Physical and Mathematical Sciences
Ukrainian Scientific Research Institute of Oil Refining Industry
«MASMA»

The analysis of regularities of formation and properties of abrasive-resistant microstructures of steel friction surfaces arising under the influence of lubricating agents with fine-dyspersated titanium dioxide and mineral hydrosilicate was carried out in stationary and specific for drilling operations dynamic conditions of friction. **Key words:** friction, surface, abrasive-resistant film, oxide type fillers.

It is known that during the machinery operations in the surface layers of friction pairs due to deformation and thermal processes occurring intensive changes in physical and chemical properties of the metal, affecting the service life [1, 2]. In a sufficiently broad range of destruction energy of the original structure of the metal the uneven unsteady processes cause different types of solid-phase transformations of the surface layer under conditions of friction [3, 4].

A specific influence way to the evolution of surface microstructure of the metal in the friction zone is the introduction to the lubricant of heterogeneous colloidal fillers [5-7]. Such fillers are expanding range of chemicals designed to drill oil and gas equipment. [8] In recent decades, in practice, are often used fillers made of powdered rock minerals (betonies, serpentine rocks, magnetite , etc.) [7]. These minerals as impurities in a very large quantity belongs to the nature of bituminous materials that may play a significant role during drilling [9]. Most of these minerals belong to the natural hydro silicate, which can easily break up in the contact friction area and due to relatively low temperature dehydration convert into oxide fillers that influence the friction synergistically with oxides of transition metals [6]. The study of the formation mechanisms of abrasive -resistant surface microstructure of the metal under the influence of said filler is problematic because of trends (risk) of coagulation their particles in the lubricant environment and, in general, long-term micro abrasive action in the initial period of friction.

The aim of the study was to explore and describe both as under stationary or dynamic conditions of friction the special abrasion-resistant friction microstructure occurring in the contact zone of high-strength steel friction pair under the influence of lubricants with specific fillers oxide type - surface modified natural asbestos and transition metal oxides.

Table 1 Average and projected cationic composition of the MF filler

Structure cation(*Kt*)	Concentration, atm %									
	Elemets									cations
	Na	K	Ca	C	Fe	Cr	Mg	Al	Si	
Kt $^{+}$	0.2	1. 0	–	? *	–	–	–	–	–	1.2
Kt $^{2+}$	–	–	1. 0	–	0.7	0.7	18.	–	–	21.2
Kt $^{3+}$	–	–	–		8.9	–	–	6.6	–	15. 5
Kt $^{4+}$	–	–	–	–	–	–	–	–	62.	62.1
Total	0,2	1, 0	1, 0	–	9,6	0,7	18,	6,6	62,	100

* Specifications of analyzer did not allow to study a carbon

Table 2 Load influence on anti-wear properties of lubricating compositions with mixtures, estimated according to GOST 9490

Lubricant	The diameter of the wear track D_3, mm			
	196 Н	392 Н	588 Н	784 Н
МС20	0,52	0,70	3,10	*
МС20+0,1 % мас. МФ	–	0,67	1,09	2,50
МС20+0,2 % мас. МФ	0,48	0,62	0,84	1,15
МС20+0,6 % MoS_2	–	–	1,00	–
Li-lubricant+2 % lubr. TiO_2	–	0,86	–	–
Li-lubricant+10 % lubr. TiO_2	–	0,98	–	–

*Intensive adhesion of a friction pair

*coagulation conditions of microparticles TiO2 and microabrasion effecet of coagulants

Objects and methods of research

During the work was studied the influence of typical oxide-type fillers:

