Tribological properties of lubricant additives of Fe, Cu and Co nanoparticles

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ABSTRACT

Tribological investigations were performed on mineral oil containing Fe, Cu and Co nanoparticles and their combinations. The tribological tests showed that each set of nanoparticles significantly reduced the friction coefficient and wear (up to 1.5 times) of friction pairs. The use of Cu nanoparticles provides the most effective reduction of friction and wear in each combination of nanoparticles. Surface analysis shows that the constituent elements of nanoparticles precipitated on the contact surface during the use of the oils with nano-additives. Different structures formed on the friction surface are observed in the contact zone and over the remainder of the ball surface. The SEM micrographs and EDX chemical analysis confirm the formation of a tribo-layer composed of the elements from the nanoparticles.

1. Introduction

Recent research papers have reported that the addition of nanoparticles to lubricant is effective for the reduction of wear and friction in mechanical systems. Because of the remarkable tribological properties of nanoparticles, nanotechnology is regarded as the most revolutionary technology of the 21st century [1].

Numerous nanoparticles have recently been investigated for use as oil additives. Nano-powders of some metals and their compounds exert an especially effective influence on the characteristics of lubricants. The use of nanoparticles that include Cu, CuO, Fe, Ni, TiO2 and other metallic nanoparticle additives in lubricating oils provides good friction reduction and anti-wear behavior [2–10]. Among these additives, Cu nanoparticles have received significant attention because they deposit on the friction surface, improve the tribological properties of the base oil and display good anti-friction and wear reduction characteristics [2–9]. When CuO was added to API-SF oil (engine oil SAE 30) and base oil for friction testing, the friction coefficients were reduced by 18.4% and 5.8%, respectively, in comparison to the oils without nanoparticles [2]. The measurements of the friction coefficient and the surface temperature during the tribological tests showed that the oils with added copper nanoparticles had lower friction coefficients than the raw oil. According to AFM and EDS analyses, oils with nano-additives fill the scars and grooves on the friction surface when the nanoparticles precipitate between the friction surfaces [3].

The tribological efficiency of metallic nanoparticles is mostly explained by the formation of anti-wear film on friction surfaces [2–4,8,9]. The formation of copper film from oil containing Cu particles is explained by two possible mechanisms: first is based on the chemical and electrochemical effects (at the onset of the rubbing, Cu nanoparticles deposit on the worn surface, which is “fresh”, having removed surface oxide layer in sliding through electrostatic adhesion caused by sliding of the friction surfaces) and the second is based on fundamentals of mechanical metallurgy (the Cu nanoparticles partly melt due to their low melting point, the local overheating and high flash temperature on friction surface in spite of the oil cooling) [4,8].

In addition to reducing the friction coefficient, liquid lubricants with solid additives increase the load carrying capacity of the lubricating fluid [3,11]. The friction-reduction and anti-wear behavior is dependent on the characteristics of the nanoparticles. Investigations of DDP-modified copper nanoparticles show that small size nanoparticles improve the tribological characteristics more efficiently [3]. Concentration of nanoparticles in oil plays significant role in tribological efficiency of such additives [7]. This shows that the formation of the tribological film takes place at certain conditions which are related to the state of nanoparticles in the lubricating fluid. Furthermore, diverse effects such as decreased friction and changes in the lubrication regime have also been reported [1].

The mechanisms by which oils with nano-additives reduce friction and wear are the colloidal effect, rolling effect, small-size effect, protective film effect and third body effect [2–4,8,9].

Chinas-Castillo and Spikes investigated the action mechanism colloidal solid nanoparticles in lubricating oils. Their study showed that colloid nanoparticles in thin film contacts penetrate
elastohydrodynamic (EHD) contacts, mainly by the mechanism of mechanical entrapment. They also found that colloids formed a boundary film in rolling contacts at slow speeds that was at least one or two times the particle size [11]. Choi et al. investigated the tribological efficiency of copper nanoparticles at different lubrication regimes. It was evident that the Cu nanoparticles were more effective in mixed lubrication than in full-film lubrication [9].

