Metrological assurance of the research on corrosion characteristics of magnetic nanodispersed lubricants

A N Bolotov, V V Novikov and O O Novikova

Tver State Technical University, A. Nikitin Emb. 22, Tver, 170026, Russian Federation

E-mail: onvk@mail.ru

Abstract. The paper proposes a new metrological assurance to study functional properties of promising magnetic lubricants: liquids and oils. They contain chemically active components to improve their tribotechnical characteristics and therefore cause corrosion of solid surfaces interacting with them. The proposed method for assessing corrosion activity of magnetic lubricants takes into account all conditions of chemical corrosion during friction. A metal filament, in which cyclic electric current and a magnetic field create alternating tension stresses and a temperature similar to the real one in the frictional contact area when using a magnetic fluid tribonode, undergoes corrosion in the magnetic medium. The theoretical justification of the method has two different cases of filament fixation. The nature of the filament movement and its tension under the influence of alternating Ampere’s force and alternating sign current pulses is analyzed. There is a diagram of a device for assessing corrosion activity of magnetic lubricant nanodispersed materials. There is a performance evaluation of the proposed method and an experimental research on the effect of corrosive magnetic and non-magnetic lubricating media on a solid copper surface. It is established that the excess of free surfactant in PES-5 organosilicone liquid and its magnetic oil is negative.

1. Introduction

Nowadays, magnetic fluids are the basis for creating new hybrid materials with special functional properties for biomedicine, chemical technology, and physical research methods [1-2]. Much attention is paid to the problems of using magnetic fluids for lubricating tribocouplings [3-6]. In order to study the properties of new magnetic lubricants and optimize their characteristics, it is necessary to create special devices that take into account their structural features and operation characteristics.

All lubricants contain a large number of components that are chemically active when it comes to a solid surface [7-12]. These surfactants are mainly introduced into a lubricant as additives to improve their functional properties. The volume concentration of additives in a lubricant is several percent. It can be significantly higher than 10% in some cases, for example, in magnetic oils.

Chemical interaction of the considered surfactants with a friction surface leads to their corrosion. As a result, both physicochemical and mechanical (including micro and macrogeometric) surface characteristics change. This affects the work of friction units negatively, if we do not consider the controlled corrosion mode during chemical surface modification in order to give it anti-wear properties.

Chemical corrosion during friction has a number of features. The corrosion process develops under mechanical activation of the surface, which means that alternating stresses in the surface layer reach hundreds of MPa, the temperature locally rises by hundreds of degrees in the places of dynamic contact of microasperities and can reach the melting temperature. Corrosion products are often destroyed and...
removed from the friction zone, thereby they facilitate surface access to new chemically active molecules.

Known methods for assessing corrosion activity of oils do not take into account its conditions during friction fully and do not give a quantitative idea of the process dynamics. The hot wire method [13, 14] allows estimating only the effect of friction temperature flashes on corrosion.

The proposed method assumes that a metal filament (wire) undergoes corrosion in the test medium while cyclically heated by electric current. In this wire, alternating tensile stresses are created under the action of Ampere’s force. It is known that tensile stresses on friction surfaces are the ones that strongly affect corrosive mechanical wear [15]. Filament vibrations provide its rapid cooling, partial removal of corrosion products and the equalization of surfactant concentration near its surface. The volume of a filament layer that enters into a chemical reaction is estimated by a change in its electrical conductivity (these values are proportional with a constant length of a filament).

The research objective is to develop metrological assurance for studying corrosion characteristics of magnetic lubricant nanodispersed materials including theoretical justification of tests, creation of device design and its testing.

2. Theoretical substantiation of research methods for corrosion characteristics of magnetic lubricants

We consider the nature of filament movement and its tension under the action of alternating Ampere’s force in two different fixation cases.