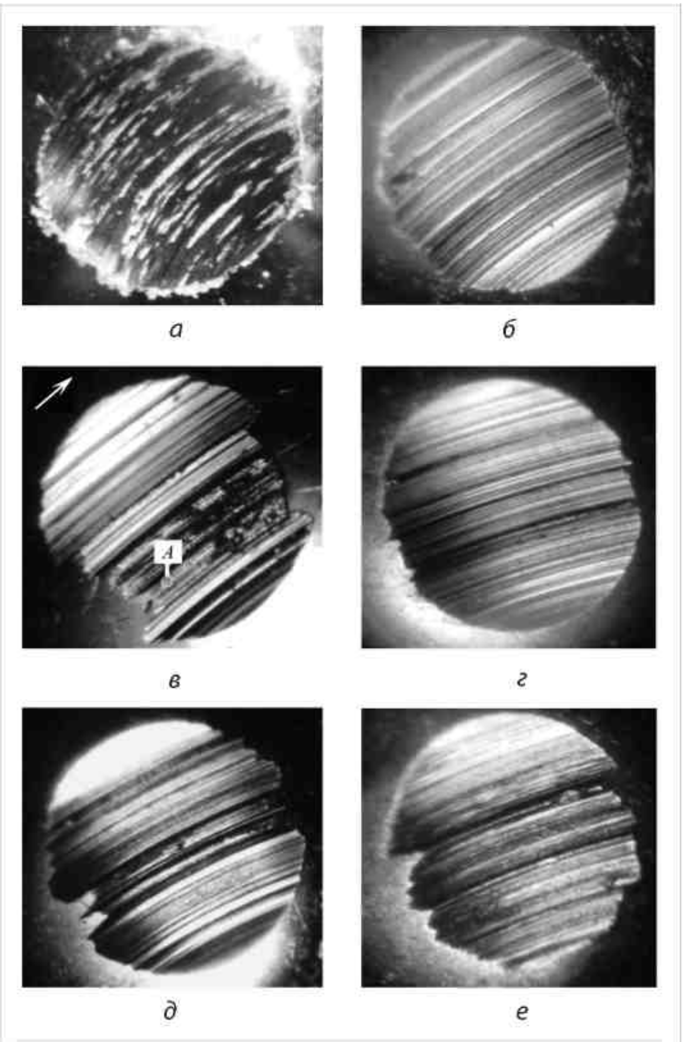

Fig. 1. The microstructure of the friction surfaces of stationary balls of 4-balls pair for cases: Base Oil МС20 (*а*); МС20+0,1 % lubr. МФ *(б);* МС20+0,2 % lubr. МФ (*в*, *д*); Li-lubricant with 2 and 10 % lubr. TiO_2 accordingly (*г*, *е*). Arrows indicate the direction of rotation of the moving ball. Load: 390 Н (*г*, *е*); 590 Н (*а*, *б, в);* 780 Н (*д*). Speed of rotation 1200 min. Friction duration 1 h.

MF sample - mineral powder of the asbestos group, modified by zinc dialkyldithiophosphate DTP Zn;

TiO_2 sample - unmodified microdispersed titanium dioxide powder.

As a comparison under the same conditions was assessed the influence of classical filler - molybdenum disulfide MoS_2.

Powder fillers at various concentrations was added to the base lubricants: oil MS20, Li-acidic grease (КЧ = 1 mgKON /g), similar under elemental composition to Litol-24, rosin oil КАВС -45. Samples of balls with a diameter of 12.7mm hardness HRC 62-64, made from steel ШХ15, tested in the test lubricant compositions on 4-balls friction devices of type Falex-6 and Shell.

Chemical composition of powdered fillers and properties of friction surfaces was studied by means of metallography, scanning electronic microscopy, Auge-electronic spectroscopy and stepped spraying of the surface metal layers by ions of argon, energy dispersive X-ray microanalysis.

To study the structural features of the wear-resistant steel surface in the friction zone was investigated its density characteristic [2, 6]:

$$\text{Characteristic } (h) = (S(h) - S_0)/S_0, \qquad (1)$$

where *S(h)* - the total intensity of the Auge-lines of chemical elements, normalized to the relative sensitivity factors of elements at depth h - layer arrangement; S0 ~ const - average value of S (h) in the metal volume.

In addition to standard methods using a four-ball pair and friction device Falex-6 was used a specially developed methodology of tribological studies in the range of typical for rapid drilling machines 100-4000 min-^{1} (vibration frequency 1-63 s-^{1}), which provided a modes of controlled-variable inequality friction conditions and the predicted microstructural reorganization of the surface steel ШХ15 [10].

Results and discussion

To clearly identify of the filler MF was made electron probe microanalysis of its sample and made conclusion according its cation composition (Table. 1).

On completion of testing was concluded the based on mineral sample MF is quite common mineral crocidolite asbestos (amphibole group of asbestos). This is a complex hydrsilicate of iron and magnesium with cations admixtures K^+, C+, Cr^{2+}, Ca^{2+}, Al^{3+}:

$(Na, K, C^+)_2(Fe^{2+}, Cr^{2+}, Mg, Ca)_3(Fe^{3+}, Al)_2[Si_8O_22](OH)_2$.