It means that the possible interaction of friction surfaces is important in the formation of copper film and its tribological efficiency. The friction reduction mechanism works when the Cu nanoparticles fill the scars and grooves of the friction surface and the physical film forms above the nanoparticles. It makes the friction surface flat and smooth resulting in a decrease of frictional force [9].

The purpose of this work is to determine the tribological effect of different mixtures of metallic nanoparticles and their compounds added to mineral oil for the lubrication of steel–steel friction pairs.

2. Experimental

2.1. Preparation of testing materials

The nanoparticles added to the tested oils were produced by the method, in which converse emulsions of water in lubricant solution (CEWLS) were used. The nanoparticles were created by the filling of minimal contents of water solutions of the reagents, according to the calculated concentration for the planned synthesis. A “water-in-oil” micro emulsion is formed when water is dispersed in a hydrocarbon-based continuous phase, which is normally located towards the oil apex of a water/oil/surfactant triangular phase diagram. In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles [12]. Spherical reverse micelles, which minimize the surface energy, are the most common form.

The CEWLS method provides a stable dispersion of nanoparticles in SAE 10 mineral oil, which was used as the base oil. The viscosity of the oil at a temperature of 100 °C was 14.1 mm²/s, and at a temperature of 40 °C it was 98.3 mm²/s. The same oil was used for the control version of the tests (in which it is called SAE 10).

To prepare the oils with nano-additives using the CEWLS method, 100 ml of SAE 10 mineral oil emulsion was prepared with 0.2 ml H₂O containing dissolved sulfates of certain metals, such as FeSO₄, CuSO₄, or CoSO₄ and 0.5 g cetyltrimethylammonium bromide (CTAB). This mixture was added to 10 ml hydrazine emulsion, and the entire volume was mixed intensively for 5 min.

The following chemical reactions took place during the CEWLS synthesis:

\[ 2\text{Fe}^{2+} + 2\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Fe} + 2\text{N}_2 + 4\text{H}_2\text{O} \]

Table 1

<table>
<thead>
<tr>
<th>Title of nano-oil</th>
<th>Nanoparticles</th>
<th>Content of metal (g/100 ml oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE 10 + Fe</td>
<td>Fe</td>
<td>0.5</td>
</tr>
<tr>
<td>SAE 10 + Cu</td>
<td>Cu</td>
<td>0.5</td>
</tr>
<tr>
<td>SAE 10 + Co</td>
<td>Co</td>
<td>0.5</td>
</tr>
<tr>
<td>SAE 10 + Fe + Cu</td>
<td>Mixture of Fe and Cu</td>
<td>0.25/0.25</td>
</tr>
<tr>
<td>SAE 10 + Fe + Co</td>
<td>Mixture of Fe and Co</td>
<td>0.25/0.25</td>
</tr>
<tr>
<td>SAE 10 + Co + Cu</td>
<td>Mixture of Co and Cu</td>
<td>0.25/0.25</td>
</tr>
<tr>
<td>SAE 10 + FeCu</td>
<td>Fe coated by Cu shell</td>
<td>0.25/0.25</td>
</tr>
<tr>
<td>SAE 10 + FeCo</td>
<td>Fe coated by Co shell</td>
<td>0.25/0.25</td>
</tr>
</tbody>
</table>

Capek [13] used a similar procedure of microemulsion preparation, which is presented in Fig. 1. However, his method does not include the mechanism of formation of mixtures and the core/shell structure of the nanoparticles.

Fig. 2(a) and (b) presents the difference between the synthesis of the nanoparticle mixtures (Fe + Cu, Fe + Co and Co + Cu) and the core nanoparticles (Fe) with shells of another metal (Cu).

