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The influence of cavitational synthesis nanodiamonds on the tribological properties of a water-oil-based cooling lubricant

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Abstract: This paper deals with the study of the influence of nanosized diamonds produced by the cavitational synthesis method on the tribological properties of a commercial water-oil-based cooling lubricant. The study is aimed at assessing the prospects for application of this type of nanodiamonds as an antifriction and antiwear additive. Tribological tests were carried out using the "indenter on a disk" friction scheme at a constant load and sliding speed. High-speed P18 steel for the indenter and 30HGSA steel for the rotating counterbody (disk) were used as friction couple materials. The studies were carried out for the base lubricant and two variants of its composition modifications using colloidal dispersion (distilled water with dispersed nanodiamonds) with a final additive concentration of 0.5 and 2.5 %. It was experimentally found that both variants of modification of the base water-oil emulsion resulted in increase of the bearing capacity of lubricating layers, decreasing the total linear wear of friction couple elements by 1.8–2.4 times. The presence of nanodiamonds in the composition enhanced as well the shielding effect of the cutting coolant. A decrease in visible damage to friction surfaces was recorded using optical microscopy. Analysis of profile diagrams of worn areas in the transverse direction showed a decrease in the size of a groove on the counterbody against the background of a decrease in roughness from *Ra*=0.49 µm in the basic variant to *Ra*=0.29–0.34 µm. Evaluation of the loss in counterbody weight for nanodiamond concentrations of 0.5 and 2.5 % showed a decrease in their value by 1.3 and 1.9 times, respectively; for the indenter, the decrease in this parameter was 1.2 and 1.5 times. Thus, the use of cavitational synthesis nanodiamonds as an additive may become a promising direction for increasing the antiwear properties of water-oil-based cooling lubricants.

Keywords: cavitational synthesis nanodiamonds; water-oil emulsion; cooling lubricant; boundary friction; wear resistance; friction ratio.

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INTRODUCTION

The use of various types of additives is an effective way to control the tribological properties of liquid lubricants. In the last decade, nanoparticles of various metals, metal and non-metal oxides, sulfides and carbonates have been widely used for this purpose [1; 2]. Modification of the base lubricant by introducing such additives, as a rule, leads to a significant improvement in its antifriction and/or antiwear properties [3; 4]. Among nanosized additives, fully carbon particles (graphenes, fullerenes, carbon nanotubes) are in high demand, allowing improving significantly the tribological properties of base lubricants [5–7].

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Among carbon nanoadditives, the use of nanodiamonds (ND) is especially promising, due to their high hardness, thermal conductivity, chemical stability and compatibility with other additives [8]. To date, many detailed studies on the tribological characteristics of various types of lubricants containing ND have been conducted. Thus, the authors of the work [9] note a significant improvement in the tribological characteristics of motor oils containing ND particles and in the quality of friction surfaces. When studying the friction process in a polyalphaolefin oil environment with the ND addition, a decrease in the friction coefficients and an increase in the antiwear effect of the lubricating film for the composition with the additive were found as well

[10]. In [11], a 3-fold decrease in the friction force and a 2-fold increase in the wear resistance of titanium hip implants were recorded when adding less than 0.2 % of ND in a weight concentration to the body fluid imitation.

An important advantage of ND is their solubility in water, which opens up opportunities for modifying both pure water and water-based lubricants. In this regard, the study of the tribological properties of aqueous suspensions with ND is an up-to-date area of scientific research. For example, a study [12] showed that the introduction of ND significantly improved the poor lubricating properties of water, reducing friction forces and wear by 70 and 88 %, respectively. A similar antifriction effect and antiwear action of water modified with ND are also noted in the works [13; 14].

A widespread category of lubricants is water-oil emulsion cooling lubricants used in cutting metals and their processing by plastic deformation methods. One of the ways for improving the operational characteristics of cooling lubricants is the introduction of various nanosized additives into the composition, enhancing their anti-scuffing effect, improving antifriction and thermophysical properties [15–17].

Currently, there are many different methods for producing ND. Examples of the most attractive of them in terms of industrial reproduction are the method of pulsed laser ablation of a specially prepared carbon target [18], the method of detonation of explosives in closed chambers [19], and some others. The method of hydrodynamic cavitation is also promising and in demand for industrial application. It consists of passing water with dispersed high-purity graphite powder through special-geometry microfluidic channels with feeding into the zone where, due to the collapse/deflation of cavitation caverns, destructive cumulative jets are formed, a buffer layer with subsequent additional effect on the collapsing caverns of fields with supercritical parameters.