1. A thin filament of length $L$ and diameter $d$ ($d \ll L$) is fixed at the ends without tension, but also without slack. From a practical point of view, it is difficult to fix the filament like that, therefore, we suppose that there are mechanical stresses in the filament, but their value is much less than the yield strength. Considering filament transverse vibrations affected by the elastic force, we can obtain the following wave equation:

$$\frac{\delta^2 y}{\delta t^2} = V^2 \frac{\delta^2 y}{\delta x^2},$$  \hspace{1cm} (1)

where $x, y$ are oscillating point coordinates, $t$ is time, $V$ is a wave velocity. The wave velocity is expressed as follows:

$$V = \left(\frac{2E}{\rho}\right)^{1/2} \frac{A}{L},$$ \hspace{1cm} (2)

where $E$ is an elastic modulus, $L$ is a filament length, $A$ is an amplitude, $\rho$ is a filament material density. As expected, the elastic wave velocity, and hence the frequency of natural vibrations depends on the amplitude since filament vibrations are nonlinear. The cyclic frequency of filament natural oscillations takes the following range of values:

$$\omega_0 = 2\pi \left(\frac{2E}{\rho}\right)^{1/2} \frac{An}{L^2},$$ \hspace{1cm} (3)

where $n = 1, 2, 3 \ldots$

Under the action of the external harmonic Ampere’s force $F_x = I_0B\sin \omega t$, where $\omega$ is the cyclic frequency of oscillations, $I_0$ is the amplitude value of the current strength, $B$ is the magnetic field induction, the filament will perform forced periodic oscillations with an amplitude, the magnitude of which depends on the frequency. We assume that $\omega = \omega_0$, then neglecting the inertia and dissipative forces, there can be the following equation: $F_x = F_y$, where $F_y$ is the projection of the stretched filament elastic force on the vibration direction. After some transformations, for the vibration amplitude $A$ we can write the following:

$$A = L \frac{3}{4} \sqrt{IB/4ES},$$ \hspace{1cm} (4)

Then the expression for the filament tension force $T$ during vibration can be represented as following:
If we know $S$ cross-sectional area of the filament, it is easy to determine tensile stresses during vibrations.

For better simulation of temperature flashes in a friction zone, current pulses of constant amplitude lasting $t \sim 1 \cdot 10^{-4}$ s must be alternated with currentless pulses, which provides more accurate simulation of a friction process. Let us suppose that the heating of the filament by electric current has occurred quickly and the process can be considered adiabatic, then the average value of the filament temperature increase with a harmonic nature of the current strength change can be estimated by the following formula:

$$\langle DT \rangle = \frac{\pi \rho_y d^2 L}{2 \rho_y S m \omega},$$

where $\rho_y$ is a filament electrical resistivity, $C_y$ is the specific heat, $m$ is the filament mass. Under real conditions, the thermal conductivity of materials and the dependence of $\rho_y$ on temperature will affect the temperature change.

In the considered example of modeling corrosion processes, the positive point is that mechanical stresses in a filament can smoothly change from zero to a certain value, similarly to friction. But in this case, there might be some difficulties in establishing basic corrosion laws due to the ambiguity in the interpretation of experimental data. Taking into account this fact, as well as technical difficulties arising when attaching a filament in an unstretched state without slack, we consider another relatively simplified version of the described method.

2. A thin metal filament of length $L_1$ and diameter $d$ ($d \ll L_1$) is fixed freely, with a deflection $h$ in the center. The filament ends are fixed at a distance $L$ from each other. Preliminary tests showed that at an $h/L$ ratio of about $10^{-2}$ V, the filament tensile stresses range from $10^5$ to $10^6$ Pa, which corresponds to the loads in the real tribocontact zone.

When passing electric current through a filament in a magnetic field, Ampere’s force will affect it and the filament will bend as an arc of a circle of finite radius. It is convenient to pass alternating rectangular current pulses so that the stresses in the filament remain constant for approximately half a period, and the filament abruptly changes a deflection direction.

Under the action of electric current, mechanical stresses of magnitude

$$\sigma = \frac{2IBL}{\pi d^2 h},$$

where $\sigma$ is the stress, $d$ is the filament diameter. The contribution of inertia forces into filament tension was not taken into account, since its mass is negligible.

In order for the filament temperature to cyclically change from ambient temperature to electrical heating temperature, there should be current-free time intervals necessary for cooling a wire. Based on the above assumption about adiabatic filament heating by electric current, the maximum temperature increase can be determined by the following formula:

$$\Delta T_{\text{max}} = \frac{16d^2 \rho_y t}{\pi^2 d^2 \rho_y c_y},$$

where $t$ is the current pulse duration.

