Á. D. Tóth

Assistant Lecturer
Department of Internal Combustion Engines
and Propulsion Technology-
Széchenyi István University
Audi Hungaria Faculty of Automotive
Engineering
Hungary

Á. I. Szabó

MSc student
Széchenyi István University
Audi Hungaria Faculty of Automotive
Engineering
Hungary

R. Kuti

Associate Professor
Széchenyi István University
Faculty of Mechanical Engineering,
Informatics and Electrical Engineering
Hungary

J. Rohde-Brandenburger

Head of Department
Department of Internal Combustion Engines
and Propulsion Technology
Széchenyi István University
Audi Hungaria Faculty of Automotive
Engineering
Hungary

Tribological Investigation of Applicability of Nano-Sized Cupricoxide (CuO) Ceramic Material in Automotive Vehicles

Due to the continuously increasing requirements of the internal combustion engines, the lubricants and their additives have to be further developed. One possible solution is the application of ceramic nanoparticles as friction modifier and wear decreaser additives. This paper presents the tribological investigation of cupricoxide (CuO) nanoparticle mixed in neat Group 3 base oil. To analyse its properties, simplified ball-on-disc friction experiments were carried out in the tribological laboratory in the Széchenyi István University in Győr, Hungary. The arisen wear scars were analysed with different, high-resolution microscopes to understand the working mechanism of the nanoparticles. The results have indicated an optimum concentration of nanoparticles at 0.5wt% where both the average friction coefficient and the wear scar diameter were reduced by 15%. The microscopical investigation revealed the reduction of copper material from the CuO material, and it has mended to the rubbing surface forming a protective film on the metal surface.

Keywords: tribology, cupricoxide, nano-ceramic, lubricant, additive, engine.

1. INTRODUCTION

The automotive industry is facing huge challenges nowadays: several international regulations are existing to reduce the emission of harmful materials from the exhaust system of passenger cars. These regulations are aiming to clean the living environment of humanity. These challenges provide huge motivation for the developing engineers of the automotive manufacturers all around the world to invest their resources into the invention and development of cleaner and more environment-friendly drivetrains. The improvement of the applied lubricants in the internal combustion engines and transmissions is also one of the key development fields. Nano-sized materials can be one of the future lubricant additives, which can lead the whole automotive industry to cleaner mobility.

Nanoparticles in lubricants are in the focus of many researchers all around the world, because they can provide a huge number of varieties in material content and particle size. Due to this variation possibility, wide research activity is obligatory to characterise their tribological properties.

Particle size is one of the key factors of the nanoparticles: some studies have revealed the property of the nanoparticles that they are only able to fill up the roughness or wear valleys on the surface if the particle size of the nanoparticles is tiny enough [1],[2]. Peña-

Paraset al. have reported the positive tribological properties of those nanoparticles, whose initial diameter is smaller than the average surface roughness [3].

Various working mechanisms have been proposed to explain how these nanoparticles can function inside the lubricants to provide positive tribological properties: acting as nano ball bearings to change the sliding motion into a rolling motion, filling in roughness or wear valleys resulting in smoother contact surfaces, polishing the surfaces and accelerate the running-in phase of the components and forming a protective tribological layer on one or both surfaces (see in: Figure 1) [1,5].

Figure 1. Different working mechanisms for increasing the tribological performance using nanoparticles [1,5]

Kato et al. studied different nanoceramic additives and showed different protective tribofilms reinforced with oxide particles [6]. Wu et al. investigated the working mechanism of the nanoparticles and showed CuO particles act as a rolling medium between the contact surfaces [7]. Manu et al. reported the optimal concentration (0.34 wt%) of nano CuO in coconut oil to achieve the rolling

presence of the particles [8]. Alves et al. showed the anti-wear behavior of the oxide nanoparticles depending on the lubricant base oil. The anti-wear mechanism is attributed to the deposition of nanoparticles in surface and physical film formation, which also can reduce the coefficient of friction [9]. Battez et al. showed the tribo-sinterization of the CuO particles in addition to the rolling effect of nanoparticles occurred on NiCrBSi coated parts. During XPS (X-ray photoelectron spectroscopy) analysis of the worn surfaces, a Cu peak was found, which was considered to be the result of a reduction based on the interaction between the cupric oxide and the Ni-containing coating [10].