This method is of the greatest interest in terms of the applicability of nanodiamonds produced with its use as a modifying additive in aqueous systems, such as gypsum, cooling lubricants, galvanics, and concrete. The advantages of the method consist in producing ND with high homogeneity of the main characteristic indicators: size, shape, charge, and functional cover. Cavitational synthesis nanodiamonds (CND-NS – Cavitation NanoDiamonds produced by the NanoSystems Company) manufactured by this method do not require additional chemical cleaning, centrifugation and other preparatory operations. Immediately after synthesis, the aqueous dispersion of ND is ready for industrial use, since ND dispersed in distilled water are completely hydrated. At present, studies have already been conducted on the influence of CND-NS on the physical and mechanical properties of building concrete. These studies have recorded a significant increase in compressive and bending strength when adding CND-NS particles to the base mixture [20].

The purpose of this study is to evaluate the influence of nanosized diamonds produced by cavitation synthesis on the tribological properties of a commercial water-oil-based cooling lubricant.

METHODS

Comparative tribological tests were carried out using the “indenter on disk” friction scheme at a constant sliding speed of V=0.4 m/s and a load of P=20 N on a T-11 tribometer (Poland). The material of the cylindrical indenter with a diameter of 4 mm and a length of 10 mm was high-speed P18 steel (HRC 65). The rotating counterbody (disk) with a diameter of 25.4 mm and a thickness of 6 mm was made of 30HGSA steel (HRC 35), the initial roughness of the friction surfaces was Ra=0.16 µm. This friction couple imitates frictional interaction during cutting (smoothing) of a difficult-to-machine structural material. At the same time, according to the previous experimental experience of the authors, the friction process without lubricating these materials is characterised by strong adhesive seizure. During testing, the friction force F(N) and the indenter displacement relative to the counterbody Δ (µm) were recorded in real time. The friction path length was L=400 m. A Mitutoyo Surftest SJ-210 profilograph-profilometer (Japan) was used to evaluate the relief of friction tracks and measure roughness. The worn surfaces of the samples were examined using a LaboMet-I4 metallographic inverted microscope (Russia). The shielding effect of the lubricating fluid was assessed based on a comparison of the wear of the softer counterbody material. An LV 210-A analytical balance (Russia) was used to measure the mass loss Δm of the samples.

The friction process was carried out in three variants of lubricating media. In the first basic case, a commercial Modus-M cooling lubricant (Trading and Industrial Company SINTEZ, Rostov-on-Don, Russia) was used. This semisynthetic water-soluble cooling lubricant in the working solution is a 5 % water-oil emulsion and contains the least amount of oil and other environmentally hazardous functional additives. In the two subsequent versions, the emulsion was modified with a colloidal dispersion consisting of ND dispersed in distilled water. The dispersion was prepared using CND-NS synthesised by Research and Production Company Nanosystems, LLC (Rostov-on-Don, Russia), which are spheroidal nanocrystals with a negative zeta potential of ζ=−44 mV. They were synthesised by the hydrodynamic cavitation method from high-purity graphite powder dispersed in distilled water with additional exposure of the system to alternating fields with supercritical parameters. By the dynamic light scattering method, it was found that the colloidal solution of the produced ND has high monodispersity with a maximum of 1 to 3 nm (Fig. 1).

To assess the influence of CND-NS ND on the tribological properties of commercial cooling lubricant, 0.5 and 2.5 % of CND-NS colloidal dispersion were added to its composition. The concentration of the aqueous colloidal dispersion of CND-NS was determined photometrically using an Expert-003 photometer by passing through a quartz cuvette with an optical path length of 1 mm and a transmission laser wavelength of 375 nm. The optical density was adjusted by diluting the concentrated CND-NS-2772 dispersion with distilled water.

