

## Article

# Investigation of the Applicability of $Y_2O_3$ – $ZrO_2$ Spherical Nanoparticles as Tribological Lubricant Additives

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**Abstract:** Long-term environmental goals will motivate the automotive industry, component suppliers, and lubricating oil developers to reduce the friction of their tribosystems to improve overall efficiency and wear for increased component lifetime. Nanoscale ceramic particles have been shown to form a protective layer on components' surface that reduces wear rate with its high hardness and chemical resistance. One such ceramic is yttria ( $Y_2O_3$ ), which has an excellent anti-wear effect, but due to its rarity it would be extremely expensive to produce engine lubricant made from it. Therefore, part of the yttria is replaced by zirconia ( $ZrO_2$ ) with similar physical properties. The study presents the result of the experimental tribological investigation of nanosized yttria–zirconia ceramic mixture as an engine lubricant additive. Yttria-stabilized zirconia (YSZ) nanoparticle was used as the basis for the ratio of the ceramic mixture, so that the weight ratio of yttria–zirconia in the resulting mixture was determined to be 11:69. After the evaluation of the ball-on-disc tribological measurements, it can be stated that the optimal concentration was 0.4 wt%, which reduced the wear diameter by 30% and the wear volume by 90% at the same coefficient of friction. High-resolution SEM analysis showed a significant amount of zirconia on the surface, but no yttria was found.

**Keywords:** tribology; nanoparticle; yttria; yttrium oxide; zirconia; zirconium oxide; nano ceramic; lubricant; additive



**Citation:** Szabó, Á.I.; Tóth, Á.D.; Leskó, M.Z.; Hargitai, H. Investigation of the Applicability of  $Y_2O_3$ – $ZrO_2$  Spherical Nanoparticles as Tribological Lubricant Additives. *Lubricants* **2022**, *10*, 152. <https://doi.org/10.3390/lubricants10070152>

Received: 30 May 2022

Accepted: 8 July 2022

Published: 12 July 2022

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## 1. Introduction

Today, energy management and environmental protection are receiving more and more attention and they are increasingly playing a key role. Transport vehicles are a major contributor to global energy consumption, and many studies are therefore focused on finding ways to reduce fuel consumption along with increasing engine performance and reducing carbon emissions. The primary causes of energy loss in vehicle engines are wear and friction of the various mechanical components. One of the ways to improve the tribological behavior of vehicle engines is the use of environmentally friendly additives, for which intensive research is currently underway. In order to improve friction and wear characteristics, various nanoparticles are being used in a number of research projects with promising results, but this field still has many challenges ahead.

One of the possibilities for the friction and wear-reducing additives of the future lies in nanoparticles. The possibility of using ceramic nanoparticles as different oil additives has received considerable attention in recent years [1]. The results of research on nanoadditives and their environmental effects and applicability have been studied by several researchers [2]. Based on the summarized tribological results, it can be said that nanoparticles are able to change the coefficient of friction, influence the type of friction, and reduce the wear of contact parts [3].

Zirconium dioxide ( $ZrO_2$ , known as zirconia) is a high hardness, naturally occurring oxide ceramic form of the zirconium metal. Zirconia has excellent mechanical properties in addition to its hardness ( $\sim 1200$  HV) being comparable to that of steels; thus, it is widely used in the industry. Numerous studies have already been published to represent the beneficial tribological effects of zirconia nanoparticles.

A complex tribological study showed that 0.5 wt% of zirconia is the optimum for friction and wear-reducing efficiency. The nanoadditive is found on the worn surface and the increasing concentration of  $ZrO_2$  increases the deposition; thereby, it reduces the metal-to-metal contacts [4]. Zirconia nanoparticles can form a hard, protective tribofilm containing zirconia nanoparticles to protect from high wear rate [5]. Surface modification is essential for the use of zirconia as an additive [6]. Shiyu Ma et al. regulated the morphology of the particles and improved the distribution of zirconia nanoparticles in the lubricating oil. Based on the four-ball test, a concentration of 0.5 wt% had an optimal anti-wear and anti-friction effect. Compared to the reference sample without additives, the coefficient of friction was reduced by 5.36% and the wear by 3.98% [7]. Zirconia additive performs well as a grease additive as well: 1 wt% of zirconia can reduce the friction coefficient by 50% on low loads [8].

Guimarey et al. investigated the thermophysical and rheological properties of three different synthetic oils doped with zirconia. They reported the dispersion stability of the nanoparticles, as well as the 8% increase of the density and viscosity of the zirconia-doped nanolubricants [9]. Kamila et al. summarized the effects of zirconia nanoparticles addition to the mechanical parameters of polymethyl methacrylate, which is a commonly used pour point modifier of modern engine lubricants [10]. The secondary particle formation in mixtures was studied by Stolzenberg et al., who described the mechanism of zirconia nanoparticles driving to aggregation and agglomeration [11].

$ZrO_2/SiO_2$  composite nanoparticles at optimum concentration (0.1 wt%) show rolling movement in the tribosystem, resulting in a reduced friction by an average of 16% and wear by a further 15% [12]. Zirconia composite materials show a self-lubricating mechanism [13]. Kerkwijk et al. tested the dry friction of different oxide ceramic composites with zirconia and showed a 40% friction decreasing effect [14]. Spherical alumina/zirconia nanocomposites produced by the sol-gel method can reduce the friction by 63% compared to the bulk alumina nanoparticles [15]. Tripathi et al. reported a synergistic yttria-stabilized zirconia (YSZ) reinforcement with boron nitride, graphene, and diamond in the Cr-matrix which had superior fretting wear resistance. Carbon nanotubes and YSZ as a coating showed a synergic effect on laser peened electrochemical chromium-based surfaces. This composite coating had high hardness and resistance to high compressive stresses [16].