Some research groups investigated the reduction of CuO in different environments [11]. Lu Yuan et al. showed that the reduction of nanosized CuO begins at 150°C in low oxygen pressure [12]. Eli et al. reported the direct reduction of CuO to Cu even at 473 K temperature if it is in carbon-monoxide environment. The experiments were supported and confirmed with thermochemical equilibrium calculations [13]. Jae et al. demonstrated that under a normal supply of hydrogen gas, CuO reduces directly to metallic copper without the formation of intermediates or suboxides [14]. Xianqin et al. investigated the complex mechanism of the CuO reduction to copper and the formation of suboxides in CO gas. The suboxides were highly disordered with extra oxygen embedded in their lattice [15]. Okayama et al. reported the tribo-reduction phenomena of the CuO on the surface of a commercial brake pad. The experiments were carried out at different temperatures (40, 80, and 120°C). There were points in the tribological system at which the local temperature was significantly higher than the nominal one. At these points, an elemental copper layer was significantly observed, which suggests that CuO is reduced more easily and faster at higher temperatures. In their research, it was hypothesized that one of the components of the phenolic resin helps to reduce CuO [16].

Sayed et al. utilized the advantages of the CuO nanoparticles to improve the tribological performance and highly recommended it for use as a nanoadditive in low wear tribosystems [17].

Battez et al. investigated the CuO nanoparticles as an additive in PAO6 lubricant and showed its low friction decreasing but excellent anti-wear effects [18]. The reduction of friction coefficient [19] and wear rate [20] were also observed by using CuO nanoadditives in different industrial lubricants.

Creating a homogeneous and time-stable mixture is crucial for the practical applicability of nanoparticles. Ettetfaghi et al. determined the method of the stabilization of nanoparticles and measured the kinematic viscosity, pour point, and flashpoint of the mixture according to the ASTM standards [21]. To ensure the stability of the mixture, the surface of the nanoparticles is often activated. Alves et al. modified the surface of the CuO nanoparticles with oleic acid and reported promising results with large potential in friction and wear decreasing on low concentrations [22]. Hao Liu et al. characterized the CuO nanoparticles by TEM, XRD and FTIR to show the surface-modified layer on the surface of the particle [23].

Mohamed et al. investigated the tribological properties of a real internal combustion engine lubricated with CuO doped 20W40 engine lubricant [24]. Sayed et al. also used an internal combustion engine to investigate the wear of aluminum, copper iron and chromium parts. It has been shown that CuO can reduce the wear of aluminum and chromium parts by 42 to 48% [25].

Ramaganesh et al. investigated the pressure distribution of nano lubricants in a journal bearing with finite element method and compared it with experimental results [26]. According to their work, the exact numerical analysis of nanoparticle-doped lubricants between sliding surfaces can be one of the investigation methods in the future. However, the method could be further developed not only for journal bearings or the calculation of the frictional or wear losses.

According to literature review, it can be stated that the experimental measurements are nowadays the most precise methods to tribologically characterise different nanoparticle-reinforced lubricant samples.

In this study, the tribological properties of nanosized cupric oxide (CuO) mixed into neat Group 3 base oil is examined. Ball-on-disc friction and wear tests were carried out with the homogenised lubricant samples with an Optimol SRV5 testing machine. The formed wear images were analysed via several microscopes to understand their working mechanism.

2. METHODOLOGY

The analysed cupric oxide nanoparticles were mixed into a neat Group 3 base oil with the kinematic viscosity of 4 cSt, which was provided by the MOL-LubKft. The homogenisation process consists of 2 steps: a 3-minute-long magnetic stirring step to homogenise the sample and a 30-minute-long ultrasonic mixing step to solve the agglomerates inside the sample. Lubricant samples with 6 different concentrations between 0.1 and 0.6 wt% were prepared for the tribological experiments.

For the friction and wear experiments, ISO-standardised ball and disc specimens were used [27]. A self-developed tribological testing program [28] was used. The specimens were moved with a 1 mm stroke and 50 Hz frequency translation movement pattern. Continuous oil flow was realised during the experiments with the continuous oil flow rate of 225 ml/h. Both the specimens and the lubricant sample were heated up to 100°C. The 30 seconds low-load phase (50 N) was followed by a high-load step (100 N) with the time duration of 2 hours. The testing specimens were cleaned in an ultrasonic bath with brake cleaner medium 15 minutes long both before and after the friction tests. The frictional testing machine enables to continuously measure the friction coefficient, both the maximum value in every stroke (COF) and the integral average value projected on every stroke (FAI).