The CEWLS synthesis process includes the reduction of any chemical residues in the oil. The added hydrazine (2–5% of oil content) reacted during the synthesis and disappeared. The salt anion-containing residues of the water emulsion were eliminated by drying with natrium sulfate.

\[ 4\text{Cu}^{2+} + 2\text{N}_2\text{H}_4 \rightarrow 4\text{Cu}^0 + 2\text{N}_2 + 8\text{H}^+ \]

\[ \text{Co(II)} + \frac{1}{2} \text{N}_2\text{H}_4 + 2\text{OH}^- \rightarrow \text{Co} + \frac{1}{2} \text{N}_2 + \text{H}_2\text{O} \]
The concentration of metal nanoparticles was 0.25 wt% in the oil. Mixtures of the nanoparticles with the same concentration of metals were used for the tribological investigations.

2.2. Tribological testing and surface analysis

The friction coefficient was measured by a four ball tribotester. Fig. 3 shows a schematic diagram of the tribotester that was used for evaluation of the friction coefficient of the raw oil and the oils with nano-additives.

The experiments were performed at room temperature. Balls with a diameter of 12.7 mm were made of 100 Cr6 bearing steel (E=21.98 x 10^11 MPa; ν=0.3; 63,..., 66 HRC). The testing procedure was adapted from the standard DIN 51 350, Part 3 [14]. A test oil sample with a volume of 22 cm^3 was poured into the sample compartment, fully submerging the stationary balls. Under an applied load of 150 N (matching 1.05 GPa pressure in contact zone of specimens in the initial test period) and a rotation speed of 1420 min^-1, the machine was run for 1 h. Before and after each experiment, all of the appropriate parts of the machine (i.e., the lower and upper ball holders, oil vessel and the test balls) were washed in an ultrasonic bath with hydrocarbon solvents and dried. The friction torque between the balls and the temperature change of a liquid sample were recorded during the test. Three identical tests were performed for each sample to minimize data scattering.

The wear was evaluated according to the wear scar diameter on the steel ball surfaces. The diameters of the circular wear spots on the three stationary balls were measured with an optical microscope (accuracy 0.007 mm). For each run, the spot measurements were reported in millimeters as an average of the wear spot diameter (WSD) of the three balls.

Surface analysis was performed by optical microscope and SEM microscopy (FEI Quanta 200 FEG). Determination of the chemical content at selected wear spots of the specimens was performed by energy-dispersive X-ray (EDX) analysis with a Bruker X-Flash spectrometer.

3. Results

3.1. Results of tribological tests

The friction coefficient was evaluated according to the friction torque measurements during the tribological tests. The results are presented in Fig. 4(a)–(c).

Each application of nanoparticles reduced the friction coefficient of the friction pairs. However, the use of different additives and the variation trends of the friction torque necessitate a discussion of the possible reasons for the effectiveness of the nanoparticles.

The graphs in Fig. 4(a) show that the cobalt nanoparticles reduce the friction torque (up to 20%) as well as the control version of the oil, but they demonstrate an increasing trend during the operation of the friction pairs. The friction torque obeys a different trend when the oils containing Fe and Cu nanoparticles are applied. After the initial increase (equivalent to the base oil and the oil with cobalt nano-additives), the friction coefficient begins to decrease after 1000 s of testing and stabilizes at a level that is significantly lower than the control version of the oil. The Fe nanoparticles reduce the friction coefficient by 39%, and the copper nanoparticles produce as much as a 49% reduction. This drop, fluctuation and later stabilization of the friction torque can be explained by the formation of a metallic nanoparticle layer on the friction surface that operates at lower friction levels.

The mixtures of nanoparticles were investigated to identify the materials that are most effective for the reduction of the friction coefficient. The graphs in Fig. 4(a) show similar tendencies for the use of iron and copper, but the friction torque measurements in Fig. 4(b) clearly show that copper is most active and plays a different role in lubrication as a nanoparticle additive. The mixture of Fe and Co nanoparticles clearly decreases the friction torque (up to 36%), but the participation of Cu in the mixture reduces the friction more quickly and to a greater degree (53%). The graph shows no differences in the friction reduction provided by the Co+Cu and Fe+Cu mixtures, but higher friction is encountered without the participation of Cu. Therefore, copper is the active component of the mixture. The Fe+Co mixture encounters increased friction at 2000 s of testing time, the same point at which the Co+Cu and Fe+Cu mixtures stabilize at a much lower level, possibly forming a tribologically active anti-friction layer.