Yttrium oxide ( $Y_2O_3$ , known as yttria) is a high hardness ceramic type material resembling zirconia in its properties that is also found in nature, although it is very rare. Yttria alone has not yet been studied as a nanoadditive, although previous research has shown a reduction in wear volume of up to 90% [17]. However, several studies reported that it has excellent results in tribology-related topics, especially wear-reducing and anti-corrosion effects as an additive in coatings and/or composites. The corrosion wear resistance of 6061 Al alloy and 304 stainless steel using commercial lubricants doped with yttrium additive was tested on a pin-on-disc tribometer. The specimen was lubricated with oil and thin grease mixed with yttrium. The lubricants were mixed with 10% sulfuric acid for the corrosion tests. The wear rate was investigated after the sliding tests from the weight loss. Results show that yttrium protects the specimen against corrosion wear and this phenomenon is confirmed by SEM analysis. SEM images show an yttrium oxide containing passive layer formed on the worn surfaces. This passive layer can increase the adhesion of the protective oxide tribofilm formed during corrosion wear [18]. In another study, Bouaeshi et al. reported the effects of an yttria additive on aluminum microstructure, hardness, wear, and corrosion wear. During the analysis of the worn surface, an  $Al_3Y$  phase was observed on the surface instead of the yttria particles. With the decomposition of yttria, a protective layer emerged that provided a higher hardness and more corrosion resistance

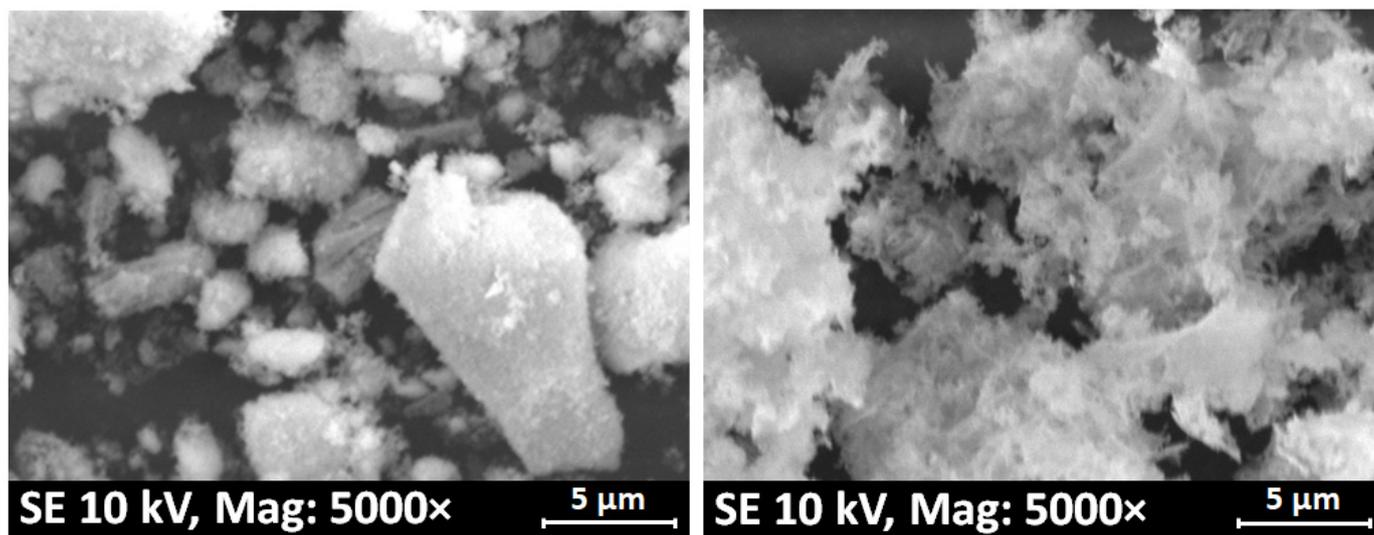
to sulfuric acid and sodium chloride solution [19].  $Y_2O_3$ -reinforced WC–10Co4Cr alloy became high erosive wear resistant, and yttria reduced the erosion wear by 45.9%. The surface analysis showed a lower tendency for material breakouts [20]. Cai et al. tested NiCrBSi– $Y_2O_3$  composite coatings prepared by plasma spraying on 45 carbon steel and showed that the coefficient of friction was reduced to 37% by the presence of yttria. The wear was reduced by 43% compared with the reference coating. The wear type of the composite was mainly adhesive with micro-cutting wear [21]. Another plasma sprayed coating from alumina–yttria was tested by Rong et al. They showed that a chemical reaction occurred during the deposition of the composite coating, during which new ceramics were formed. The yttria-containing coatings thus formed lower friction, so the wear surface temperature was also lower. Microscopic analysis revealed that yttria increased the crack propagation resistance of the composite coatings [22]. Two-dimensional sheet-like yttria nanosheets could improve the mechanical and flow properties of lubricants: 0.1 wt% of the yttria nanosheets could reduce the friction coefficient and viscosity by ~40% and ~5%, respectively. The results were confirmed by the simulation of the fluid shear stress [23].

## 2. Materials and Methods

Both the yttria (CAS-number: 1314-36-9) and zirconia (1314-23-4) used in the studies were purchased from Reanal Laborvegyszer Kereskedelmi Ltd., Budapest, Hungary. The parameters of the applied nanoceramics are shown in Table 1. Figure 1 shows the SEM images of the investigated nanoparticles with 5000x magnification.

**Table 1.** Properties of the investigated zirconia ( $ZrO_2$ ) and yttria ( $Y_2O_3$ ) nanoparticles.

Nanoparticle	Purity	Density	Particle Size	Morphology	Crystal Structure
$ZrO_2$	99%	5.89 g/cm <sup>3</sup>	15–25 nm	Spherical	Monoclinic
$Y_2O_3$	99.999%	5.01 g/cm <sup>3</sup>	50 nm	Spherical	Body-centered cubic



**Figure 1.** SEM images of the used nanoparticles: left, zirconia ( $ZrO_2$ ); right, yttria ( $Y_2O_3$ ).

Both yttria and zirconia nanoadditives show excellent tribological effects. However, no research could be found about the synergy of the two ceramic additives. As yttria is a rare and expensive ceramic, a synergy should be sought in which it exerts its previously beneficial effects even at lower concentrations [17]. The weight ratio of yttria stabilized-zirconia (YSZ), which is very common in practice, was used to study the synergy. In practice, yttria is often used to stabilize zirconia so that its crystal lattice does not change at high temperatures, without its properties changing significantly. Depending on the

yttria–zirconia ratio, a distinction is made between partially and fully stabilized zirconia. An amount of 8 mol% of yttria is able to completely stabilize the crystal lattice of zirconia. According to multiple literature sources, zirconia crystal structure can be stabilized with the addition of 8 mol% of yttria material. An amount of 8 mol% yttria means 13.75 wt% in the ceramic mixture, resulting from the higher molar mass of yttria (yttria: 225.81 g/mol; zirconia: 123.22 g/mol). The new yttria–zirconia ratio thus created is from 11 to 69. The aim of the research is to investigate the synergism between zirconia and yttria, and thus the possibility to use lower yttria concentrations in mixtures.