The wear scars formed on the surface of the ball and disc specimens were investigated by a Keyence VHX-1000 digital microscope with the magnification of 100 and 200. With the help of these images, the wear scar diameter on the ball specimen can be identified. The whole wear images on the surface of the disc specimen were digitalised by a Leica DCM 3D confocal microscope to

characterise the different lubricant samples according to their anti-wear properties. This confocal microscopic analysis enables to calculate the wear volume of each experiment on the surface of the disc specimen. The worn surfaces were also analysed via scanning electron microscope completed with energy-dispersive X-ray spectroscopy to analyse and identify the working mechanism of the investigated nano-additive and the element distribution on the worn surface of the specimens.

3. RESULTS AND DISCUSSION

During the tribological measurements, two different friction coefficient values were continuously recorded: the COF value represents the maximum value in every stroke of the oscillating movement, and the FAI value is the integral average value of friction coefficient. Because of the natural properties of the translation movement, the measured COF-value refers to the frictional properties of the system under boundary layer lubrication regime, while the FAI value represents the property of the system under mixed lubrication regime.

At least 3 independent experimental measurements were carried out to analyse the tribological properties of the lubricant samples. The evaluation of the experiments is illustrated in Figure 2.

Figure 2. Evaluation of the identified tribological properties of the investigated oil samples

The bar chart in Figure 2. clearly shows the difference in the tribological properties of the oil concentrations: slight friction (blue and red bars) reduction can be determined by the concentrations of 0.1, 0.5 and 0.6 wt%. However, the observed wear scar diameters on the ball specimens show a clear tendency: the cupricoxide nanoparticles can reduce the wear on the specimens and the higher NP-concentrations have reduced the wear significantly. An optimal concentration can be identified by tribological results: the lubricant sample with the CuO-concentration of 0.5 wt% have provided the lowest friction coefficients and wear scar diameter. This sample has provided COF-decrease by 15%, FAI-decrease by 8% and WSD-decrease by 17%.

The worn surfaces of the experiments with different nanoparticle concentration (Figure 3) describe an interesting phenomenon: the addition of cupricoxide nanoparticle into the base oil reduces the wear and decreases the damage of the rubbing surfaces. On the digital microscope images, a yellow layer can be identified, especially in the presence of higher cupricoxide concentrations. This yellow layer can be observed usually in the wear valleys

of the surfaces, as the 0.5 wt% microscopic image represents. This yellow layer can be the sign of some copper protective film on the surface, which might take part in the positive tribological influence of the investigated lubricant samples. The exact material content of this protective layer must be further analysed.

Figure 3. Digital microscope images about the worn surfaces of the disc specimens with different CuO-concentrations

One of the main disadvantages of the measurement of the wear scar diameter (WSD) on the ball specimen is that this result cannot consider the wear depth. To receive higher and more precise information from the wear surface, confocal microscopy measurements were carried out via Leica DCM 3D microscope. This microscope enables to scan and analyse the surface of the specimens. The wear scars including a certain unworn area of the disc specimen were scanned by this microscope, and they were evaluated with the Leica Map software to define the volume value of the worn surface: the worn surfaced was enclosed by a certain amount of lines, the average height-value of the unworn areas (around the enclosed area) was calculated and the volume below this height-value in the enclosed area is considered as the wear volume. Figure 4 is an example of the scanned surface which enables the evaluation of the wear volume inside the enclosed area.

Figure 4. Confocal microscopic image of the worn surface on the disc specimen with 0.5 wt% CuO-dosed lubricant

With the help of this calculation method, the lubricant samples with different nanoparticle concentrations can be compared based on the missing volume on the disc specimens. The result of the confocal microscopic analysis is illustrated in Figure 5. A clear tendency can be established from the bar chart: the identified wear volume has decreased until the concentration level of 0.3 wt% with 69% wear volume decreasing property. By higher amounts of additive concentration, the wear volume has raised for a relatively high value. This tendency can be supported with the cross-section profile analysis of the worn surfaces (see in Figure 6): the amount of average wear depth is decreasing until 0.3 wt%, and by higher concentrations, the wear starts to increase. A significant amount of adhesive material can be clearly seen at 0.5 wt% value, which influences the measured wear volume significantly.

