Investigation of the tribological properties of nano-scaled ZrO$_2$ and CuO additive in automotive lubricants

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Abstract. To improve the fuel efficiency and the lifetime of the internal combustion engines, the lubricants and their additives have to be developed further. One of the possible future engine lubricants can be the nano-sized ceramic particles, which can provide positive tribological properties also in the presence of non-metallic surface materials. This paper presents the results of investigations with the help of ZrO$_2$ and CuO nano-sized ceramic particles. To define the tribological properties of these additives, lubricant samples with different additive-concentrations were prepared and tribologically analysed. The frictional losses of these lubricant samples were analysed by a ball-on-disk sliding friction machine. The worn surface on the test specimens was analysed by different high-resolution microscopes. To define the functional mechanisms of the nano-additives, the worn surfaces were investigated by high resolution scanning electron microscopes. The ZrO$_2$ additive has experimentally shown an excellent wear reduction property (over 40% wear reduction compared with the neat Group 3 base oil) at the optimum mixing concentration of 0.4wt%. Both frictional and wear reduction properties could be determined at the application of CuO additive (15-15% friction coefficient and wear scar diameter reduction) at its optimum concentration (0.5wt%). A copper-yellow layer can be seen on the worn surface of the disc specimens with CuO, which indicates the mechanism of chemical transformation to elementary copper from the cupric-oxide nanoparticle and this elementary copper can be melted on the surface, because of the applied high temperature and high loads during the experiments.

1. Introduction

The emission regulations in Europe are becoming continuously strict which requires the development of the different components of the vehicles on the road. One of the most important development topics is the reduction of the different losses in the internal combustion engines, e.g. thermal and mechanical losses including frictional losses. During the last years, the engineers and researchers have elaborated several solutions to increase the efficiency of the engines, e.g. low-viscosity lubricants, low-friction coatings, etc. To take advantage of the maximum potential of these solutions, the different solutions have to be suited together.

The lubricants are one of the most important components of the piston engines. Their roles are to separate the rigid surfaces, prevent them from wear, corrosion, and decrease the frictional losses. To fulfill these challenges, the modern engine lubricants have to be formulated with the use of different additives. The lubricant additives of today are usually function due to polarity difference and they can form a protective nano-scale layer on the rubbing surfaces. In the last years, the compatibility of the
lubricant additives and the exhaust gas after-treatment systems became vital to the harmful emission products. Some additives can form ash during their burning process and this ash can seal the channels in the particle filters, or they can cause damages in the catalyst systems of the vehicles.

These tribological losses will lead to different energy losses and failures in the mechanical systems due to friction and wear, and these losses can strongly influence the fuel consumption and component lifetimes of the engines and vehicles. Different statistics are existing, which show a third of the world’s primary energy consumption due to friction, and the wear is responsible for 60% of the damage of machine parts. Besides the lubrication failure can cause more than 50% of accidents involving machinery equipment. [1]

One of the possible solutions for the future lubricant additive can be the nano-particles. These particles can be made of a huge variety of materials. According to their material, they can offer quite different properties. However, this huge amount of variety requires research activities to map their properties and their optimal mixing concentration in different types of lubricants. These types of particles can have lots of influence factors regarding tribology, e.g. particle size, material, the property of building agglomerations, concentration, or attendance of surface-active solving agents.

2. Nano-sized ceramic particles as lubricant additives
The existence of powder form nano-materials can be very useful for different applications: they can be the starting material for different coatings (e.g. atmospheric plasma spray) or they can be sintered into new and complex material and geometry. The research activities to use this kind of additives in lubricants of machines have started in the recent few years. During this research time plenty of nano-particle material, size, and form were investigated by many institutes which shows until now encouraging.

The most widely investigated size of these particles is the nano-scale with spherical form, which means the average particle size is between 1 and 100nm [2]. These size of additives results in the best homogenization properties: between the particles, there are always secondary Van der Waals forces which can be separated via e.g. ultrasonic homogenizer resulting in a homogeneous lubricant-additive mixture. Besides, these secondary forces can also increase the adhesion property of the nano-particle additives to the rubbing surfaces [3].