The oil mixtures used for the measurement were based on a Group III base oil with a kinematic viscosity of 4 cSt at 100 °C temperature (provided by MOL-LUB Ltd., Almásfüzitő, Hungary). To create a more homogeneous and stable mixture, 1% Triton X-100 (TX100) nonionic surfactant dispersant was added to the mixture (purchased from Reanal Laborvegyeszer Kereskedelmi Ltd., Budapest, Hungary). In the previous research activities of the authors [17], neat yttria nanoparticles were investigated with the same methodology and the negative effects of yttria nanoparticles were only defined without the addition of extra nonionic surfactant dispersant by formulating agglomerates. According to this result, the yttria–zirconia mixture was only investigated with the addition of Triton X-100 dispersant.

The role of homogenization is key, because nanoadditives are only able to interact between the tribological interfaces and show their effects there if they have a sufficiently small particle size and a homogeneous distribution in the lubricant [24]. The specified ratio of nanoceramics was added to the base oil in 5 different concentrations (0.1, 0.2, 0.3, 0.4, and 0.5 wt%) and then the 1 wt% TX100 dispersant was added. The resulting mixture was prepared in two steps. First, the mixture was stirred for 3 min at 1000 rpm on a magnetic stirrer to separate larger bulks of ceramic nanopowder. In the second step, the mixture was placed in an ultrasonic homogenizer at 50 °C for 30 min. Ultrasonic homogenization separates the particles from each other to produce a mixture that is sufficiently homogeneous for measurements. To prevent settling, the mixture was kept on a magnetic stirrer until it was filled into the measuring tribometer.

The tribological experiments were carried out with the help of an Optimol SRV<sup>®</sup>5 tribometer [25] (Optimol Instruments GmbH., Munich, Bavaria, Germany) in the Tribological Laboratory of Széchenyi István University. For the experiments, standardized ball and disc specimens (provided by Optimol Instruments GmbH.) were used which correspond to the ISO 19291:2016 standard [26]. The applied ball specimens were 10 mm diameter ball bearings from 100Cr6 material (1.3505 material), were hardened up to 61 HRC, and their surface was polished (Ra 0.025 µm). The used disc specimens (24 mm diameter and 7.9 mm height) were also standardized and made of 100Cr6 material (1.3505 material). They were vacuum melted, their hardness was 62 HRC, and their flat surfaces were grinded and lapped (Ra 0.035 µm). The applied tribometer provides a 1 mm and 50 Hz sinusoidal oscillation movement of the ball on the contacting surface of the disc specimen and the ball was pressed on the disc with a given normal force. The specimens were heated up to 100 °C to simulate the usual circumstances a lubricant would experience in an operating engine. The standardized measurement method was extended with an oil circuit with an external peristaltic pump to simulate the conditions of the lubricant in a real mechanical system [27]. The prepared nanolubricant samples were tribologically investigated with the described investigation method; its detailed investigation parameters can be observed in Table 2.

**Table 2.** Investigation parameters used for the tribological tests.

Parameter	Stroke	Frequency	Specimen T	Oil T	Oil Flow Rate	Load	Time
Step 1	1 mm	50 Hz	100 °C	100 °C	225 mL/h	50 N	30 s
Step 2	1 mm	50 Hz	100 °C	100 °C	225 mL/h	100 N	2 h

The applied tribometer measures the friction coefficient every 20  $\mu\text{s}$  and the FAI (friction absolute integral) value is calculated for each stroke according to the following formula:

$$\text{FAI} = \frac{1}{s_{\text{max}}} \cdot \int_{s_0}^{s_{\text{max}}} |\mu(s)| ds \quad (1)$$

where 's' is the applied stroke and ' $\mu$ ' is the measured friction coefficient.

Further microscopical analyses were carried out to define the wear values on the ball and disc specimens. The wear scar diameter (WSD) values were measured with a Keyence VHX-1000 digital microscope (Keyence International, Mechlin, Belgium), according to the measurement process described in the ISO 19291:2016 standard [26]. To measure the missing metal volume on the worn surface of the disc specimen, a Leica DCM 3D confocal microscope (Leica Camera AG, Wetzlar, Germany) was used. A scanning electron microscope investigation was also carried out to produce high-resolution and high-magnitude images of the worn surface. These images were supplemented with EDX element distribution measurement to understand how the additive influences the tribological properties of the investigated ball-on-disc tribosystem. For these investigations, both a Hirox SEM-4000M in the Surface Analytic Laboratory at Széchenyi István University (Hirox Europe, Limonest, France) and a Thermo Fisher Helios G4 PFIB CXe microscope in the 3D Lab of the University of Miskolc (Thermo Fisher Scientific, Waltham, MA, USA) were used.

### 3. Experimental Results and Discussion

In the previous article of the authors [17], a surface-active dispersant additive was necessary for the yttria nanoparticles to avoid the formation of larger nanoparticle agglomerates. These larger agglomerates of nanoparticles could decrease the tribological performance of the oil by increasing the three-body abrasion wear on the contacting surfaces. In the case of the yttria–zirconia investigations, each lubricant sample was prepared with 1 wt% Triton X-100 dispersant additive. Six different lubricant samples were prepared for the investigation, each containing the previously described dispersant additive, and their nanoparticle content varied between 0 and 0.5 wt% with 0.1 wt% steps. A minimum of three independent tribological ball-on-disc measurements were carried out with each lubricant sample to compare their friction decreasing property and their protection against wear. For the evaluation of the results, the average and standard deviation values of friction coefficient, wear diameter, and wear volume parameters were calculated for each nanoparticle concentration in Excel, using the AVERAGE and 'STDEV.P' functions.

The comparison of the measured friction coefficient can be observed in Figure 2. The bar chart diagram clearly shows a slight increase in the tribological values adding 0.1 wt% of nanoparticles in the lubricant sample. By increasing the nanoparticle concentration, the friction coefficient starts to decrease slowly (the only exception was the 0.2 wt% sample, but its deviation range was higher compared to the 0.1 wt% sample, so they can be considered as equals) and the only concentration where the measured friction coefficient value was lower than the reference sample was 0.5 wt%. The maximal friction coefficient decrease was defined as 6% in the case of the lubricant sample with a 0.5 wt% yttria–zirconia nanoparticle concentration.

The comparison of the wear scar diameters measured on the contacting surfaces of the ball specimens is presented in Figure 3. The same tendency can be defined in this bar chart as in case of the previously discussed friction coefficient values: the 0.1 wt% sample produced a slightly increased WSD value, but in the case of increased nanoparticle concentrations the wear scar diameter was significantly decreased. The maximal wear scar decreasing property was observed for the 0.4 wt% sample, where the WSD value dropped by 30%. However, the 0.5 wt% sample showed excellent anti-wear properties with its 26% decrease of wear compared to the reference sample.

