A research on magnetic properties of magnetic nanodispersed lubricants

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Abstract. The paper presents the results of theoretical and experimental studies of the magnetic properties of magnetic lubricating oils. It shows oil magnetization curves in the initial state and after tests in the boundary friction mode. Oil properties were measured by an original magnetometer with Hall sensors. It has been established that triboeffects change oil composition and structure and decrease its magnetization. The results will help determine the optimal operating conditions of magnetic oils while maintaining their magnetic and lubricating properties.

1 Introduction

Magnetic lubricating oils that are used in friction units of modern high technology equipment increase their life, energy performance and improve their friction characteristics [1-5]. The range of tribounits with magnetic oils as a lubricant and a working fluid is wide: sliding bearings, guides, sealants, magnetic couplings, etc. [6, 7]. Such devices have a wide range of applications and operating conditions, therefore there are some load and temperature requirements imposed on them. High temperatures, pressure, and shear stresses in the friction zone that affect magnetic oils during operation lead to changing their chemical composition as a result of molecular destruction, chemical interaction of molecules with the surface and atmospheric gas, loss of magnetic properties by magnetic particles, and violation of oil colloidal stability [8, 9].

After studying switching curves of magnetic oils, we can obtain the information that will become a basis for tracing the dynamics of changes in the content of magnetic and nonmagnetic phases in a carrier fluid, estimating the effective particle size of a dispersed phase, investigating oil colloidal stability, and determining the main magnetic characteristics necessary to design friction units with magnetic oils. The analysis of magnetic oil magnetization curves, which are taken during simulation of real tribological effects, will help evaluating the possibility of using magnetic oils in various friction units quickly and efficiently, as well as improving their functional properties purposefully.

The aim of this study is to research magnetic properties of magnetic lubricating oils in the initial state and after tribological effects, taking into account their composition and structure.

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2 Theoretical issues of the experimental research

In the initial approximation, without taking into account the interaction between single-domain particles and polydispersion of particles, we can represent magnetic oil as a superparamagnetic fluid, the magnetization of which obeys the Langevin theory [10]. In this case, the Langevin function describes the theoretical curve of the dependence of the magnetic oil magnetization M on the magnetic field strength H as follows.

$$M = M_S \left[cth \left(\frac{\mu_0 m H}{kT} \right) - \frac{kT}{\mu_0 m H} \right] \quad (1)$$

where $M_S = \varphi J_S$ is magnetic oil saturation magnetization; φ, J_S is volume concentration and magnetic phase (magnetite) saturation magnetization, μ_0 is a magnetic constant, m is a particle magnetic moment, k is the Boltzmann constant, T is temperature.

Real magnetic oils (liquids) are characterized by polydispersity of magnetic particles. In weak fields, the magnetization is mainly due to large ferromagnetic particles, which are easily oriented by a magnetic field; the attainment of saturation is determined by small ferroparticles that require large fields for orientation. Within this framework, based on theoretical dependences, it is possible to determine the size of the largest and smallest particles of the magnetic oil dispersed phase according to magnetic measurements from the experimental magnetization curve [10, 11].

Based on the magnetogranulometric method [10], the diameter d_0 of large magnetic particles in a liquid is determined from the formula (1) at a magnetic field strength $H \rightarrow 0$ using the formula:

$$d_0 = \sqrt[3]{\frac{18xkT}{\mu_0 \pi M_S J_S}} \quad (2)$$

where x is the initial magnetic susceptibility determined from the initial part of the experimental magnetization curve. The diameter d_∞ of the smallest magnetic particles can also be determined from the formula (1) provided that $H \rightarrow \infty$:

$$d_\infty = \sqrt[3]{\frac{6kT}{\pi \mu_0 H_0 J_S}} \quad (3)$$

where $1/H_0$ is the abscissa intercept of the a line tangent to the initial part of the magnetization versus field strength converse experimental curve.

3 Research methods and materials

Laboratory magnetometers that are commonly used to study magnetic properties of magnetic fluids [12–15] have significant drawbacks. In some cases, when studying a magnetization curve (for example, by the ballistic method), the magnetizing field value in a solenoid is not big enough and the accuracy of measuring magnetic characteristics is low. This is due to the fact that the measurements are carried out in an open magnetic circuit. Nowadays, magnetometers with Hall sensors are used more often to study magnetic properties of solids. This method meets the whole range of demands for studying the magnetic properties of magnetic fluids. Therefore, we used the Hall magnetometer developed by ourselves in the studies [16].