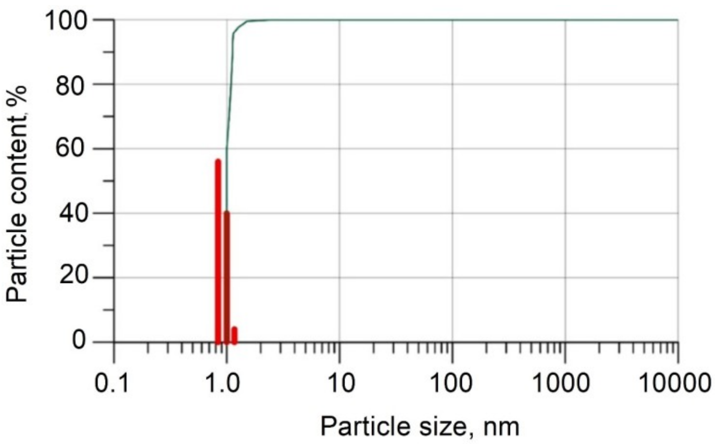

Fig. 1. Particle size distribution of nanodiamonds [24]
Рис. 1. Распределение размеров частиц наноалмазов [24]

Lubricants were supplied directly to the friction track using the drop-by-drop method with a flow rate of about 2 ml/min. The number of experiment implementations for each lubrication option was 5 experiments, statistical processing of the results was carried out using reliability theory methods in the MathCAD program. To calculate the values of the confidence limits for the estimated parameters, the Student's method was used at a specified reliability level of 95 %.

RESULTS

Evaluation of the tribological properties of the lubricant samples showed that both variants of CND-NS concentration in the base cooling lubricant lead to an increase in the average values of friction forces. Fig. 2 shows examples of the evolution of the friction ratios f during the experiments. According to the results of statistical processing, the average value of the friction ratio for the base lubricant variant was f_{av}=0.08; with the addition of 0.5 and 2.5 % of CND-NS, the value of this parameter increased to 0.11 and 0.13, respectively (Table 1).

Evaluation of the change in the tribocontact geometry relative to the initial position using the $\Delta(L)$ curves showed that the addition of additives contributed to a slowdown in the convergence of the friction couple elements due to wear processes (Fig. 3).

The lowest total linear wear of the tribo-couple elements was recorded at a concentration of 2.5 % and averaged δ_3≈3.4 μm, while for the base cooling lubricant this value reached δ_1≈7.8 μm.

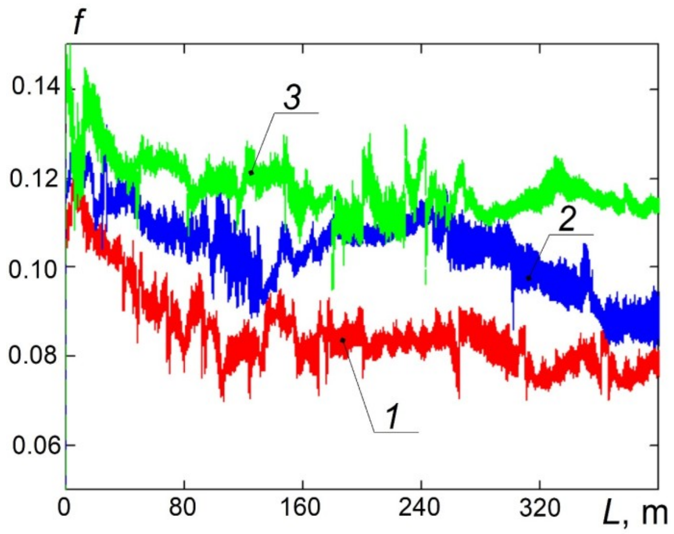

Fig. 2. Change in friction ratios f(L) in various environments:
1 – base cooling lubricant; 2 – cooling lubricant + 0.5 % of CND-NS; 3 – cooling lubricant + 2.5 % of CND-NS
Рис. 2. Изменение коэффициентов трения f(L) в различных средах:
1 – базовая СОЖ; 2 – СОЖ + 0,5 % КНА-НС; 3 – СОЖ + 2,5 % КНА-НС

Table 1. *Tribological characteristics of the friction process in various lubricating environments*
Таблица 1. *Трибологические характеристики процесса трения в различных смазочных средах*

Lubricant type	F_{av}	Counterbody				Indenter
		δ, µm	h_{max}, µm	$\Delta m_c \cdot 10^{-3}$, g	Ra, µm	$\Delta m_{in} \cdot 10^{-4}$, g
Base cooling lubricant	0.08±0.02	7.88±0.99	7.49±1.67	3.21±0.64	0.49±0.16	9.2±0.75
Cooling lubricant + 0.5 % of ND	0.11±0.03	4.45±0.59	4.81±0.86	2.33±0.56	0.34±0.07	7.6±0.81
Cooling lubricant + 2.5 % of ND	0.13±0.02	3.41±0.46	3.22±0.73	1.67±0.40	0.29±0.05	5.8±0.98

The greatest damage was suffered by the surface of the samples during friction in unmodified cooling lubricant (Fig. 4 a). The width of the friction tracks in thiscase reached 1000 µm, the wear depth was h_{max}≈7.5 µm, and the roughness of the friction tracks in the transverse direction was Ra=0.49 µm. Evaluation of the mass losses of the samples also showed the highest values of these parameters during friction in the base cooling lubricant (Table 1).