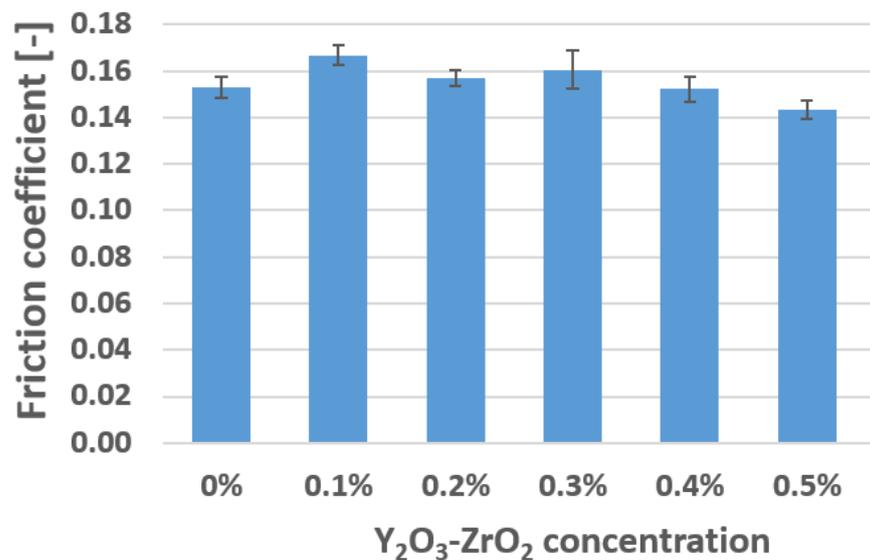


Figure 2. Comparison of the measured friction coefficient values at each nanoparticle concentration.

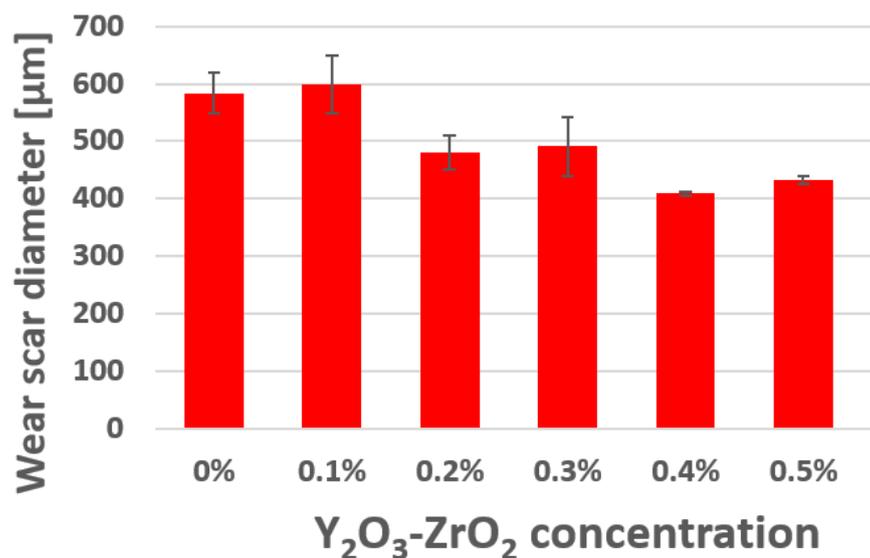
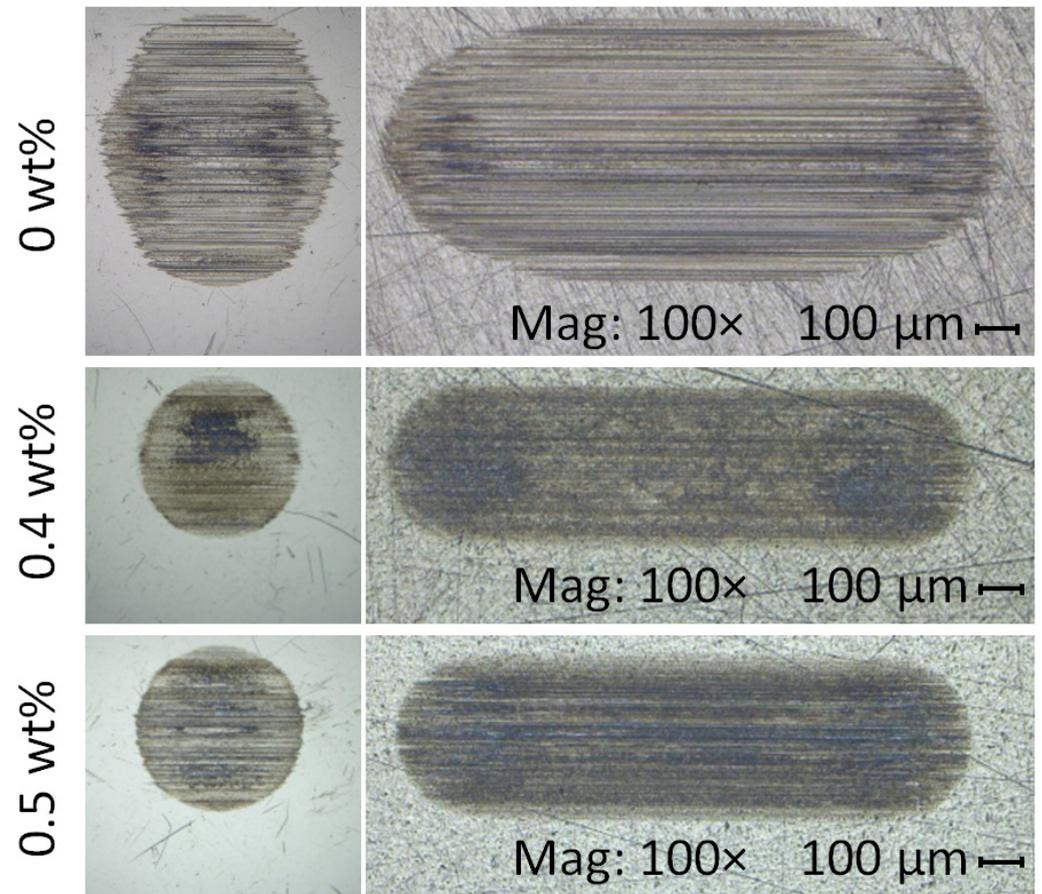


Figure 3. Comparison of the measured wear scar diameter values at each nanoparticle concentration.