Friction and wear tests under boundary friction conditions were carried out on a MTP finger-type friction machine [17]. We studied the following magnetic lubricating oils: MM1-PES4 (base is PES-4, dispersed phase is magnetite (10 vol%) stabilized by a fatty acid), MM-

PESV (PES-V-2 and 10 vol% magnetite stabilized modified by chlorosiloxane), MM-I (industrial oil and 8 vol% magnetite stabilized by an oleic acid), MM-PES5 (PES-5 and 5 vol% magnetite stabilized by a fatty acid), MM2-PES4 (PES-4 and iron 2.5 vol% stabilized by modified chlorosiloxane), MM-P (perfluoropolyether PEF-240, magnetite stabilized by a fatty acid). The magnetic properties of oils were compared with the similar properties of a classical low-viscosity magnetic fluid that has good colloidal stability and based on kerosene containing 7 vol% magnetite stabilized by an oleic acid.

The changes in oil magnetic properties after long-term availability (about 140 hours) in friction units were analysed on the example of MM-P oil, which has magnetization of ~20 kA/m, density 1.3 g/cm³. The oil is based on perfluoropolyether that has high thermal and oxidative stability. It was found that in present certain metals (for example, iron) ether thermal stability is significantly reduced.

During friction, a lubricant accumulates magnetic and nonmagnetic wear particles, tribopolymerization products, and lubricant degradation [18, 19]. In addition, oil formulation might include various additives and fillers to improve oil lubricating properties. All this can affect an oil structure, colloidal stability and, therefore, bulk magnetic properties.

To study the effect of magnetic and non-magnetic fillers, we added dispersed additives into a model magnetic oil based on kerosene. We introduced solid lubricant powder of molybdenum disulfide with a particle size of about 1 μm at the rate of ~1.5 vol% (typical for composite lubricants) into the base oil. The multidomain barium ferrite powder with a 1÷5 μm dispersiveness was introduced into the same magnetic oil. Its load in 1 cm³ oil was 120 mg.

4 Research results and discussion

Figure 1 shows the theoretical and experimental magnetization-strength curves of the oil based on kerosene with 7% magnetite volume content stabilized by oleic acid. Curve 1 was obtained using a magnetometer, curve 2 is the dependence theoretically calculated by formula (1). There is some discrepancy between the calculated and experimentally established dependencies. However, it is possible to use a magnetization curve according to the formula (1) if it is necessary for design calculations of bearing assemblies lubricated with magnetic oil.

Fig. 1. Kerosene-based magnetic oil magnetization curves with 7% magnetite: 1 is the observed dependence, 2 is a theoretical dependence.

Fig. 2. Oil magnetization curves: 1 – MM-PES4, 2 – MM-PESV, 3 – MM-I, 4 – MM1-PES5, 5 – MM2-PES5.

The average size of magnetite colloidal particles determined by the electron micrograph was 12 nm. The diameters of ferriparticles calculated by formulas (2) and (3) were $d_0 = 12.5$ nm and $d_\infty = 9.6$ nm, respectively.

There are two reasons that might explain the discrepancy between the experimental magnetization curve and the calculated one, as well as the underestimated value of an average ferriparticle size obtained from magnetic measurements compared with the data of electron microscopic studies. First, there might be a chemical interaction of oleic acid molecules with magnetite accompanied by an iron oleate nonmagnetic layer, or the conversion of magnetite into compounds with less spontaneous magnetization after oxidation. Therefore, the content of dispersed particles, which was determined by the gravimetric method and the experimental saturation magnetization of magnetic oil, might differ by 1.4–1.8 times. Second, there is interparticle magnetostatic interaction that causes stable agglomerates with mutual compensation of magnetic moments. Magnetization of agglomerates is due to the rotation of a magnetization vector held by the anisotropy field, which requires increased magnetic fields.

Figure 2 shows the experimentally obtained magnetization curves of a number of magnetic oils used to optimize the tribological parameters of friction units with magnetic lubrication. The quantitatively reduced curves differ significantly in the values of the initial permeability and saturation magnetization. At a qualitative level, the magnetization curve run is explained by the magnetic dispersed phase concentration and composition. As the magnetic dispersed phase concentration increases, magnetic saturation is observed in higher fields exceeding $1.5 \cdot 10^4$ A/m.