The surfaces of the samples are damaged to a lesser extent during frictional interaction in the cooling lubricant + 2.5 % of CND-NS environment. The width of the friction track in this lubrication option does not exceed 600 µm; the depth of the worn area is h_{max}≈3.2 µm. The roughness of the friction tracks for this concentration was Ra=0.29 µm. A high shielding effect is found as well when adding a much smaller amount of additive – at a concentration of 0.5 % of CND-NS (Fig. 4 b). In this case, an improvement in all the studied tribological indicators is also observed (Table 1, Fig. 4 c).

DISCUSSION

The introduction of CND-NS nanoclusters into a water-oil emulsion in various concentrations significantly reduces the wear rate relative to the basic tribosystem configuration, but leads to an increase in friction forces. At the same time, the values of the friction ratios in all cases show that the boundary lubrication condition is maintained in the tribosystem.

The method and mode of producing ND, which determine their shape, average size and other statistical indicators of geometric characteristics, significantly affect the tribological behaviour of the lubricant when these particles are introduced into it. The antifriction effect of adding ND, according to the results of modern studies, is mainly associated with a partial replacement of sliding friction with rolling friction due to the presence of particles in the gap that are large enough in comparison with the sizes of surface microasperities, close to a spherical shape [21]. Smaller ND particles, being in the lubricant and penetrating into surface microasperities,

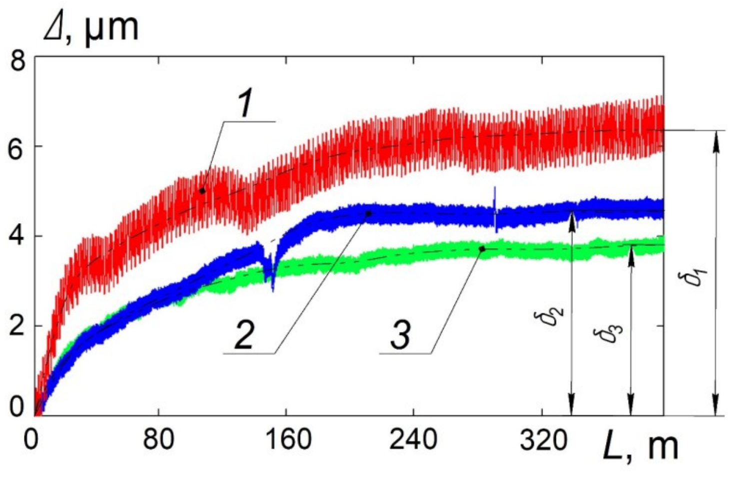

Fig. 3. *Total linear wear of tribocouple elements:*
1 – base cooling lubricant; 2 – cooling lubricant + 0.5 % of CND-NS; 3 – cooling lubricant +2.5 % of CND-NS
Рис. 3. *Суммарный линейный износ элементов трибопары:*
1 – базовая СОЖ; 2 – СОЖ + 0,5 % КНА-НС; 3 – СОЖ + 2,5 % КНА-НС

