THE EFFECT OF COPPER OXIDE NANOPARTICLES ADDITION ON THE FRICTION COEFFICIENT OF CALCIUM-BASED GREASE

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In this work, copper oxide nano-metric powders were synthesized via a manual method called Electric Discharge, and the effect of CuO nanoparticle additives on the tribological behavior and friction coefficient of the Ca^{2+} *grease has been investigated. CuO nanoparticles were fabricated through different current intensities of 100, 250, and 500 Ampere, and various wire dimeters of 0.2, 0.3, and 0.5 Millimeter. After that, a certain percentage of the nanoparticles were added to the grease, so that their effects on the coefficient of friction of the* Ca^{2+}*grease could be examined. The microstructures of the nanoparticles were studied using a Field Emission Scanning Electron Microscopy (FESEM). To investigate the crystal structure of the copper oxide nanopowders, X-ray diffraction (XRD) was performed. In addition, the friction coefficient of the greases that were modified by nanoparticles were examined using a horizontal pin on disc wear testing machine, and wear tests showed that CuO nanopowders produced in 500 A and less wire diameter resulted in better tribological properties and reduced friction coefficient of the grease, in respect to those nanoparticles which were synthesized in lower current densities and more wire diameters. In summary, reducing the diameter of the wire and increasing the current density causes the coefficient of friction to decrease.*

Keywords: Nanoparticles; Copper oxide; Electric discharge; Coefficient of friction

1. Introduction

Metal oxide nanostructures (MOs) play a very critical role in many fields of science such as physics, chemistry, material science, engineering and medicine. Today, MOs are being implemented vastly in the construction of solar cells, sensors, microelectronic circuits and piezoelectric devices. Metal oxide nanostructures possess unique physical, chemical, magnetic, electric and biological properties mainly because of their high surface to volume ratio. Due to these unique features, MOs have attracted wide range of various applications such as lithium-ion batteries, solar and fuel cells, magnetic storage devices, biosensors, cancer cell treatments and antibacterial agents [1-7].

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In industry, the fuel energy consumed in combat friction and wear amounts to approximately30%–40%. Thus, numerous scientists have developed lubrication additives and low-friction materials[8, 9]. In fact, less friction coefficient between different parts of vehicles results in longer lifespan, and less thrust force for running the tools. Therefore, reducing the friction force can cause the vehicle to have improved properties, mechanical durability, and more accurate function[10, 11]. Recently, nanoparticles have been investigated as additives for lubricants in order to reduce wear and friction. Nanomaterials have emerged as potential environment friendly lubricant additives to upgrade the conventional lubricants such as automotive oils, industrial oils, grease, and metal working fluids[12, 13].A significant advantage of nano lubricants over other conventional anti-wear and anti-friction additives is that they do not require tribo-active elements such as phosphorus and sulfur to improve the tribological properties of the base oil, exhibiting excellent friction and wear reduction characteristics [14].According to many investigations, adding certain nanoparticles to lubricants causes a very thin film to be created on the rubbing surfaces which results in decreasing the friction coefficient and improving lubricative properties[15-17].For instance, in one study, 2.0 wt% of CuO nanoparticles were incorporated into Poly-alpha olefin 8 (PAO 8) base oil, and antiwear results showed a decrease of up to 18% on coefficient of friction[18]. Furthermore, in another study, CuO, ZrO2, and ZnO nanoparticles were dispersed in a polyalphaolefin (PAO 6), and results proved that all nanoparticle suspensions exhibited reduction in friction and wear compared to the base oil[19].Moreover, another research showed that 1 wt% of CuO blend resulted in low wear and coefficient of friction with improved lubricity of oil [20].