The iron nanoparticles covered with cobalt and copper were created to identify the most effective nanoparticle additive. The friction behavior of these additives can contribute to an understanding of the action of nanoparticles made from different metals and the possibilities for tribo-layer formation. Fig. 4(c) confirms the greater effectiveness of copper for friction reduction. Iron nanoparticles coated with copper (FeCu) reduce the friction torque by 55% relative to the base oil, and they stabilize at 2000 s. Although FeCo exhibits a friction increase at the beginning, it later decreases to 50% less than the control. There is an interesting fluctuation in the friction torque at 1500 s (for the FeCo nanoparticles) and a less-clear fluctuation at 2500 s (for the FeCu particles). These fluctuations could be explained by the uneven formation of a tribo-layer because two metallic components participate in this process.

Wear measurements according to the wear spot diameter on test balls (Fig. 5a–c) show that the anti-frictional efficiency of the nanoparticles reflects the longevity of friction pairs. Fig. 5(a) shows a comparison of the wear results between the base oil (SAE 10) and the same oil with nano-additives of the investigated metals. Similar to the friction results, the oil with copper nanoparticles exhibits the most improved tribological results,
reducing the wear by 47%. Fe and Co nanoparticles also reduce the wear by 23% and 11%, respectively. The mixture of copper and iron nanoparticles (Fig. 5b) decreases the wear by nearly a factor of two (50%), and the Co\(^+\)+Cu and Fe\(^+\)+Co mixtures are also very effective (44% and 32% lower wear, respectively). Interestingly, the use of iron nanoparticles coated with Cu and Co shells (Fig. 5c) has almost the same influence on the longevity of the friction pair (approximately 20% lower wear), but it is less effective than the mixtures of single-metal nanoparticles. However, the shell nanoparticles more effectively reduce the friction coefficient.

Measurements were made with SAE 10 oil containing the surfactant CTAB but no nano-additives to exclude the tribological influence of CTAB itself. The results show that the pure CTAB without nanoparticles does not influence the friction torque (the fluctuations of this value fall within a range of 2%). The wear of samples using the SAE 10 oil with CTAB is higher (for 18%) than that of the pure SAE10 oil. This result confirms that the tribological effectiveness of the investigated nano-additives is based on the impact of the nanoparticles, and the surfactant CTAB itself does not influence the tribological results.

In summary of the wear test results, we conclude that the wear reducing ability of copper nanoparticles (pure, in mixtures and with an iron shell) is the most pronounced among all of the tested nano-additives. This ability may be related to the properties of copper as an active metal. However, the effectiveness of all metallic nano-additives shows that the tribological impact of nanoparticles is primarily related to the unique properties of nanoparticles as materials with very large comparable surfaces and increased surface energy as a result of their free atomic bonds.

The results of tribological testing show that Co nanoparticles as a separate additive are not as effective as their combination with Fe nanoparticles (mixtures and shells). However, the most effective strategy is the use of Cu nanoparticles, which are also the most effective additive in each combination. Fe nanoparticles are not as effective as the Cu nanoparticles, but they influence the tribological efficacy of the Cu and Co nanoparticles. Mixtures of Fe with Cu nanoparticles reduce the friction and wear of specimens more than pure Cu nanoparticles, which could mean that Fe nanoparticles are important for the formation of a friction and wear reducing layer and its better adhesion with the bulk material of the steel balls.