Figure 5. Comparison of the investigated lubricant samples according to the measured wear volume on the disc specimen

Figure 6. Cross-section analysis of the wear scars on the disc specimens under different nanoparticle concentrations

As one of the main disadvantages of the optical microscopy can be considered the fact that it cannot differentiate the original material of the testing specimen from those materials, which was adhered to the surface during the frictional tests. However, the cross-section diagrams (Figure 6.) can reveal it clearly: at 0.5 wt% concentration a significant amount of adhesion can be established. The material content of this adhered material cannot be identified with this microscope, its source

can be the ball specimen, lubricant additive material, or contamination.

The wear was also analysed both via a scanning electron microscope (Hirox-type SEM) and a focused ion beam scanning electron microscope (Helios-type FIB-SEM) to define the working mechanism of the applied research additive. Both the reference surface (disc surface tested with neat Group 3 base oil) and the CuO-added worn surfaces were analysed via SEM and the results (in Figure 7.) showed a significant amount of copper on the rubbed surfaces even after a precise ultrasonic cleaning. The distribution of copper on the surface is various: both smaller and larger agglomerates can be established.

Figure 7. Scanning electron microscope image including element analysis about the worn disc surfaces, A) reference oil middle-stroke, B) reference oil dead-centre, C) and D) 0.5 wt% CuO sample

The applied scanning electron microscope enables to define the quantitative element distribution on the investigated surface. The results of this analysis are shown in Table 1. It can be clearly considered that a significant amount of copper element covers the surface. However, the number of oxygens does not linearly correlate with the number of coppers: more copper than oxygen can be found on the surface. The atomic weight of the copper is 4-times the atomic weight of the oxygen, which can cause this difference. Besides, the iron base material can also be oxidized which also leads to a higher oxygen content of the surface. Further element investigation is necessary to decide the precise correlation between the copper and the oxygen.

Table 1. Mass % element analysis results about the optimal concentration, 0.5 wt% CuO, according to the SEM measurements

Wt%	Fe	Cr	Si	O	C	Cu
0	82.21	1.16	1.88	8.14	6.61	0.00
0.5	75.23	1.20	0.69	7.18	6.45	9.25

The FIB-SEM analysis was carried out in the 3D Lab of the University of Miskolc. Both a small section and a lamella was machined out from the worn surface which can be analysed. To protect the surface during the machining, a platinum-layer was applied on the surface. The result of the lamella investigation can be observed in Figure 8. The element distribution was investigated through a linear line and the result indicates no correlation between the copper and the oxygen material: the

amount of copper is increasing around the surface, but this phenomenon cannot be detected in case of the oxygen. This leads to the conclusion that the yellow layer on the surface of the worn specimens does not consist of cupric oxide nanoparticles, but the copper had to be reduced via a chemical process. The distribution of the oxygen can be explained with the small amount of oxidation of the basic iron material.

Figure 8. SEM Linear element analysis of the machined lamella from the surface with the 0.5 wt% oil sample

The element analysis of the ion-machined section (see in Figure 9.) shows a similar tendency as the lamella analysis: no correlation can be found between the Cu and O elements. However, the clear correlation between Fe and Cu reveals the information that the copper can cover the iron base material. The almost constant oxygen-content can be established by the tiny amount of corrosion on the investigated area.

Figure 9. SEM Linear element analysis of the ion-machined section on the tested surface with the 0.5 wt% oil sample

To define the form and the compound of the copper on the surface, further investigation methods had to be used. The XPS (X-ray photoelectron spectroscopy) is a very good solution for this measurement, because the binding energies of the electrons of the material can be identified and the chemical element can be identified by this method [29]. The specimens were cleaned 3-3 minutes in acetone and chloroform and were dried with dry nitrogen. The non-solvable materials on the surface were removed by ion vaporization surface cleaning process right before the XPS measurement.

According to the summarised whole spectrum, the different Cu-compounds could not be differentiated, so

the LMM Auger spectra were used, and the result can be observed in Figure 10. The LMM Auger spectra of the measured surface (disc specimen tested with 0.5 wt% CuO lubricant sample) illustrates a clear correlation with the Cu₂O and Cu spectra.