There are various techniques for synthesizing nanostructured materials such as chemical co-precipitation, sol-gel, hydrothermal decomposition, thermal decomposition, Electro-Explosion of Wire (EEW) and Electric Discharge method. For example, Petcharoen et al. successfully synthesized magnetite nanoparticles via chemical co-precipitation method, ranging from 10-40 nm, suitable for various biomedical applications[21]. In another study, spherical-shaped zinc oxide nanoparticles with smooth surfaces were fabricated through sol-gel method using zinc acetate as a precursor[22]. In the present study, copper oxide nanoparticles were produced via electric discharge method. The electric discharge method involves the application of a potential difference between a cathode and anode in a conductive electrolytic solution to create a discharge plasma between the electrodes. When a certain material is used as the cathode, small droplets are emitted with the discharge, and the melted droplets are rapidly cooled in the solution to form nanoscale particles of the material[23]. In this work, the negative pole of a welding machine was attached to a copper plate, which plays the role of the cathode, and it was immersed in distilled water as the electrolyte solution, and the positive pole was connected to a copper wire as the anode. When the electrically conductive wire hits the copper plate, the copper plate disintegrates in the distilled water because of electric discharge action, resulting in the production of the nanoparticles.

2. Materials and Methods

A base grease (Ca^{2+}grease) without additives was reinforced with a certain concentration of CuO nanoparticles produced via electric discharge method. Three samples were synthesized in a constant current intensity of 500 A via the explosion of the copper wire in different diameters of 0.2, 0.3, and 0.5 mm in distilled water. On the other hand, two samples were produced in varying amperages of 100 and 250 A via the explosion of the copper wire with a constant diameter of 0.2 mm. In order to identify and compare different phases in samples, X-ray diffraction (XRD) was employed using a Philips PW1730 equipment and X'Pert software. Moreover, all XRD experiments were performed using Cu-Ka radiation with the wavelength of 1.5404A°. In addition, A Philips XL 30 equipment was applied as the Field Emission Scanning Electron Microscope (FESEM) to investigate the size and morphology of CuO nanoparticles. Finally, wear tests were carried out via a horizontal pin on disc wear testing machine, in order to examine the coefficient of friction of the reinforced greases. All CuO nanoparticles samples (S1 to S5) were synthesized according to the experimental conditions listed in table 1.

Table 1.

The experimental conditions for the synthesis of samples S1 to S5

Samples	Amperage (A)	Wire Diameter (mm)
S1	500	0.5
S2	500	0.3
S3	500	0.2
S4	250	0.2
S5	100	0.2

3. Results and Discussions

3.1. XRD results

According to the XRD plots presented in Fig. 1a-c, the Copper and Copper Oxide phases are distinguished in the patterns of the samples S1, S2 and S3.