Figure 3 shows the results of the analysis of changes in the MM-P oil magnetic properties after long-term availability. It also shows the magnetization curve of the base oil (before testing). Tribological effects on magnetic oil lead to the fact that the magnetization curve of the oil collected from the friction track after 140 hours of work as a lubricant goes much lower. This indicates that spent oil partially loses its magnetic properties. We should note that there was oil near the friction track that did not react to the magnetic field at all.

Fig. 3. Magnetization curves of the magnetic oil MM-P: 1 is the base oil, 2 is after heating at 100°C for 10 hours, 3 is after heating at 100°C for 50 hours, 4 is after 140 operating hours.

Fig. 4. Magnetization curves of the magnetic oil: 1 is with the molybdenum disulfide additive, 2 is the base oil, 3 is with ferrite additive, 4 is with the excess oleic acid.

If we take into account the fact that the content of the dispersion medium has decreased in the spent oil, which means that the content of ferriparticles has increased, then the decrease in magnetic properties will be higher than it follows from the graph in Figure 3. It is known [20] that friction causes large pressures on friction contact spots and local temperature flashes up to 600°C and higher for 10^{-6} s. Therefore, the deterioration of oil magnetic properties

might be due to desorption and destruction of surfactant molecules covering ferriparticles that stimulates particle agglomeration. In this case, there might be oil dispersed phase oxidation to low magnetic iron oxide compounds and particle coagulation with the formation of agglomerates and loss of magnetic properties. Artificial heating of magnetic oil leads to a similar result (see Fig. 3).

Figure 4 shows the results of studying the effect of fillers with different magnetic properties on the magnetization curves run. The kerosene-based magnetic fluid was the model oil. After thorough mixing, the resulting suspension was settled. We have selected a relatively stable fluid with a filler liquid for research.

The studies (see Fig. 4) have shown that the magnetization curve of the kerosene-based model oil with the diamagnetic molybdenum disulfide powder additive runs higher (Fig. 4, curve 1) compared to the initial curve for magnetic fluid without additives (Fig. 4, curve 2). This is somewhat unexpected and might be due to an increase in the dispersed phase concentration in the magnetic fluid colloidal solution due to a decrease in the dispersion medium removed by molybdenum disulfide particles separated in the gravity field.

Introducing polydomain powder of barium ferrite into magnetic oil decreased the saturation magnetization of the gravitationally stable part of the oil (Fig. 4, curve 3). Apparently, here this is due to the gravitational force between oil monodomain colloidal ferriparticles and filler particles. The effect of these forces increases the size and mass of filler particles due to adding magnetite particles to them, which precipitate during gravitational sedimentation, which in turn decreases the bulk magnetic properties of the oil.

Boundary and hydrodynamic friction causes thermal destruction and tribopolymerization of dispersed media accompanied by an increase in diphenyl molecules in the colloidal solution, which was modeled by introducing an excess surfactant-oleic acid into the oil. An increase in the oleic acid content leads to changing in the oil base polarity. Therefore, the ability of the oil to maintain colloidal stability in external magnetic fields decreases [8, 9]. As a result, irreversible flocculation of dispersed particles can occur in magnetic oil (they can be separated magnetically or gravitationally). Floccules (agglomerates) in the oil cause a slower increase in magnetization with increasing magnetic field (see Fig. 4, curve 4), i.e. permeability decreases.

5 Conclusion

The paper shows that tribological effects on magnetic oil cause its magnetization decrease due to the oxidation of magnetic dispersed particles and separation of the dispersion medium in oils with low colloidal stability. Changing the polarity of an oil dispersion medium during friction can cause flocculation of magnetic particles, which in turn reduces oil magnetic permeability. The introduction of solid additives into magnetic oil changes its magnetic properties in various ways, which depends on the dispersiveness of additive particles, their density and magnetic state. The paper confirms that the concentration of magnetic dispersed particles in oil determined by magnetization is slightly lower than the one determined by the gravimetric method due to a non-magnetic shell of the particles.

Thus, the design and operation of friction units lubricated by magnetic oils require taking into account the established change in their magnetic properties and not allowing operation in extreme conditions that lead to a loss of magnetic properties.

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