Table 3 Average diameter of D wear scar of fixed balls and the average coefficient of friction f of 4-balls pair after the initial breaking-in stage: breaking-in time is 20 min, load 588H, rate of turn-over 1200 min 1

Lubricant	*D*, mm	*f*
MC20	0,42	0,049
MC20+0,1 % lubr. MF	0,44	0,054
MC20+0,2 % lubr. MF	0,44	0,053

Table 4 Average diameter of the D wear scar of fixed 4-balls pair after the rate of turn-over growth in the range 100-3800 min-^{1}

Lubricant	Load, H	*D*, mm
MC20	390	0,54
MC20+0,1 % lubr. MF	390	0,43
MC20+0,2 % lubr. MF	390	0,43
КАВС+5 % lubr. TiO_2	490	0,92

Zinc, phosphorus and sulfur content (surface-active elements of the modifier DTF Zn) were very low and registered only within an error of the electron probe microanalysis.

The ultimate composition of the sample TiO_2 was confirmed by Auge-spectral studies. Also found that in the normal state the powder particles of this hydrated have a dioxide surface.

Study of tribological characteristics of lubricating compositions within given in GOST 9490 testing duration (1 hour) was found some antiwear and antiscuff significant efficiency of the MF filler even in comparison with the classic filler MoS_2 (Table 2).

Trends of the initial friction period is illustrated in Table. 3. Analysis of the received variables indicates that the processes of a friction pair setting in the case of base oil MC20 (Table 2, 588 W) and the final formation of abrasion-resistant surface metal microstructure under the influence of filler MF (Fig. 1, b) develops not at the early break-in period of a friction pair, and later, between the 20 and 60 min of friction.

In Fig. 1 is shown the microstructure of wear scar of fixed 4-balls pair (diameter values are given in Table 2.) for different lubricant compositions. The comparison reveals certain similarities of the influence of powdered natural hydro silicate and transition metal oxides, relatively shifted under concentrations scales fillers and loads on the friction pair. For the case of base oil MC20 was formed microstructure of wear scar surface (Fig. 1, a) is the result of a series of sequential micro and macroprocesses flow activated by prior setting of surface friction pair.

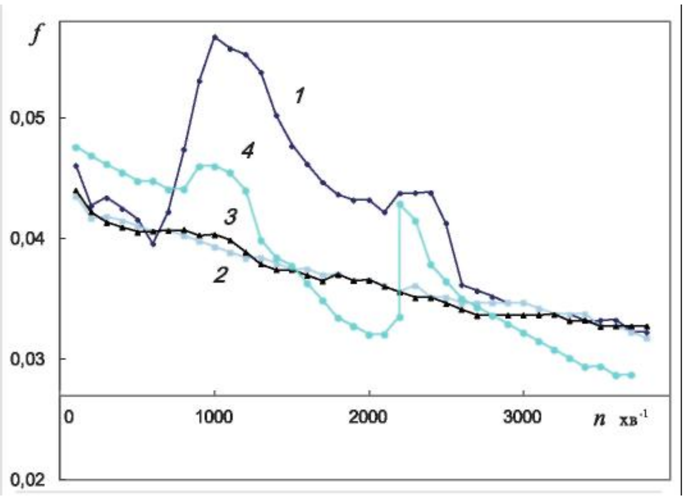

Fig. 2. The dependence of the friction coefficient f of n braking –in of 4-balls friction pair for the case of: oil MC20 (*1*); MC20+0,1 % lubr. MФ (*2*); MC20+0,2 % мас. MФ (*3*); lubr KABC+5 % lubr. TiO_2 (*4*). Load: 390 H (*1–3*); 490 H (4). Step-up of *n* with average speed 75 min^{-1}