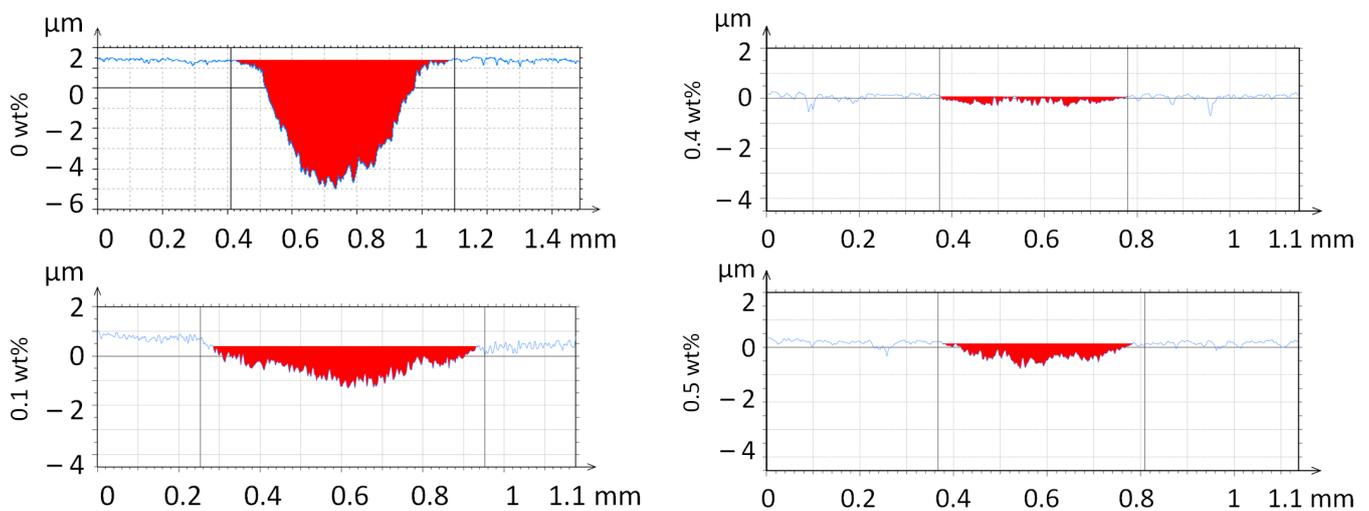
Figure 4 presents the acquired digital microscopic images of the 0.4 and 0.5 wt% nanoparticle concentration measurements. The wear images show a relatively low wear rate with a similar dominant wear mechanism. Abrasive wear can be observed on both worn surfaces: in the case of 0.4 wt% there is a surface polishing effect, while at 0.5 wt% the worn grooves seem to be deeper and the wear scar on the disc specimen is darker, which indicates a higher thermal load of the used lubricant (so the lubricant molecules were burned on the surface at a higher ratio).

To understand the exact wear mechanism, the whole worn surface on the disc specimens had to be scanned with the confocal microscope. During the evaluation of the scanned results, the average wear cross sections were plotted, and the wear volume data were calculated. The acquired cross section diagrams can be observed in Figure 5, while the comparison of the wear volume results is presented in Figure 6. For the calculation of the wear volume, the worn surface area and its surroundings were digitalized with the help of the confocal microscope. The average starting surface height was calculated from the surrounding results with the least squares method. All of the area which was under

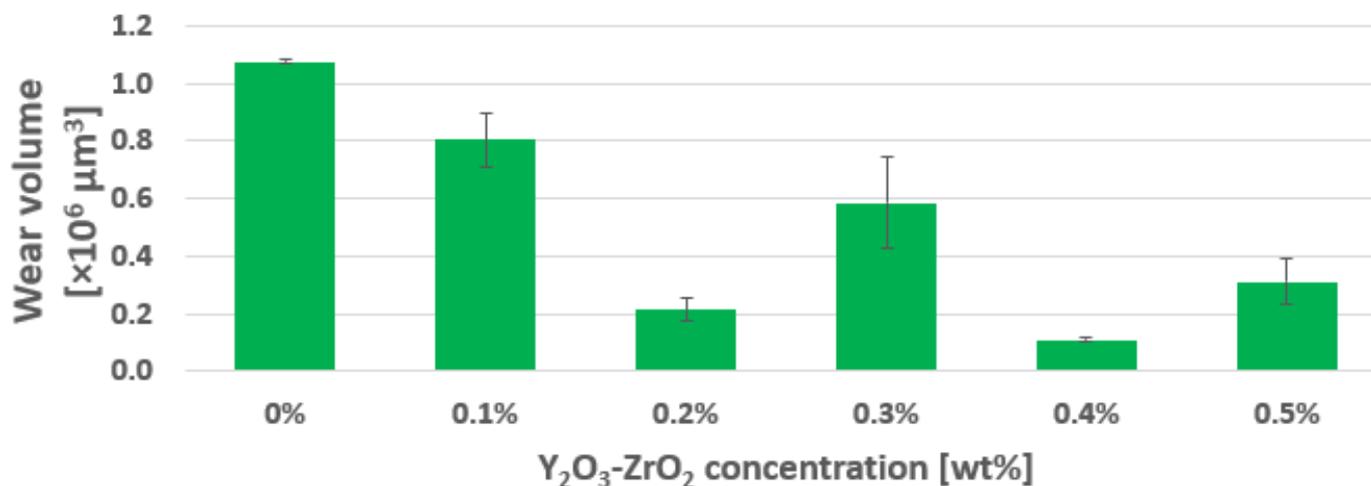
this plane of average starting surface was considered as a worn surface and its volume was calculated with the help of the evaluation program of the used microscope.



**Figure 4.** Digital microscope images about the worn surfaces with 0 (top), 0.4 (middle) and 0.5 wt% (bottom) nanoparticle concentration oil sample (ball specimens on the left, disc specimens on the right).



**Figure 5.** Cross-sectional profile of the worn surfaces with different  $Y_2O_3-ZrO_2$ -concentrational lubricant samples.