The formation of an effective tribo-layer as a result of the properties of the nanoparticles is confirmed by the investigations of other researchers [2–4,8,9]. However, these premises should be verified by the analysis of the friction surfaces.
Fig. 5. Wear-test results according to the wear-spot diameter when using the basic oil (SAE 10) and oils with nano-additives: (a) with metallic nanoparticles; (b) with the mixtures of nanoparticles and (c) with iron nanoparticles coated with Cu and Co.

Fig. 6. Pictures of wear scars on the balls that operated with SAE 10 oil with metallic nano-additives: (a) Fe nanoparticles; (b) Cu nanoparticles and (c) Co nanoparticles.
3.2. Investigation of surface and nanoparticles

Surface investigation by optical microscopy shows that different wear surface form when the nano-additives are used, including the copper nanoparticles. The pictures in Fig. 6 present the wear scars on the balls that operated with SAE 10 oil with Fe, Cu and Co nanoparticles. The images of the balls that operated with Fe and Co nanoparticles (Fig. 6a and c) show that the wear scars completely abraded ball processing traces and formed new a surface with the scars from the ball contacts. The contact zone on the ball that operated with Cu nanoparticles is covered by wear scars, but it is also covered by remaining ball processing traces. In addition to abrasion wear, zones of adhesion wear are also visible in Fig. 6(b). This result suggests that a different wear mechanism took place during operation when oil with copper nanoparticles was used that is indicative of more effective wear resistance. This result also indicates that copper nanoparticles play an active role in the contact zone.

The SEM image of the control version of the tests (Fig. 7) shows the different character of the wear that occurred during the use of the pure SAE 10 base oil. The surface at the wear spot does not show any features indicating an additional layer or a surface transformation.

Fig. 8 shows the SEM images that indicate the chemical elements of wear scarring on the balls that operated under the oils with Cu and Co nanoparticles. The layer of metal visibly depends on the nanoparticles that were formed in the contact zone of the balls. The layer of Co nanoparticles (Fig. 8c) is less thick, but the area of the cobalt layer extends past the contact spot. The edge picture shown in Fig. 8(b) demonstrates that the layer of Cu formed exactly in the wear spot, and no copper is present over the rest of the ball surface. Fig. 8(d) also displays the difference in the character of the surface structure between the contact zone and the remaining surface of the ball when Co nanoparticles were used.

The surface investigation of the wear scars produced with mixtures of nanoparticles is important because those versions of the tests exhibited the best results for the reduction of the friction and wear. Fig. 9(a) and (e) indicates the presence of copper on the surface when the mixtures of Fe or Co nanoparticles with Cu nanoparticles were used in the operation of the friction pairs. Fig. 9(c) show the concentration of Co on the contact zone. Those images show that the elements of the corresponding nanoparticles precipitated on the contact surface during the operation.

Fig. 7. SEM image of wear scar on the ball operated with base SAE 10 oil.

Fig. 8. Selected images indicating the chemical elements of the wear scars on the balls that operated under the oil with Cu nanoparticles (a and b) and Co nanoparticles (c and d).
of the oils with nano-additives, and Fig. 9(b), (d) and (f) display the different structures of the formed friction surfaces.

When Cu particles were used in the oil, the copper layer always exhibited daubed corners (Figs. 8b and 9b and f). This phenomenon clearly confirms the formation of a copper layer. Interestingly, a lubrication-friendly porosity of the surface formed when Co nanoparticles participated in the friction process. This modification could be observed when pure Co nanoparticles were used (Fig. 8d) and when the mixture of Fe and Co nanoparticles were tested (Fig. 9d). All of the pictures in Figs. 8 and 9 confirm the formation of layers of the elements from the nanoparticles.

The EDX spectra of the wear scar surfaces (Fig. 10) confirm the presence of the corresponding chemical elements when the friction pairs were operated with oils with nano-additives. The selected spectra show Cu and Co, which originated from the nanoparticles, but they also show chromium (which is an element of the ball alloy) and sulfur (which is usually present in oil).

Fig. 10(c) and (d) confirm that the elements of the nanoparticles also precipitate in the wear spot also Fe nanoparticles with Cu and Co shells are used, proving that a tribo-layer also forms from the elements of the nanoparticles.