Figure 10. LMM Auger spectrum of the disc specimen tested with 0.5 wt% CuO lubricant sample

The clear correlation was proved with the boundary energy and atomic concentration measurements which is summarised in Table 2. The copper element can be found on the worn surface in two different compounds: Cu₂O in almost 70% and Cu in 30% presence. Some of the Cu₂O can be derived from the reoxidation of elemental copper on the surface. This measurement did not reveal any copper with the original compound (CuO) of the nanoparticles. This information proves the following hypothesis: the copper has reacted with the hydrocarbon content of the applied base oil (neat Group 3) and was reduced. This reduction could be completed under the applied temperature circumstances (heated up to 100°C and the frictional losses were also converted into extra heat locally) during the tribological test or even in the homogenised phase before the experiments. The copper in this form is quite soft and can easily be adhered to the rubbing surfaces resulted in a protective copper-layer which can provide the above-defined positive tribological properties.

Table 2. Type of copper-compounds and their distribution on the worn disc surface tested with 0.5 wt% CuO lubricant sample

Compound	Bounding energy (eV)	Atomic concentration (%)
Cu ₂ O	570.43	69.6
Cu	567.83	30.4

The explanation for this phenomenon is the triboreduction of the CuO. Copper is an unreactive metal, it can be easily reduced with heating from its oxide in the presence of carbon or hydrogen. During the reduction, carbon/hydrogen removes the oxygen from the compound, leaving the metal as gaseous carbon dioxide, carbon monoxide or water vapour.

In the tribological system, due to the initial high pressure, temperature, little lubricant between the contact surfaces, high mechanical activity, and the hydrocarbon content of the base oil, CuO could be partially reduced to elemental copper. The reaction rate was also

induced by the small size(30-50 nm) of the cupric oxide used as an additive. Copper as a very soft metal spread on the contact surfaces and forms a protective layer.

Based on the Boudouard reaction, according to the high pressure and temperature values in the contact zone of the tribological system, if CuO is reduced with carbon, a carbon monoxide product is obtained with elemental copper. The two stipulations of the calculations:

- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}} > 0$
- The universe always strives for the energy minimum and the entropy maximum.

The direction of the processes is determined by the minimum of free energy. The thermodynamic definition of entropy can be given by the amount of heat Q (thermal energy) of the materials. Whether it is a gas, a liquid or a solid, its atoms or molecules perform disordered movements to which kinetic energy belongs. The sum of these forms is the thermal energy, i.e. the quantity of heat. The ratio of thermal energy divided by the temperature defines entropy:

$$S = \frac{Q}{T} \quad (1)$$

Thermodynamic potential functions represent the energy that can be maximally converted into another form of energy in one process. Gibbs free energy can be calculated from the amount of enthalpy and entropy:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (2)$$

If the pressure and temperature of the system are constant, then:

$$dG \leq \mu \cdot dN \quad (3)$$

From this, it can be concluded that the free enthalpy G can change at most as much as the chemical work of μdN . Thus, free energy shows how much of the internal energy can be converted into chemical work in isobar and isothermal processes. Thus, with the help of the formula (2), the possibility of the hypothetical processes can be determined.

- A negative sign of free energy change means that the process can occur spontaneously in the given direction.
- A positive change in free energy means that the process does not occur voluntarily, spontaneously.
- If the free energy change is zero, the system is in equilibrium.

The base oil manufacturer has indicated by CAS numbers (64742-54-7 and 72623-87-1) that the oil consists of a mixture of hydrocarbons having 20 to 50 carbon atoms. The more precise composition of the used base oil is unknown, so it was substituted to the decane. The required thermodynamic data of decane can be found in the literature [30]. Hydrocarbons of the lubricant crack during the operation under the pressure, mechanical and thermal stress. These cracks can release shorter hydrocarbons or even free carbon atoms. Decane ($C_{10}H_{22}$) is often used in fuels, sometimes as a base for low viscosity lubricating oils, as a component. Table 3 shows the thermodynamic measured values found in the literature [30].

Table 3. Summary of the thermal parameter, necessary for the calculation of the Gibbs-potential[30]

T = 400 K	CuO	Cu	C	CO	$C_{10}H_{22}$	C_9H_{20}	H_2
S [J/molK]	55.727	40.481	8,754	206.25	518.314	477.245	139.216
ΔH [kJ/mol]	-	0	0	-	-	-	0
	155.551			110.129	312.086	285.578	

The hypothesized reactions:

Cupric oxide reacts with decane and reduces it with the help of carbon in the alkane. This shortens the carbon chain of the alkane by one (nonane) while forming elemental copper in the presence of carbon monoxide and hydrogen gas. The operating temperature of the tribometer measurement is 373.15 K however, the thermodynamic values are only uniform at 400 K, so the Gibbs free energy values were calculated on this temperature. The for the calculations necessary values are shown in Table 3.