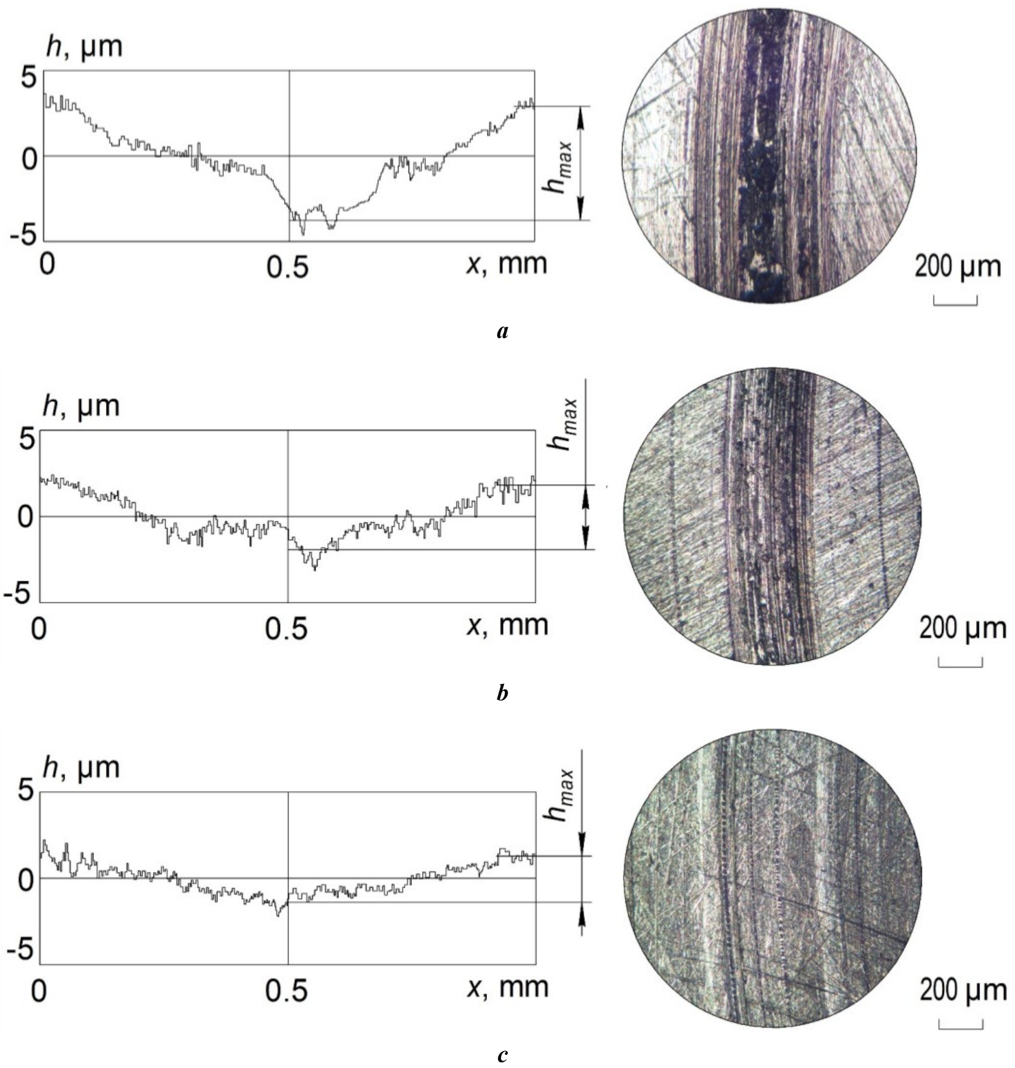

Fig. 4. *Worn surfaces of disks during friction in various environments:*
a *– base cooling lubricant;* ***b*** *– cooling lubricant + 0.5 % of CND-NS;* ***c*** *– cooling lubricant +2.5 % of CND-NS*
Рис. 4. *Изношенные поверхности дисков при трении в различных средах:*
а *– базовая СОЖ;* ***b*** *– СОЖ + 0,5 % КНА-НС;* ***c*** *– СОЖ + 2,5 % КНА-НС*

microasperities, can have a polishing effect. In this case, on the areas of surfaces separated by the lubricant, the presence of ND leads to the formation of a homogeneous and thick tribofilm, which reduces the wear of the contacting bodies [10; 21]. These mechanisms of action on the tribological properties of the lubricant have been proven for particles obtained by the detonation method; they are most often studied as additives [21]. In comparison with CND-NS, these ND usually have a larger size range. Thus, when adding detonation ND, the lubricant contains particles close to a spherical (oval) shape within the range of 5–10 nm. For ND with a diameter in this range, the ball-bearing effect has been proven, including by molecular modelling [12].

When introducing CND-NS, which are significantly smaller in diameter, characterised by higher monodispersity, the ball-bearing effect from the use of ND decreases, giving way to other mechanisms of action. Small-diameter diamond particles (1–3 nm) will fill surface microasperities more easily and remain fixed in them. This type of introduction, on the one hand, protects the faces of the tribo-couple elements from destruction due to the presence of a periodically regenerated protective layer of ND on them; on the other hand, the frictional interaction of surfaces with hard inclusions, accompanied by a polishing effect, is the cause of the increase in the friction force. Concurrently, the ND particles modify the lubricating film, promoting its compaction, increasing abrasion resistance and shear resistance, which leads to an increase in the friction ratio even with the addition of 0.5 % of CND-NS.