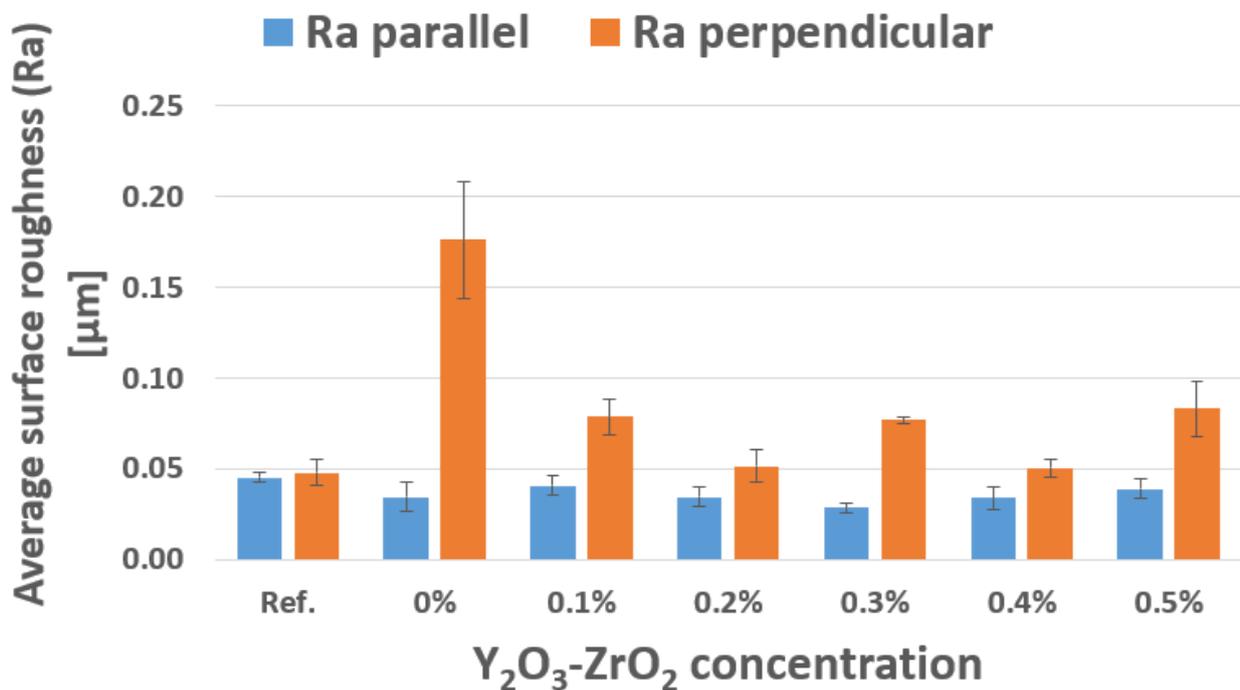


**Figure 6.** Comparison of the measured wear volume data of the disc specimen's surface with confocal microscope.

The wear volume analysis from the confocal microscope revealed an interesting difference in results compared with the wear scar diameter analysis. The lowest amount of additional nanoparticles in the neat base oil could reduce the wear volume and the wear depth. A significant difference can also be observed from the results of the 0.4 and 0.5 wt% sample: the wear volume was larger for the 0.5 wt% sample. The highest wear volume decrease can be shown for the 0.4 wt% sample, where the volume was reduced by almost 90% compared to the reference sample. Moreover, the cross-sectional profile of the 0.4 wt% sample also suggests the same as the previously mentioned statement, that the 0.4 wt% yttria–zirconia nanoparticle mixture can slightly modify the wear mechanism and the worn surface was polished rather than abrasively worn.

A surface roughness analysis was also carried out on the worn surfaces of the disc specimens to prove the polishing mechanism of the investigated nanoparticles. The average surface roughness values were measured in the directions parallel and perpendicular to the sliding direction according to the standard ISO 4287. The graphical presentation of the average surface roughness results can be observed in Figure 7. As reference, the surface roughness of the clean starting surface of the disc specimen was also measured, and these results can be seen with the name of Ref. The Ra values correlate with the cross-section profiles (Figure 5) and wear volume evaluation (Figure 6). Due to the lack of additives of the reference sample, a relatively high surface roughness was measured for the 0% sample. With the addition of the investigated nanoparticles, both the wear volume and the average surface roughness were significantly decreased, mainly in the values of Ra, measured perpendicular to the sliding distance. In the case of the so-called optimum concentration (0.4 wt%), the measured average surface roughness values were equal to the values of the reference, even after 2 h of tribological test under the 100 N loading condition. The Ra values also prove the polishing working mechanism of the yttria–zirconia nanoparticle mixture.

It is necessary to compare the acquired results of the yttria–zirconia nanoparticle mixture with previous research results, in which these nanoparticles were separately tested with the same investigation method. The currently presented result tendencies correlate with both the zirconia results [28] and the yttria results [17], but the results of this mixture of nanoparticles are nearer to the zirconia results. In the case of neat yttria nanoparticles, there were concentrations (between 0.2 and 0.4 wt%) where the wear volume was increased compared to the reference, while the zirconia nanoparticles showed similar tendencies to the current yttria–zirconia mixture results; nevertheless, the neat zirconia particles were only investigated without Triton X-100 extra dispersant additive. This can be explained with the mixing ratio of the yttria and zirconia nanoparticles: almost 8 times more zirconia was used for each research lubricant sample than yttria.