![Figure 1. Different working mechanisms using nanoparticles, a) rolling mechanism, b) mending mechanism, c) polishing mechanism, d) protective film [4] [5]](image)

Different working mechanisms were reported in the literature to describe the investigated results. Zhang et al. [4] summarized the different mechanisms for nanoparticles (Fig. 1):

- **Rolling (or ball bearing) mechanism:** the nanoparticles will work as nano-scale balls to roll between the rubbing surfaces and change the sliding friction to sliding-rolling one.
- **Mending mechanism:** the nanoparticles can be collected in the grooves of the rubbing surfaces resulting in a smoother contact surface.
- **Polishing mechanism:** the nanoparticles will polish the roughness peaks of the surface leading to a smoother surface, which reduce the running-in phase of the rubbing surfaces
- **Protective film mechanism:** the nanoparticles can attach to the rubbing surfaces (e.g. with secondary forces or via polarity difference) and they can form a protective tribofilm between the sliding surfaces.

3. Investigation method
The aim is this paper is to analyse the friction and wear influencing properties of the selected ZrO₂ and CuO nano-particle. The average size of the particles is between 15-25 and 30-50nm respectively. To
characterise the tribological behaviour of these nano-ceramic particles, a homogeneous particle-lubricant sample has to be prepared. To the characterisation, a base oil (classification Group 3, kinematic viscosity 4cSt) without any additives was chosen. The chosen lubricant is worldwide used to produce engine lubricant with relatively low viscosity class (SAE 0W-20). The nanoparticles with the proper concentration have to be mixed and homogenised and for this task, a two-phase method was used, which contains a 30-minute homogenisation phase (ultrasonic homogeniser) and a 30-minute magnetic stirring.

The friction and wear influencing behaviour of the nanoparticles was investigated with an Optimol SRV5 friction machine. This tribometer enables to produce the necessary oscillation movement pattern between the used testing specimens and measures the most important tribological values (e.g. friction coefficient of the system). As testing specimens, ISO-standardised 10mm balls and 24mm discs were used (material: 100Cr6, Ra 0.020 and 0.047 µm respectively) [6]. For the tribological test, a self-developed testing method and setup parameters were used [7], which can be seen in Tab.1.

| Parameter | Stroke | Frequency | Specimen T | Oil T | Oil circulation speed | Load | Time |
|-----------|--------|-----------|------------|-------|-----------------------|------|------|
| Step 1    | 1mm    | 50Hz      | 100°C      | 100°C | 225ml/h               | 50N  | 30s  |
| Step 2    | 1mm    | 50Hz      | 100°C      | 100°C | 225ml/h               | 100N | 2h   |

After the tribological experiments, the worn surface was analysed with both digital- and scanning electron microscopes to define the wear behaviour of the investigated nanoparticles. The recordings made with these microscopes can carry important information to understand the working mechanisms.

### 4. Investigation results

During the investigation, the following three main measured values are considered as a comparison base:

- Coefficient of Friction (COF): The maximum value of the friction coefficient in one sliding stroke, measured by the Optimol SRV5 tribometer
- Friction Absolute Integral (FAI): the absolute integral value of the measured friction coefficient in the function of the stroke, measured by the Optimol SRV5 tribometer
- Wear scar diameter (WSD) from the ball specimen, measured by a digital microscope

#### 4.1. Results with the reference lubricant sample

For the evaluation of the measurements, a neat Group 3 base oil was chosen as the reference sample. This base oil is widely used in the lubrication industry to produce low-viscosity engine lubricants for modern passenger cars. This base oil enables to produces lubricants according to the SAE 0W-20 viscosity classification and the engine manufacturers (OEMs) are also specify this kind of lubricants as official engine oil in their products. The reference oil was delivered by the MOL-Lub Kft. from Hungary.