Further saturation of the cooling lubricant with nanodiamond particles enhances to an even greater degree the effect of the antiwear and polishing action of CND-NS. The increase in the average friction ratio relative to a concentration of 0.5 % in this case, taking into account the values of the confidence limits, can be considered insignificant (Table 1). Thus, the properties, shape and size of cavitation nanodiamond particles, as well as their high monodispersity, allow achieving significant antiwear and polishing (smoothing) effects when modifying water-oil-based cooling lubricants with them against the background of a slight decrease in anti-friction properties, which generally makes the application of CND-NS as an antiwear additive promising.

CONCLUSIONS

1. Addition of diamond nanoclusters to the studied water-based cooling lubricant resulted in a significant change in the tribological characteristics of the friction system. Modification of the lubricating layers contributed to an increase in their load-bearing capacity, which ensured a decrease in the total linear wear of the friction-couple elements by 1.8 and 2.4 times at colloidal dispersion concentrations of 0.5 and 2.5 %, respectively.

2. Intermediate layers containing CND-NS increased the shielding effect of the lubricant in comparison with the base version, reducing the average roughness of the friction tracks by 1.4 and 1.6 times, which indicates an improvement in the surface quality after using the modified cooling lubricants.

3. Addition of nanosized diamonds enhanced the antiwear properties of the lubricant. The reduction in mass losses of the rotating counterbody for colloidal dispersion concentrations of 0.5 and 2.5 % was 1.3 and 1.9 times, respectively, for the indenter – 1.2 and 1.5 times. The observed reduction in wear of the friction-couple elements was accompanied by an increase in the shear resistance of the lubricating layer, contributing to an increase in the friction force in the system by 1.4 times even with the addition of 0.5 % of nanodiamonds. A further increase in the amount of additive to 2.5 % led to an insignificant increase in the friction ratio relative to the minimum concentration of nanodiamonds.

The use of cavitational synthesis nanodiamonds as an additive in water-oil-based cooling lubricants can become a promising direction for further improvement of tribological properties and enhancement of their performance characteristics. The development of new compositions of cooling lubricants based on the studied commercial brand with the addition of nanocrystalline diamonds in various concentrations and subsequent studies of the performance characteristics of these experimental compositions in various metal cutting operations, plastic deformation processing, and knurling are considered as up-to-date sectors of further research in this area. The expected effects from the lubricant modification in this case will be an increase in the service life of the tools used and an improvement in the quality of the microrelief of the treated surfaces.

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Влияние наноалмазов кавитационного синтеза на трибологические свойства смазывающе-охлаждающей жидкости на водомасляной основе

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Аннотация: Статья посвящена изучению влияния наноразмерных алмазов, полученных методом кавитационного синтеза, на трибологические характеристики коммерческой смазывающе-охлаждающей жидкости на водомасляной основе. Исследование направлено на оценку перспектив применения наноалмазов данного типа в качестве антифрикционной и противоизносной присадки. Трибологические испытания проводились по схеме трения «индентор по диску» при постоянной нагрузке и скорости скольжения. В качестве материалов пары трения использованы быстрорежущая сталь Р18 для индентора и сталь 30ХГСА для вращающегося контртела (диска). Исследования проведены для базового смазочного материала и двух вариантов модификаций его состава коллоидной дисперсией (дистиллированная вода с диспергированными наноалмазами) с окончательной концентрацией присадки 0,5 и 2,5 %. Экспериментально установлено, что оба варианта модификации базовой водомасляной эмульсии привели к увеличению несущей способности смазочных слоев, снизив суммарный линейный износ элементов пары трения в 1,8–2,4 раза. Присутствие наноалмазов в составе также усилило экранирующий эффект смазочно-охлаждающей жидкости. Посредством оптической микроскопии было зафиксировано снижение видимых повреждений поверхностей трения. Анализ профилограмм изношенных участков в поперечном направлении показал уменьшение размеров борозды на контртеле на фоне снижения шероховатости с Ra=0,49 мкм в базовом варианте до Ra=0,29–0,34 мкм. Оценка потери массы контртел для концентраций наноалмазов 0,5 и 2,5 % показала снижение их величины в 1,3 и 1,9 раза соответственно, для индентора уменьшение этого параметра составило 1,2 и 1,5 раза. Таким образом, использование наноалмазов кавитационного синтеза в качестве присадки может стать перспективным направлением повышения противоизносных свойств смазывающе-охлаждающих жидкостей на водомасляной основе.

Ключевые слова: наноалмазы кавитационного синтеза; водомасляная эмульсия; смазывающе-охлаждающая жидкость; граничное трение; износостойкость; коэффициент трения.

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