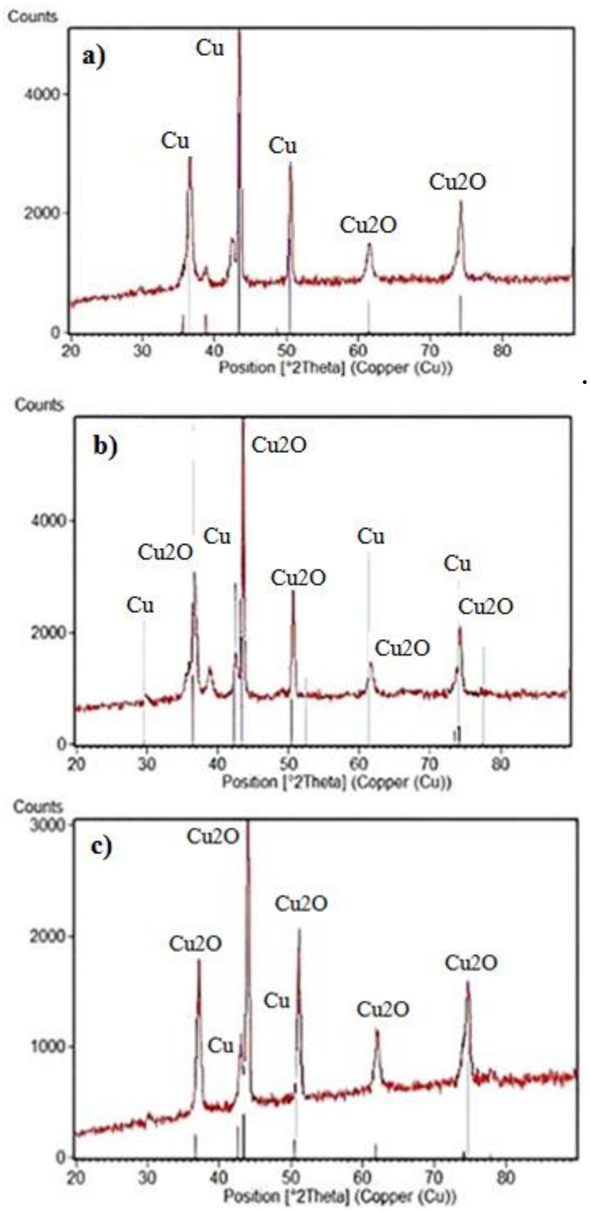
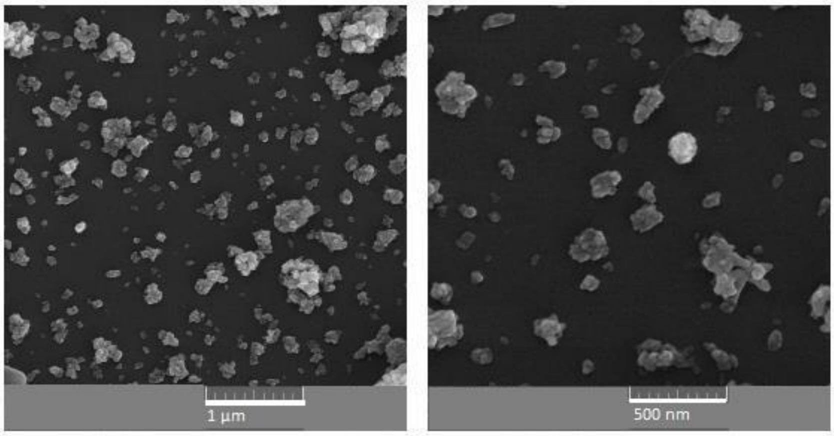


Fig.1. The XRD patterns of a) sample S1, b) sample S2 and c) sample S3.

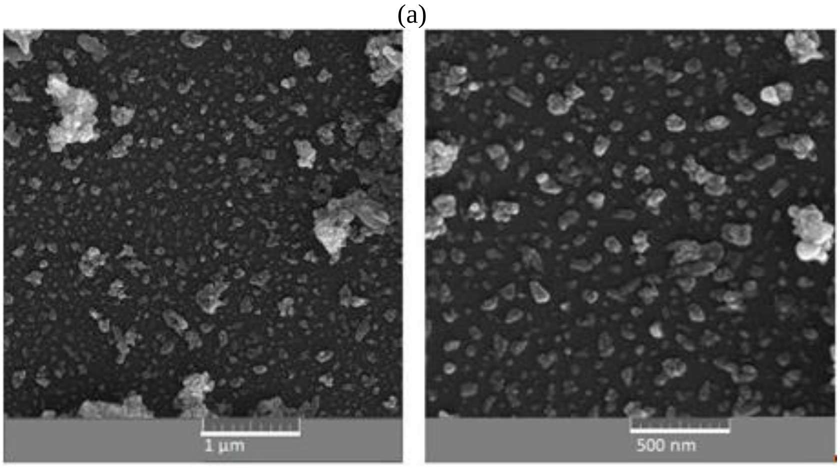
According to the XRD patterns the nanoparticles comprise of Cu and O elements, and nothing else. The X-ray diffraction analysis via the Rietveld method shows that as the wire diameter decreases, the percentage of the Copper Oxide phases increases (table 2). This is due to the fact that when the wire is thicker, the copper atoms located in the center of the wire are better protected from the atmospheric Oxygen.As it is shown in XRD patterns of samples S1 to S3 and table 2, with decreasing the diameterof the copper wire, the percentage of CuO increases from 20% to 50%.