The change of entropy during the reaction with decane at 400 K temperature:

$$\Delta S = \sum S_{\text{out}} - \sum S_{\text{in}} \quad (6)$$

$$\Delta S = (40.481 + 206.25 + 139.216 + 477.245) - (55.727 + 518.314) = 289.151 \left[\frac{J}{mol \cdot K} \right] \quad (7)$$

which indicates a spontaneous chemical reaction.

The change of enthalpy during the reaction with decane at 400 K temperature:

$$\Delta H = \sum \Delta H_{\text{out}} - \sum \Delta H_{\text{in}} \quad (8)$$

$$\Delta H = (0 - 110.129 + 0 - 285.578) - (-155.551 - 312.086) = 71.93 \left[\frac{kJ}{mol} \right] \quad (9)$$

which indicates an endotherm process.

The change of the entropy during the reaction with carbon at 400 K temperature, according to (6):

$$\Delta S = (40.481 + 206.25) - (55.727 + 8.754) = 182.25 \left[\frac{J}{mol \cdot K} \right] \quad (10)$$

which is also a spontaneous reaction.

The change of the enthalpy during the reaction with carbon at 400 K temperature, according to (8):

$$\Delta H = (0 - 110.129) - 155.551 + 0 = 45.422 \left[\frac{kJ}{mol} \right] \quad (11)$$

which is also an endotherm process.

The Gibbs free energy of the reaction with decane at $T = 400$ K temperature can be calculated by following, according to (2):

$$\Delta G = 71930 - 400 \cdot 289.151 = -43730.4 \left[\frac{J}{mol} \right] = -43.73 \left[\frac{kJ}{mol} \right] \quad (12)$$

The Gibbs free energy of the reaction with carbon at $T = 400$ K temperature can be calculated by following, according to (2):

$$G = 45422 - 400 \cdot 182.25 = -27478 \left[\frac{J}{mol} \right] = -27.48 \left[\frac{kJ}{mol} \right] \quad (11)$$

It is important to notice this reaction idealizes the chemical composition of the base oil. The real hydrocarbons, which are the components of the base oil, have a higher atomic number, but the process of reduction is the same. According to the manufacturer of the used base oil, these are hydrocarbons (mainly alkanes) having 20 to 50 carbon atoms. Thus, at the actual operating temperature, the entropy of the materials is much higher (approximately ~ 1000 - 1200 J/mol·K), but their rate of increase is almost the same, so this only slightly affects the rate of ΔS .

The values of entropy and enthalpy change in the reactions are also positive. This shows that the reaction is a spontaneous endothermic process. Thus, the tribological system has a special temperature value, above which the free energy value turns negative and the reaction begins.

4. CONCLUSION

This paper summarises the performed tribological experiments and the results with nano-scale cupric oxide particles. Experimental measurements with a ball-on-disc tribometer were carried out to define the frictional properties of the additive homogenised with different concentrations in neat Group 3 base oil. The tribological measurements were supported with several microscopical investigations to define the wear properties and the working mechanisms of the investigated lubricant samples.

The results can be summarised by the following:

- An optimum concentration can be established at the concentration value of 0.5 wt%. With this lubricant sample, the average friction coefficient value was reduced by 8% and the wear scar diameter on the surface of the ball specimen by 17%. However, the results of the wear volume measurements showed relative deep wear with this sample. The wear volume measurements with 0.3 wt% lubricant sample have revealed a significant, 69% wear reduction with relative flat wear scar.
- A significant amount of copper can be defined on the worn surfaces with cupric oxide nanoadditives even after ultrasonic cleaning. The FIB-SEM analysis of the surfaces revealed no correlation between the copper and oxygen element on the surface. Further XPS analysis was carried

out and the results have indicated that the copper on the surface can be found in Cu_2O and neat Cu state.

- CuO reduction with decane and atomic carbon proved with the calculation of Gibbs free enthalpy.

The investigations have revealed positive tribological properties of CuO nanoparticle additive which can improve the surface protecting and low-frictional properties of the applied lubricants, not only in case of internal combustion engine applications. Further investigations should be carried out to understand the functionality of this cupric oxide nanoadditive. These measurements have to be nearer to the reality, e.g. fired engine test bench measurements including exhaust gas analysis.

ACKNOWLEDGMENT

The authors would like to thank Ms Dóra Olimpia Csepregy, Ms Boglárka Nagy and Dr. József Perger for their general support.