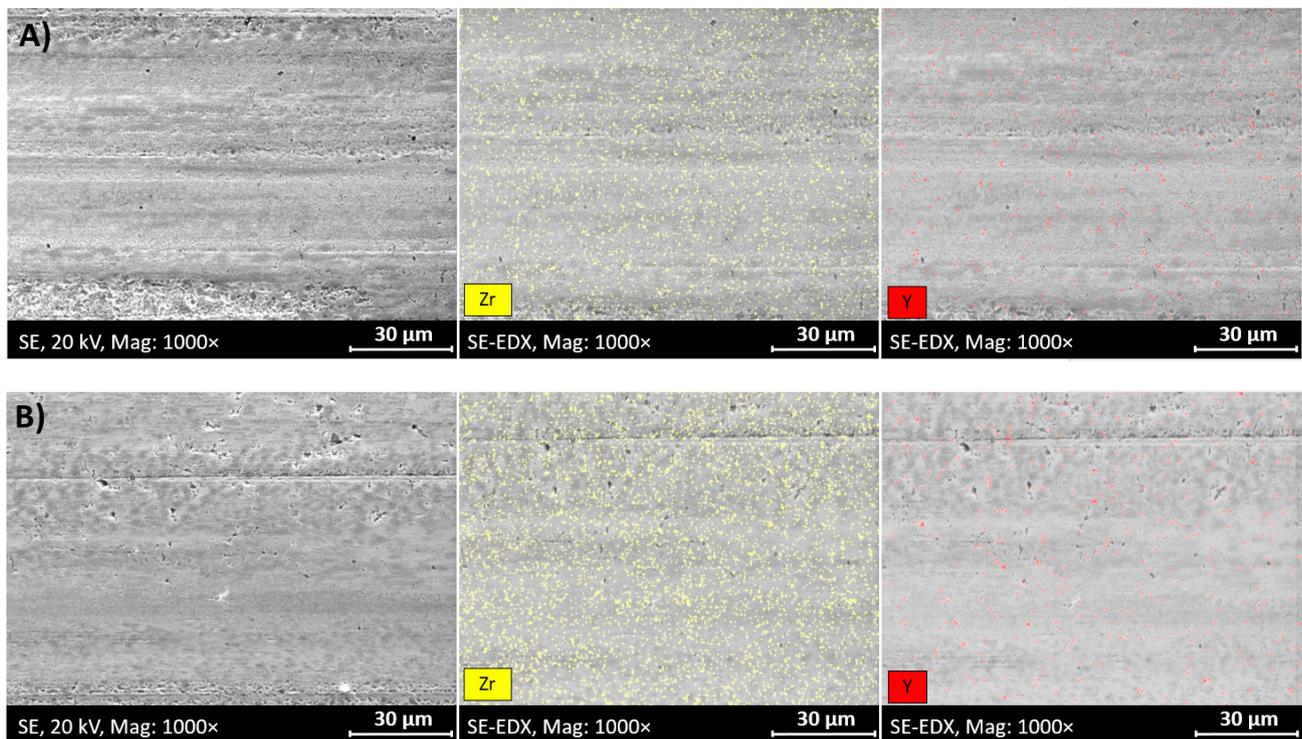


**Figure 7.** Comparison of the measured average surface roughness values on the worn surface of the disc specimens.

To understand the working mechanism of the yttria–zirconia nanoparticle mixture, further scanning electron microscope analysis was carried out with high magnification. Figure 7 represents the acquired SEM images with yttrium and zirconium distribution on the dead center and middle stroke area of the disc specimen measured with 0.4 wt% yttria–zirconia nanoparticles. The SEM images show a relatively smooth worn surface with some deeper grooves which can come from abrasion wear. The whole worn surface presents a polished surface which also reflects the main working mechanism of the used nanoparticles. The acquired EDX images illustrate that a significant amount of zirconium can be found on the worn surfaces, while the yttrium distribution is quite low. Table 3 shows the results of the quantitative EDX element analysis from the areas of the SEM images in Figure 8. The quantitative results prove the EDX images: 1.7 wt% and 0.76 wt% zirconium was found on the dead center and middle stroke area of the measurements, respectively; however, no yttrium could be defined (the yttrium distribution can be defined as a signal from the background).

**Table 3.** Results of the quantitative EDX element analysis on the worn surface of the disc specimen measured with 0.4 wt% yttria–zirconia nanoparticles.

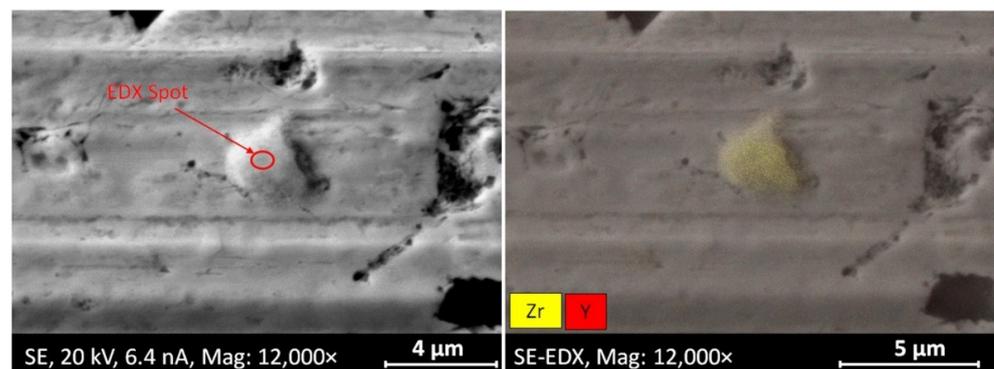
Element	(A) Dead Center	(B) Middle Stroke
Fe	90.86%	93.30%
Cr	1.25%	1.12%
Si	1.41%	1.16%
O	3.01%	1.95%
C	1.78%	1.71%
Y	0.00%	0.00%
Zr	1.70%	0.76%



**Figure 8.** SEM images of the worn surface of the disc specimen in case of the 0.4 wt% lubricant sample: (A) dead center area and (B) middle stroke area.

The previously presented SEM images with 1000× magnification provided important information about the general yttrium and zirconium content of the worn surface; however, they could not provide the necessary information about the local distribution of the nanoparticles. To acquire the necessary information, further SEM analysis with significantly higher magnification was necessary. The high magnification SEM analysis of the worn surface of the disc specimens was carried out with a Thermo Fisher Helios G4 PFIB CXe microscope (Thermo Fisher Scientific, Waltham, MA, USA) in the 3D Lab of the University of Miskolc.

Figure 9 presents the acquired SEM images and the distribution of Zr and Y elements on the worn surface of the disc specimen that was measured with a 0.4 wt% nanoparticle concentration. Several areas were found where zirconium enrichment was defined, and a small amount of yttrium could also be measured in these areas. According to the quantitative element analysis (see Table 4), a significant amount of zirconium (over 16 wt%) and yttrium (0.8 wt%) could be found there, while the average zirconium content of the worn surface was defined between 0.7 and 1.7 wt%.