When carrying out tests according to the scheme from the second example, it is necessary to monitor mechanical stresses in the filament heated to a significant temperature carefully. The resulting stresses should not exceed the yield strength of the filament material under tension. It is possible to create mechanical stresses in the sample similar to those arising during frictional interaction on a friction surface by varying magnetic field induction.

When a sample is attached like this, the periodically changing directions of filament bending accelerate test material corrosion providing easier access for chemically active molecules of a magnetic fluid to the filament solid surface. In addition, all tests include applying a uniform magnetic field to
create Ampere’s force affecting the filament. In contrast to traditional dielectric lubricating oils, a magnetic field significantly changes physical and chemical properties of nanodispersed magnetic lubricating fluids. It is also necessary to consider this factor.

When using both measuring circuits, the frequency of filament current pulses is selected from the operating modes of a real tribocoupling simulating the real time of roughness interaction in a friction zone. The filament heating temperature corresponding to the “flash” temperature is determined by the strength of the current passing through it.

3. A schematic diagram of a device for assessing corrosion activity of magnetic lubricant nanodispersed materials

The studied metal filaments (samples) 1 are fixed on busbars 2 inside a rectangular cuvette 3 made of fluoroplastic. To fix the filament correctly, the cuvette is closed with a lid 4 and sealed with a gasket 5. The cuvette is filled with magnetic lubricating nanodispersed liquid or oil 6 so that the sample is completely coated with it. The device is placed in a magnetic system that creates a magnetic field with the induction vector perpendicular to the filament axis.

The magnetic system of the device provides a magnetic field with inhomogeneity of not more than 5%. It includes a permanent magnet 7 and two flat magnetic cores made of soft magnetic steel 8 linked with the magnets pole surfaces. The magnitude of the magnetic field induction in the studied area can be set by varying the distance of the plate 9 made of soft magnetic material from the permanent magnet 7. The ratio between the utilized magnetic flux and the diffusion flux changes. A non-magnetic gasket 10 separates the plate 9 and the magnet 7. Due to its small size, the device can be placed in a heating cabinet.

![Diagram of a device for studying corrosion activity of magnetic lubricants.](image)

Figure 1. A device for studying corrosion activity of magnetic lubricants.

The choice of magnetic system geometric dimensions corresponds to the following formula for the magnitude of the magnetic field induction $B$ in the working gap:

$$B = \frac{\alpha \mu_0 I_y S_m l_m}{S_m l_z + S_z l_m},$$

where $\mu_0$ is a magnetic constant, $I_y$ is the remanent magnetization, $l_m$ is the magnet height, $l_z$ is the magnetic gap magnitude, $S_m$, $S_z$ is the magnet cross-sectional area and the working magnetic gap area, respectively. $\alpha$ is the coefficient taking into account diffusion magnetic fluxes, in our case $\alpha = 0.8–0.85$. If it is supposed to carry out measurements at volumetric temperatures up to 500 K, then it is reasonable to use heat-resistant magnets made of a rare earth alloy with cobalt, in which the residual induction is about 0.8 T.

4. Testing the proposed method

The assessment of the utilization efficiency of the proposed method is based on experimental studies on the significance of the temperature and surface mechanical state influence on corrosive chemical processes in tribounits with magnetic nanodispersed lubricating media.
Transmission oil TAD-17, organosilicon fluid PES-5, magnetic fluid based on PES-5 fluid and magnetic fluid modified by 10% stearic acid were used as corrosive lubricants. The sample is made of copper wire with a diameter of 0.075 mm. Alternating rectangular current pulses with an amplitude of 2.9 A and a period of 0.2 s were passed through the sample. The induction magnitude of a uniform magnetic field was 0.035 T. The maximum tensile stresses in the sample were $2.6 \times 10^7$ Pa. The installation was placed in a heating cabinet with a temperature of 370 K, the calculated increase of the filament temperature was about 200 K. The duration of the tests is relatively short, it does not exceed several tens of hours.

During the experiment, the ends of the copper wire (filament) were soldered to the current conductors in the cuvette providing a central deflection of 1-2 mm. We filled the cuvette with the studied lubricant, set the required parameters of the magnetic system and placed in a heating cabinet. After measuring the thread initial resistance, alternating current was applied to it and the current values of the wire resistance were fixed at specified intervals. Corrosion process activity was evaluated by the relative change in the resistance $\Delta R/R$ of a copper wire, since $\Delta R/R = \Delta d/d$, where $\Delta d$ is the doubled thickness of the corrosion layer.