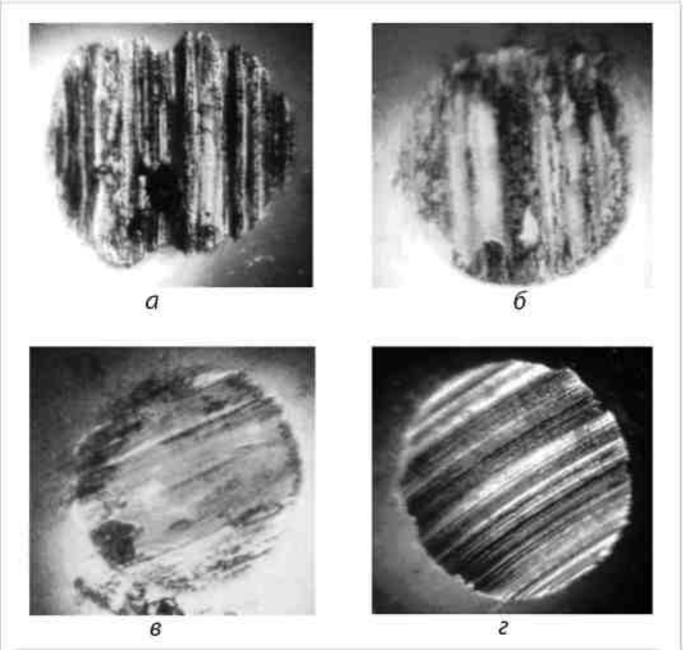

Fig. 3. The microstructure of the friction surfaces of fixed balls of 4- balls pair provided the growth in the range 100-3800 min.for the cases: oil MC20 (*а*); MC20+0,1 % lubr. MФ (*б*); MC20+0,2 % lubr. MФ (*в*); lubr. KABC+5 % lubr. TiO_2 (*г*). Load: 390 H (*а, б, в); 490* H (*г*)

Fillers in lubricating compositions prevent setting of surfaces, but cause the microabrazive influence on metal (Fig. 1*б, г*). Increase of their concentrations in relation to surface-active components in an oil composition leads to the local formation of structures, which are particularly resistant to microabrazive wear (Fig. 1, *в*, line in the vicinity of microstrip line A), reducing the wear surfaces (Table 2), but also enhance their apparent their heterogeneity (Fig. *1, в, д, е)*.

Let us assume that indicated structure results from buckling of friction mode and corresponding adjustment of the surface layer . In the following studies, we apply variable test conditions [10]. Dependence of friction coefficient on the rate of turnover (Fig. 2), registered for the studied oil compositions show regular oscillation coefficient of friction. Their amplitude is the smallest in the case of filler MF (curves 2 and 3), indicating the effective inhibition under the influence of its micro particles of specific critical transformation of the steel microstructure [10].

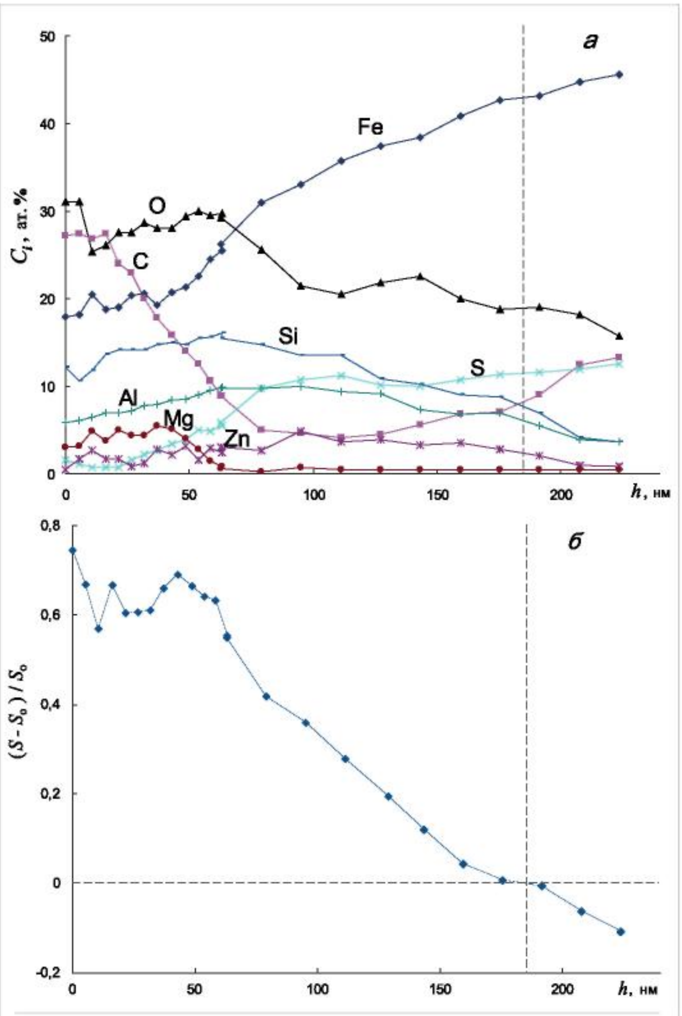

Fig. 4. Concentration profiles of C_i elements (*a*) and density (Equation (1)) of segments (*б*) in a wear-resistant surface structure investigated within the microstrip line A (see. Fig. 1, *г*) of the surface friction of fixed steel ball of the 4-balls pair. Oil MC20 with addition of 0,2 % lubr. МФ

Estimated value of fixed balls of the 4-balls pair wearing (see Table. 4) showed significant anti-wear performance of mineral hydrosilicate МФ during almost the same study duration, as in the case of GOST 9490 (Table 1). The effective value of volumetric balls wear, which is proportional to the cube of the average diameter of the wear strap decreased twice in the presence of filler МФ: $(0,54)^3 / (0,43)^3 = 2$.