REFERENCES (HELVETICA 9 BOLD, ALIGN LEFT)

- [1] Lin J., Wand L., Chen G.: Modification of graphene platelets and their tribological properties as a lubricant additive, *Tribology Letters*, Vol. 41, pp. 209-2015, 2011.
- [2] Tomala A., Vengudusamy B., Rodríguez Ripoll M. et al.: Interaction between selected MoS_2 nanoparticles and ZDDP tribofilms. *Tribology Letters*, Vol. 59, Art. Nu. 26, 2015.
- [3] Peña-Parás L., Geo H., Maldonado-Cortés D. et al.: Effects of substrate roughness and nano/micro particle additive size on friction and wear in lubricated sliding, *Tribology International*, Vol. 119, pp. 88-98, 2018.
- [4] Zhang Z., Simionesie D., Schaschke C.: Graphite and hybrid nanomaterials as lubricant additives, *Lubricants*, Vol. 2, No. 2, pp. 44-65, 2014.
- [5] Shafi W.K., Raina A., Ul Haq M.I.: Friction and wear characteristics of vegetable oils using nanoparticles for sustainable lubrication, *Tribology – Materials, Surfaces and Interfaces*, Vol. 12, No. 1, pp. 27-43, 2018.
- [6] H. Kato, K. Komai: Tribofilm formation and mild wear by tribo-sintering of nanometer-sized oxide particles on rubbing steel surfaces, *Wear*, Vol. 262, pp. 36-41, 2007.
- [7] Y.Y. Wu, W.C. Tsui, T.C. Liu: Experimental analysis of tribological properties of lubricating oils with nanoparticle additives, *Wear*, Vol. 262, pp. 819-825, 2007.
- [8] Manu V.T., Rajendrakumar K.P. and Prabhakaran N.K.: Experimental Evaluation on the Tribological Properties of Coconut Oil by the Addition of CuO Nanoparticles, *International Journal of Precision Engineering and Manufacturing*, Vol. 13, No. 1, pp. 111-116, 2012.
- [9] S.M. Alves et al.: Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions, *Tribology International*, Vol. 65, pp. 28-36, 2013.