![Figure 2](image.png)

**Figure 2.** Tribological results of the reference oil sample: friction coefficient and wear results (left) and the wear scar on the disc specimen (right)

Fig. 2 demonstrates the experimented and evaluated results of the used reference oil sample. The evaluation of the reference sample was carried out with 8 independent experiments and their average value and their deviation were statistically calculated. The measured frictional coefficient values have shown a normal operation of the system. The wear scar image on the disc specimen presents high wear with heavy abrasion and adhesion. The signs of burned lubricant cannot be considered on this worn surface, which can be explained with this high wear velocity: the lubricant may have burned on the surface but the high abrasive and adhesive wear have removed these oil molecules.
Figure 3. SE-Scanning Electron Microscope image and EDX Mapping picture about the surface of disc specimen with neat Group 3 reference oil, A) middle-stroke area, B) dead-centre area

The SEM-images of the disc specimen with reference oil sample (neat Group 3 base oil) can be seen on Fig. 3. The SEM-images can show a high amount of fatigue wear, which is called also pitting. This demonstrates the lack of the tribological additives of the used oil sample: there are no additives which can protect the rubbing surfaces against overload and high wear. These pittings can be established by the following process: the high load causes micro-cracks in the surface-near material of the specimens, resulting in a grid of cracks in the material. Further load and sliding of these surfaces produce wider and deeper cracks, which can lead to a solid material particle departure from the surfaces resulting in these craters on the surface [8]. The amount of the pitting is higher at the dead centre areas, because of the direction change in these areas. The EDX-analyse of the surfaces shows a small amount of Cu and Zr on the surface, which can be considered as the natural background spectrum of the measurement method. According to the quantitative analysis of the electron microscope, this amount can be considered as zero.

4.2. Results with ZrO₂ nano-particle

Figure 4. Tribological results of nano-sized ZrO₂ additive
Fig. 4 illustrates the results of the investigated ZrO$_2$ additive. This additive could decrease the WSD, up to 40% at the concentration of 0.4wt%. However, the friction coefficient values have shown a slightly increasing tendency. Only the optimum 0.4wt% concentration was able to reach the coefficient of friction value of the reference sample without any additive.

The wear scars on the disc and ball specimen (Fig. 5.) show a relatively smooth surface with a low level of surface damages. Even some roughness valleys can be seen on the worn surface. It can also be considered that on the edges the colour of the wear is different compared with the middle-areas. A very low amount of burned lubricant can also be seen on the surface of the disc specimen, with this blue-colour area in the middle of the width.

![Figure 5. Wear scars on the surface of ball and disc specimen with the lubricant sample including 0.4wt% ZrO$_2$](image)

The worn surfaces were also analyzed by a scanning electron microscope located in the laboratory of the department in Győr. Two different areas were selected for the analysis: one middle-stroke and one dead-centre area. The images can be seen in Fig. 6. On the worn surface, slight abrasive wear scars and tiny fatigue craters (pitting) can be found. The relatively small amount of heavy abrasion wear can show the existence of a protective tribological layer between the rubbing surfaces and the pits are the signs for the reciprocating movement pattern and the fatigue of the surface. On the EDX images, the amount of the founded Zr and O material can be seen with the colour of red and green. On the images from the dead-centre areas can be measured less particle which means that the dead-centre areas were loaded more heavily because of the slowing-stopping-restarting movement pattern of the oscillation.

![Figure 6. SE-Scanning Electron Microscope image and EDX Mapping picture about the surface of disc specimen with ZrO$_2$ nano-additive, A) middle-stroke area, B) dead-centre area](image)
The ZrO$_2$ nano-particle has the hardness value of 1200 HV, that’s why it is very difficult to decrease the average size of the particles during the loading and rubbing phase of the tribosystem. These particles are also not able to be solved into the used mineral base oil (G3, 4cSt). The EDX-SEM images show the existence of the Zr and O material on the worn surface even after a thorough ultrasonic cleaning in brake cleaner medium. This shows the sign of the existence of secondary bonding force (van der Waals) between the nano-particles and the rubbing surface. The ZrO$_2$ nanoparticles can be collected in the roughness valleys, fill them up resulting a smoother rubbing surface with the lower surface distribution of the load. Besides they can be pressed into the metal-matrix via deformation of the metal. During the loaded and rubbing phase on the surfaces of the two testing specimens, this protective layer can be formulated and that’s why the specimens are only in contact with each other via this layer. Of course, as from the SEM-images of the middle-stroke and dead-centre areas can be seen, the higher tribological load results in less particle on the surface at the end of the test.