Since copper wire resistance is relatively small, we used four probe schemes to measure it more accurately. In this case, the current of a given value passes through the filament by two conductors, and the sample voltage was measured using two other conductors.

Figure 2 shows the experimental results, which make it possible to estimate the copper wire corrosion rate in various lubricating media. The experimental points correspond to the average value of the resistance change over three threads. The above data implies that surface tensile stresses and its temperature significantly change corrosion dynamics. Without taking these factors into account (using traditional methods) corrosion rate values are underestimated.

When analyzing the corrosive activity of PES-5 organosilicon liquid and magnetic oil based on it, one can see the negative role of the excess surfactant (stearic acid) in the free state.

5. Conclusion
The metrological assurance considered in the paper will allow more reliable studying chemical interaction processes during friction of magnetic oil components and a structural material under study. The proposed method for assessing chemical corrosion can reduce test time, and therefore the cost of researching expensive magnetic lubricating media. The experiments on the proposed equipment allow predicting the operability of real tribonodes with magnetic lubricants, as well as evaluating the effectiveness of new magnetic lubricant nanofluids, their additives and fillers.

![Figure 2](image-url)  
*Figure 2. The chronogram of oil corrosive activity: 1, 2, 3 - TAD-17; 4 - PES-5; 5 - magnetic oil with 10% stearic acid, 6 - magnetic oil. Test conditions: 1 - without magnetic field and current, 2 - when passing current; 3, 4, 5, 6 - when passing current and applying a magnetic field.*
References

[1] Odenbach S 2002 Ferrofluids: Magnetically controllable fluids and their applications. LNP (Springer-Verlag) 594 253

[2] Orlov D V, Mikhalev Yu O and Myshkin N K 1993 Magnetic Fluids in Mechanical Engineering ed D V Orlov and V V Podgorkov (Moscow: Mashinostroenie) 272

[3] Ochoński W 2007 Sliding bearings lubricated with magnetic fluids Industrial Lubrication and Tribology 59(6) 252–65

[4] Bolotov A N, Novikov V V and Novikova O O 2010 Researching tribological properties of piezomagnetic fluid bearings Friction and Lubrication in Machines and Mechanisms 10 23–9

[5] Bayburtsky F S 2010 Magnetic Fluids: Production Methods and Applications Retrieved from: http://magneticliquid.narod.ru/autority/008.htm

[6] Uhlmann E 2002 Application of magnetic fluids in tribotechnical systems J. of Magnetism and Magnetic Materials 11 336–40

[7] Bolotov A N, Novikov V V and Novikova O O 2009 Tribotengineering magnetic oils Physical and Chemical Aspects of Studying Clusters, Nanostructures and Nanomaterials 1 5–9

[8] Ermakov S F 2012 The effect of lubricants and additives on tribological characteristics of solids. Part 2. Active friction management Friction and Wear 3 275–83

[9] Mishchak A 2006 Tribological properties of ferrofluid Friction and Wear 27(3) 330–6

[10] Bolotov A N, Novikov V V and Novikova O O 2016 Development of a modified technology for producing nanostructured magnetic oil Physical and Chemical Aspects of Studying Clusters, Nanostructures and Nanomaterials 8 69–75

[11] Huang Wei, Wang Xiaolei, Ma Guoliang and Shen Cong 2009 Study on the synthesis and tribological property of Fe₃O₄ based magnetic fluids Tribology Letters 3(3) 187–92

[12] Bolotov A N, Novikov V V and Novikova O O 2011 Magnetic oil for friction units with boundary lubrication Friction and Lubrication in Machines and Mechanisms 9 27–32

[13] Klamann D 1984 Lubricants and Related Products: Synthesis, Properties, Applications, International Standards (New York: Wiley-VCH) 489

[14] Matveevsky R M, Lashkhi V L, Buyanovskya IA et al. 1989 Lubricants. Antifriction and Antiwear Properties. Test Methods: Reference Guide (Moscow: Mashinostroenie) 224

[15] Chichinadze A V, Berliner E M, Braun E D and Bushe N A 2003 Friction, Wear and Lubrication (Tribology and Tribotechnology) ed A V Chichinadze (Moscow: Mashinostroenie) 576