Detailed investigation of nanoparticles has not been performed. However, it is important to ascertain the formation of nanoparticles. According our CEWLS method the nanoparticles are prepared in oil. Due the complicated micrography of nanoparticles in oil, the samples for SEM imaging are prepared according to special methodology. After washing of the sample from oil with the acetone the solution with nanoparticles is coated on silicon plate and dried with hot air. The SEM micrograph of this sample is presented in Fig. 11.
The complicated sample preparation by oil removal causes the presence of halo around the nanoparticles. Taking into consideration that the same method is used for the preparation of all nano-additives the size of nanoparticles could be confirmed in the range of 50–80 nm. Similar size of the nanoparticles prepared according to this synthesis methodology is presented in literature [13,15].

4. Discussion

The tribological efficiency of our suspensions with nanoparticles is considerably higher in comparison to results of former investigations of metallic nanoparticles in oil [2,4,8–10]. Our investigated nano-additives in oil reduces the friction coefficient and wear up to 1.5 times compared to the oil without such additives.

Fig. 10. EDX spectra of wear scars on the balls that operated under the oil with: (a) Cu nanoparticles; (b) Co nanoparticles; (c) iron nanoparticles with Cu shell (FeCu) and (d) iron nanoparticles with Co shell (FeCo).
The mechanism of friction and wear reduction should be different due to the use of different nanoparticles of Fe, Cu, and Co, their mixtures and nanoparticles with core/shell structure. As the nanoparticles are most efficient at boundary and mixed lubrication regimes [2,9] two basic mechanisms of nano-additives efficiency are considered.

The first mechanism includes the filling of the microasperities (scars and grooves) of the friction surface with the nanoparticles from the lubricating fluid. It causes the increase of contact area of friction surfaces, the decrease of the contact pressure and the replacement of sliding friction with the rolling effect in contact zone [2]. Such mechanism may explain the efficiency of different metallic nanoparticles (Fe, Cu, and Co).

The other mechanism is related to formation of ultrathin protective film of oil-copper when the temperature and real contact pressure are high enough to cause an electrochemical reaction and electrostatic adhesion of Cu nanoparticles with friction surface. Such deposition is possible due to high plasticity of copper and removal of surface oxide layer due to the attrition of the friction surfaces [8]. The investigations of the traces of copper residues exactly in the area of the wear scar confirm this mechanism of copper film formation. Such ultrathin copper film operates as a soft surface film on hard substrate and reduces the friction force thanks to lower shear strength of weaker metal. Such film makes the friction surface flat and smooth and it causes the reduction of mechanical component of friction force as well.

The wear resistance ability of such nano-additives (especially those which includes Cu nanoparticles) should be related to compensation of substrate wear by the third-body wear in friction area and regular renewal of protective metallic film of the nanoparticles when they get to contact zone because of electrochemical reactions. Possible increase of plasticity and dispersion range of nanoparticles in oil could enable the controlled shift of lubrication regime from mixed lubrication to full-film lubrication despite the increasing loading.

5. Conclusions

- The tribological investigation of oils with nano-additives shows that each application of Fe, Cu and Co nanoparticles significantly reduces the friction coefficient and wear (up to 1.5 times) of friction pairs. The trends of the varying friction coefficients show that a friction- and wear-reducing layer of the nanoparticle material forms during the application of friction. Tribological testing shows that the use of Cu nanoparticles is most effective for the reduction of friction and wear, both alone and in each combination of nanoparticles. The use of mixtures of nanoparticles is more effective than the use of pure nanoparticles.
- Surface analysis of the wear spots shows that the elements of the according nanoparticles precipitate on the contact surface during the operation of the oils with nano-additives. The different structure of the formed friction surface is clearly observed in the contact zone and over the rest of ball surface. The SEM images and EDX chemical analysis confirm the formation of a tribo-layer of the elements from the nanoparticles.

References