4.3. Results with CuO nano-particle
The tribological properties of CuO nano-particle were also investigated according to the same process. Fig. 7 describes the results of this type of additive. This chart shows a slight reduction in friction coefficients and WSD as well. Both values have been decreased by 15\%, compared with the reference oil. The optimum concentration can be established at 0.5wt\%. After 0.5wt\%, a slight increase in friction and wear could be measured.

![Figure 7. Tribological results of nano-sized CuO additive](image)

The wear scars on the disc and ball specimen (Fig. 8.) illustrate the signs of a middle-loaded surface. There are some valleys with relative higher depth, but the whole worn surface can be described as normal wear of these systems. The speciality of this wear scar is the cooper-yellow colour. This colour may be formatted from the CuO additive. Burned lubricant cannot be seen on the surfaces.

![Figure 8. Wear scars on the surface of specimens with the lubricant sample including 0.5wt% CuO](image)

The worn surface of the disc specimen was also analysed via a scanning electron microscope (Fig. 9.), both at middle-stroke and dead-centre area. The surfaces show slightly worn areas by abrasion wear and polished areas as well. The material content of the surfaces was also analysed via EDX SEM and the results can show that there are 2 different areas: one with higher abrasion wear and higher Cu content and one with smoother, polished surface with lower copper on the surface. It can be defined that in the dead-centre areas less amount of Cu and O material was found which can be explained with the higher tribological loads and with the worse lubrication properties because of the oscillation motion.
The CuO additive has significant lower hardness value compared with the ZrO$_2$, which enables the formation of the spherical additives. After the homogenization of the CuO and the base oil, the colour of the sample was black, but the colour of the additive on the worn surface is significantly different, copper-yellow. To formulate this elementary copper, the following hypothesis was founded: the cupric-oxide can be reducted with the carbon-hydrogen content of the base oil (the Group 3 base oil is formulated from different carbon-hydrogens between C20 and C50. With these long-chain molecules, the cupric-oxide may react, resulting in CO, CO$_2$ or H$_2$O. One possible reaction equation can be presented with the decane (C$_{10}$H$_{22}$), which is widely used in fuels and low-viscosity lubricants [9][10]. During the reaction, the decane can be reduced to nonane (C$_9$H$_{20}$):

\[
CuO + C_{10}H_{22} \xrightarrow{\text{reduction}} Cu + CO + H_2 + C_9H_{20}
\]

Further analysis is required to verify this chemical reduction equation which can be proved with the calculation of Gibbs free enthalpy values.

In case the copper has already been formulated near the rubbing surfaces, this material is enough soft to be mended on the surface, forming a tribological protective sliding film between the two rubbing specimens. This copper-layer can fill up the roughness valleys resulting smoother contacting surfaces (see on Fig. 1, d) and this layer provides an increase of the contacting area which decreases the load pressure of the ball and disc specimen. To verify the hypothesis, further investigation has to be carried out in the future via FIB-SEM microscope or XPS method. Besides the valid transformation equation and the starting temperature have to be clarified.

5. Summary
This paper presents the investigation results with the ZrO$_2$ and CuO nanoparticles as lubricant additives. The tribological properties were analysed via Optimol SRV5 tribometer and the worn surfaces via digital and scanning electron microscopes.
The following results can be summarised:

- Both the ZrO$_2$ and CuO nanoparticles have shown positive tribological properties, compared with the neat Group 3 base oil: friction decrease by 3 and 15%, wear reduction by 40 and 15%, respectively. These values belong to the optimum concentration values, 0.4 and 0.5wt% respectively.

- The worn surface after the investigation with ZrO$_2$ 0.4wt% shows a significant smooth character. With SEM analysis a relatively huge amount of Zr was found on the worn surface. The ZrO$_2$ NP could adhere to the rubbing surfaces via mending mechanism, which resulted in a protective tribological layer between the specimens.

- On the surface after the CuO 0.5wt% experiment Cu was also found, however, in a different form: it was melted in the valleys of the worn surface. This melted layer could be formulated by the reaction of CuO and the carbon-hydrogen content of the Group 3 base oil.

To understand the exact working mechanisms of these additives, further investigation is necessary, with both tribometers and microscopes. Further experiments with these additives and lubricants with higher additive content (both active and inactive additives) is also obligatory.

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