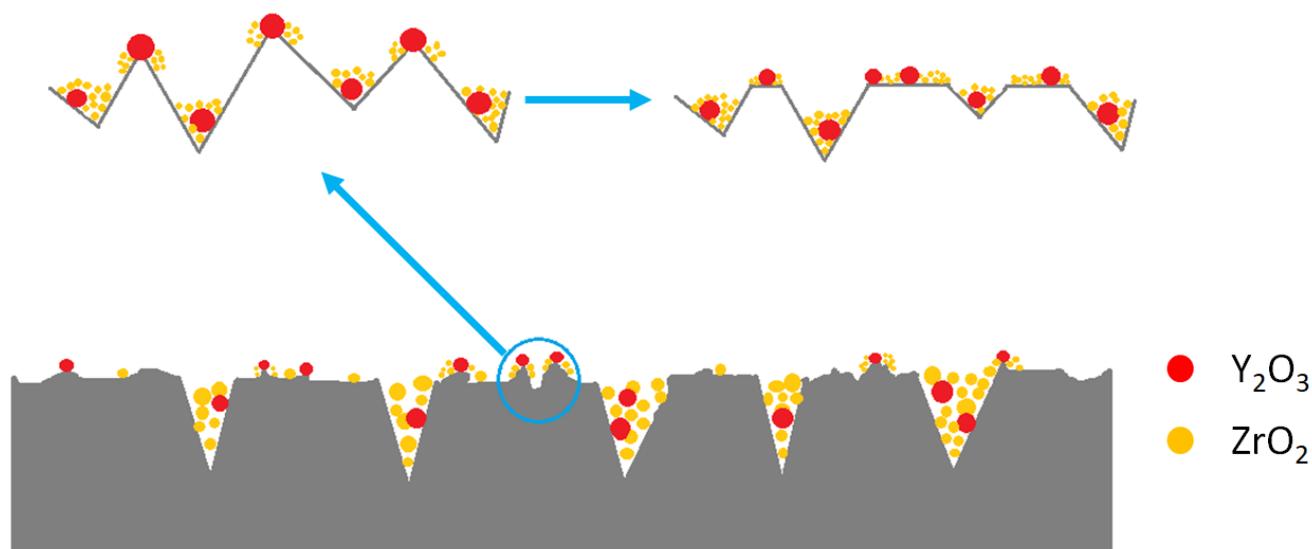


**Figure 9.** SEM image and EDX map of a zirconium enrichment on the worn surface of the disc specimen, measured with 0.4 wt% yttria–zirconia nanoparticles.

**Table 4.** Results of the quantitative EDX element analysis of the EDX spot on the worn surface of the disc specimen.

Element	EDX Spot
Fe	72.6%
Cr	0.9%
Si	1.3%
O	8.2%
Y	0.80%
Zr	16.20%

According to the acquired information, the yttria–zirconia nanoparticle mixture can provide promising tribological properties to the investigated base oil. Because of the yttria content of the prepared lubricant, extra dispersant additive had to be used (Triton X-100) to avoid the building of large agglomerates. The SEM images and EDX element analysis revealed the working mechanism of the nanoparticle mixture; the nanoparticles were attached to the contacting surface, forming a protective tribological layer by tribo-sintering, and they additionally were collected in the surface grooves, resulting in a smoother contact surface which could decrease the wear volume. Furthermore, a small amount of yttria nanoparticle in the lubricant decreased the wear depth significantly and increased the polishing effect of the lubricant, accelerating the running-in process of the contacting surfaces. Figure 10 represents a schematic illustration of the working mechanisms of the investigated yttria–zirconia-reinforced lubricants. Compared with the research results with only zirconia and only yttria-doped lubricants of the authors [17,28], the data of the yttria–zirconia nanoparticle mixture was nearer to the yttria than the zirconia-doped lubricant.



**Figure 10.** Schematic illustration of the working mechanisms of the lubricant samples with yttria–zirconia nanoparticles: mending, tribo-sintering, and polishing.

With regard to economy, the currently investigated nanoparticle ratio also has its advantages. According to the purchase prices of the nanoparticles, the cost increase of 1 L of engine lubricant was calculated with regard to the optimum concentrations: an extra cost of approximately EUR 13.5 is needed to formulate 1 L of engine oil using yttria–zirconia nanoparticles, while approximately EUR 38 should be paid to obtain the same amount of engine oil with only yttria nanoparticles.

#### 4. Conclusions

This article presents the experimental research results carried out with yttria–zirconia-reinforced nanolubricant. The main aim of this paper was to prove the positive tribological behavior of the investigated nanoparticle mixture as a lubricant additive and define its working mechanisms. The lubricant samples were prepared in the Tribological Laboratory of the Department of Internal Combustion Engines and Propulsion Technology at Széchenyi István University, Győr, Hungary, and the tribological experiments were also carried out in the laboratory. The thorough microscopical analyses of the worn surfaces were executed in the Surface Analytic Laboratory of the department, and in the 3D Lab of the University of Miskolc, Hungary.

The results of this research can be summarized as follows:

- The yttria–zirconia nanoparticles provided positive tribological effects to the used neat Group III 4 cSt base oil. For the proper homogenization of the nanoparticles, extra dispersant additive (1 wt% Triton X-100) was also added into the nanolubricant samples. The nanoparticles caused a slight friction coefficient increase with a significant amount of wear reduction. The optimum concentration was defined at 0.4 wt%, which provided a 30% wear scar diameter and almost 90% wear volume reduction without friction coefficient increase, compared to the reference oil sample.
- The executed SEM analysis revealed a significant amount of zirconium (between 0.76 and 1.7 wt%) on the worn surfaces of the disc specimen measured with 0.4 wt% nanolubricant; however, no yttrium was found on these surfaces. The acquired high-magnification SEM images revealed local zirconium enrichments on the surfaces which could be found on the worn surfaces after multiple thorough ultrasonic cleaning processes.
- The signs of multiple working mechanisms were detected during the research: due to the small amount of yttria, the lubricant sample increased the polishing effect of the nanoparticles, accelerating the running-in process, and the particles were also tribo-sintered into the surfaces, forming a protective tribolayer; by mending, the nanoparticles were also collected into the wear and roughness grooves of the surface.

The results of the investigation prove that the research field of nanoscale ceramic particles used as lubricant additives is an interesting and valuable area, which has potential to be further researched. It is also important to understand whether these nanoparticles are adaptable to mass production. The nanoparticles can provide positive tribological effects to a lubricant, but as they increase the purchasing costs of the engine oil significantly, it is not possible to sell them to customers.

As the future of these research fields, further nanoparticle variations should be investigated to understand their working mechanism and to find the most suitable nanoparticle variant for the lowest possible cost increase. Engine oils always contain several other additives as well (e.g., viscosity modifier, dispersant), and it should also be investigated whether the nanoparticles can work together with these additives. At the end of this research, a proper engine lubricant could be formulated that originally contains nanoparticles with all their tribological benefits.

**Author Contributions:** Conceptualization, Á.D.T. and H.H.; methodology, Á.D.T. and Á.I.S.; formal analysis, Á.D.T. and H.H.; investigation, Á.D.T., Á.I.S. and M.Z.L.; resources, Á.D.T. and H.H.; data curation, Á.D.T. and Á.I.S.; writing—original draft preparation, Á.D.T., Á.I.S. and M.Z.L.; writing—review and editing, Á.D.T., Á.I.S. and H.H.; visualization, Á.D.T., Á.I.S. and M.Z.L.; supervision, H.H.; project administration, Á.D.T.; funding acquisition, Á.D.T. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to thank Dóra Olimpia Csepregy, Boglárka Nagy, Valéria Mertinger, and Jan Rohde-Brandenburger for their general support.

**Conflicts of Interest:** The authors declare no conflict of interest.

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