The microstructure of the balls friction surfaces (Fig. 3) also significantly varied under the influence of admixtures. In the case of oxide filler TiO2 in rosin oil КАВС (Fig. 3, *г*) typical critical transformations of the steel microstructure are interrupted, probably under the influence microabrazive action of the filler (Fig. 2, curve *4*).

Under the influence of lubricating compositions with filler МФ on the surface friction we witnessed a presence of, fine wear-resistant and, obviously, abrasion-resistant surface film that is best seen in Fig. 3 *г*. Decrease of the concentration of МФ filler causes deterioration of the homogeneity of this film (Fig. 3, *б*).

The results of Auger analysis of the surface, resistant to wear microabrazive wear (Fig. 1, *г* , microstrip line A) for the case of lubricating compositions with filler МФ we witnessed its complex thin-film structure. Analysis of the profile (Fig. 4a) shows that the modifier ДТФ Zn acts synergistically with hydrosilicate of iron and magnesium, which promotes the formation of a new structure of steel surface [11].

Study of density characteristics of silicon-containing surface (Fig. 4, a) in equation (1) showed the presence of condensed steel ШХ15of surface oxide structure type compared to the volume (Fig. 4b). Investigated surface (Fig. 4) does not reach the volume of steel, as evidenced by the relatively low values of the iron concentration in it. Between the compacted surface and the volume of steel is seen also the transition layer with "disperse" structure.

Abrasive resistant surface microstructure created in friction conditions under the influence of oxide filler TiO_2 were thoroughly investigated in [6]. We found that the microstructure of the surface formed by carboxy ща iron and titanium and have also relative increased volume density relative to the volume of steel ШХ15 (density characteristic in equation (1) reaches to 0,4-0,5).

The similarity of the generated surface microstructures for both studied fillers (TiO_2 and МФ) under different loads of friction pair raises questions about the role of the processes of dehydration of МФ filler in conditions of transient friction.

Conclusions

We witnessed an analogy between surface microstructure of steel, created in conditions of friction as a result of such fine heterogeneous oxide fillers such as hydro and natural oxides of transition metals. Under the influence of fillers on the friction surface of steel ШХ15 may form a surface film, resistant to microabrazive wear. The results of the study proved that its formation occurs in certain modes of friction (close to setting or dynamically change of the wear mechanisms) due to the simultaneous transformation of the microstructure of the critical surface layer and the influence of microparticle filler. Abrasive resistant film is a complex surface microstructure of the oxide type, which has a higher density compared to the bulk steel structure.

By the method of periodic changes of moving balls turnover rate of 4-balls friction pair were made conditions of nonequilibrium mechanical and chemical activation of the steel surface, specific to the dynamic characteristic of the drilling of oil and gas wells in which the effects of formation of abrasive-resistant microstructures are shown the most effective way. The latter, in particular, makes the possibility of on-line diagnostics and research.

Authors

Tsapliy Maksym Petrovych

Research Engineer, post-graduate UkrNDINP "MACMA." Fields of research - friction and wear of metals under the influence of lubricant.

Yudina Vita Vasylivna

Senior Researcher of UkrNDINP «MACMA», candidate of Technical Sciences, Fields of research - development of production technologies and study the properties of lubricants.

Pavlovskiy Anatoliy Petrovych

post-graduate UkrNDINP "MACMA». Fields of research - friction and wear of metals, production technologies of lubricants.

Mishuk Oleg Oleksandrovych

Senior Research Engineer UkrNDINP "MACMA" candidate. Sci. sciences. Fields of research - spectroscopy, physics and chemistry of solids surface, friction and wear of metals.

New search well on the Romanian shelf

Petroseltic International PLC, a subsidiary of Melrose Resources Romania BV, began drilling of search wells in promising areas of Cobalcescu South, located on the Black Sea at the distance of 170 km to the southwest of Constanta. The well has a complex trajectory, its purpose is to open promising horizons of the Miocene. The company has a 40% shares in the concession areas of the Est Cobalcescu and Muridava. In the first area its partners are the Beach Petroleum SRL and the Petromar Resources SA, each of which owns 30 % of shares.

Conducted by Petroseltic set of studies has shown promising areas as of high gas and of oil. After drilling of search wells in this area , the company plans to drill exploration drill hole in the nearby area of Muridava

Romania: Petroceltic group spuds Black Sea wildcut. Oil & Gas Journal/16.10. 2013