- [10] A. Hernández Battez, J.L. Viesca, R. González et al.: Friction reduction properties of a CuO nanolubricant used as lubricant for a NiCrBSi coating, *Wear*, Vol. 268, pp. 325-328, 2010.
- [11] S. Poulston, P. M. Parlett, P. Stone et al.: Surface Oxidation and Reduction of CuO and Cu₂O Studied Using XPS and XAES, *Surface and Interface Analysis*, Vol. 24, pp. 811-820, 1996.
- [12] Lu Y., Qiyue Y., Yiqian W. et al.: CuO Reduction Induced Formation of CuO/Cu₂O Hybrid Oxides, *Chemical Physics Letters*, Vol. 570, pp. 92-96, 2013.
- [13] E.A. Goldstein, R.E. Mitchell: Chemical kinetics of copper oxide reduction with carbon monoxide, *Proceedings of the Combustion Institute*. Vol. 33, pp. 2803-2810, 2011.
- [14] J.Y. Kim, J.A. Rodriguez, J.C. Hanson, et al.: Reduction of CuO and Cu₂O with H₂: H Embedding and Kinetic Effects in the Formation of Suboxides, *Journal of the American Chemical Society*, Vol. 125, No. 35, pp. 10684-10692, 2003.
- [15] Wang X., J.C. Hanson, A.I. Frenkel et al.: Time-resolved Studies for the Mechanism of Reduction of Copper Oxides with Carbon Monoxide: Complex Behavior of Lattice Oxygen and the Formation of Suboxides, *Journal of Physical Chemistry B*, Vol. 108, pp. 13667-13673, 2004.
- [16] Okayama K., Hiratsuka K.: Verification of tribo-reduction of copper oxide in phenolic composite material through visualization of friction surface, *Transactions of the JSME (in Japanese)*, Vol. 84, Issue 866, pp. 231-244, 2018.
- [17] S.Y. Akl, A.A. Abdel-Rehim, S. Elsoufy: An Experimental Investigation of Tribological Performance of a Lubricant Using Different Nano Additives, *SAE Technical Paper* 2018-01-0833, 2018.
- [18] A. Hernández Battez et al.: CuO, ZrO₂ and ZnO nanoparticles as antiwear additive in oil lubricants, *Wear*, Vol. 265, pp. 422-428, 2008.
- [19] Vijaykumar S. Jatti, T.P. Singh: Copper oxide nano-particles as friction-reduction and anti-wear additives in lubricating oil, *Journal of Mechanical Science and Technology*, Vol. 29, No. 2, pp. 793-798, 2015.
- [20] S. Bhaumik, S.D. Pathak: Analysis of Anti-Wear Properties of CuO Nanoparticles as Friction Modifiers in Mineral Oil (460cSt Viscosity) Using Pin-On-Disk Tribometer, *Tribology in Industry*, Vol. 37, No. 2, pp. 196-203, 2015.
- [21] Ehsan-o-llah E., Hojjat A., Alimorad R. et al.: Experimental evaluation of engine oil properties containing copper oxide nanoparticles as an nanoadditive, *International Journal of Industrial Chemistry*, Vol. 4, Art. Nu. 28, 2013.
- [22] S.M. Alves et al.: Nanolubricants developed from tiny CuO nanoparticles, *Tribology International*, Vol. 100, pp. 263-271, 2016.
- [23] Hao L., Yujuan Z., Shengmao Z. et al.: Preparation and evaluation of tribological properties of oil-soluble rice-like CuO nanoparticles, *Industrial Lubrication and Tribology*, Vol. 67, No. 3, pp. 276-283, 2015.
- [24] Mohamed K.A.A., Hou X.: Improving the tribological behavior of internal combustion engines via the addition of nanoparticles to engine oils, *Nanotechnology Reviews*, Vol. 4, Issue 4, pp. 347-358, 2015.
- [25] S.Y. Akl, A.A. Abdel-Rehim, E.A. Khafagy: Tribological Properties of Engine Lubricant with Nano-Copper Oxide as an Additive, *SAE Technical Paper* 2016-01-0487, 2016.
- [26] R. Ramaganesh, S. Baskar, G. Sriram et al.: Finite Element Analysis of a Journal Bearing Lubricated with Nano lubricants, *FME Transactions*, Vol. 48, pp. 476-481, 2020.
- [27] Lubricants – Determination of tribological quantities for oils and greases – Tribological test in the translator oscillation apparatus, *ISO 19291:2016(E)* (2016).
- [28] Tóth Á.D., Paulovics L., Hanula B. et al.: Development of testing methodology for tribological characterisation of different engine lubricants (in German), in *Proceedings of the German Tribological Conference 2017*, Göttingen, Vol. 2., pp. P8/1 – P8/11.
- [29] Siegbahn, B., Nordling C., Fahlman A. et al.: *ESCA: Atomic, Molecular and Solid State Structure Studied by means of Electron Spectroscopy*, Almquist & Wiksells, Uppsala, 1967.
- [30] Barin I., Knacke O., Qbaschewski O.: *Thermochemical Data of Pure Substances*, 3rd Edition, VCH Verlagsgesellschaft mbH., Weinheim, 1995.

NOMENCLATURE

G	Gibbs free energy
H	enthalpy of a system
N	particle number
Q	heat or thermal energy
S	entropy of a system
T	temperature

Greek symbols

μ	chemical potential
-------	--------------------

ТРИБОЛОШКА ИСТРАЖИВАЊА МОГУЋНОСТИ ПРИМЕНЕ КЕРАМИЧКОГ МАТЕРИЈАЛА НА БАЗИ БАКАР ОКСИДА СА НАНОЧЕСТИЦАМА

А.Д. Тот, А.И. Сабо, Р. Кути, Ј.Р. Бранденбургер

Стални пораст потребе за моторима са унутрашњим сагоревањем намеће даље развијање мазира и њихових адитива. Једно од могућих решења је примена керамичких наночестица као модификатора трења и редуктора хабања. Приказано је трибо-

лошко истраживање наночестица бакар оксида у смеши са базним уљем групе 3. Анализа својства добијене смеше извршена је испитивањем трења типа куглица-на-диску у триболошкој лабораторији Универзитета Сечењи из Ђера у Мађарској. Настали трагови трошења су испитани микроскопима високе резолуције да би се разумео рад наночестица.

Резултати су показали да је оптимална концентрација наночестица при 0,5 теж.%, при чему су коефицијент трења и пречник трага трошења опали за 15%. Микроскопирањем је откривено опадање садржаја бакра из CuO као и да је поправио тарну површину формирајући заштитни филм на металној површини.