3.2. FESEM results

The results of microstructure analysis of samples S1 to S3 shows that in a constant current density of 500 A, with decreasing the wire diameter from 0.5 mm to 0.2 mm, the mean size of the CuO nanoparticles decreases from 73.50 nm to 23.15 nm. This is due to the fact that reducing the wire diameter causes the amount of energy stored in the wire for electrical discharge to increase; thus, resulting in the formation of small initial Cu embryos. Since the cooling rate of these small Cu atoms is quite high comparing to bigger ones, the final particle size lessens. FESEM images of samples S1 to S3 are presented in Fig. 2a-c.



(a)



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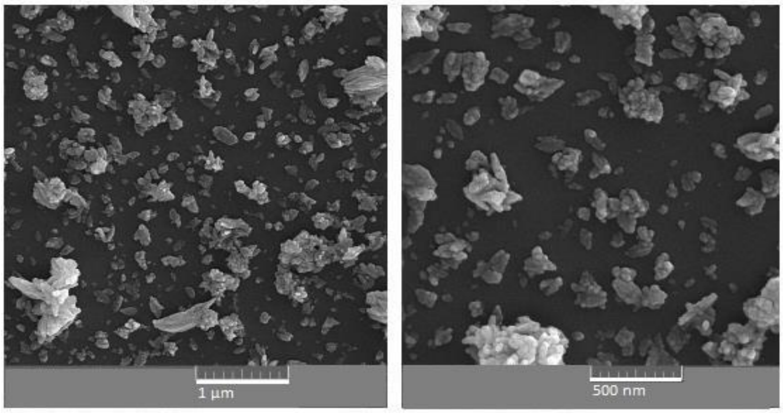
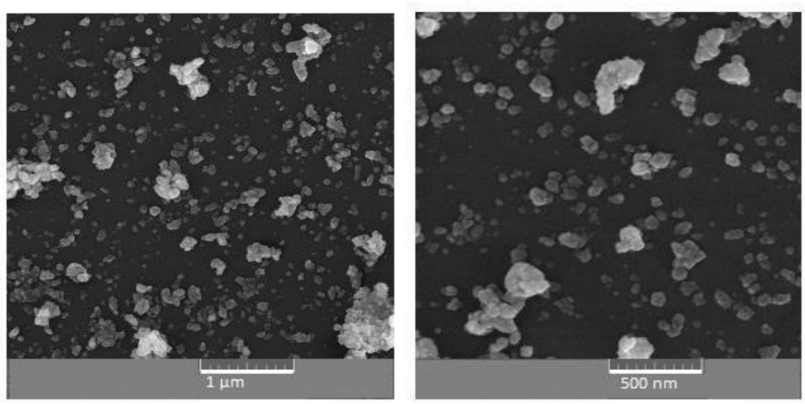


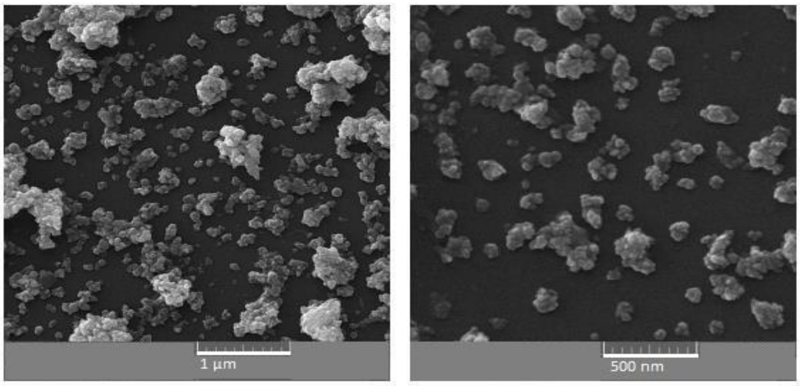
(c)

Fig.2 The FESEM images of samples a) S1, b) S2 and c) S3

For samples S3 to S5, the effect of current intensity on the size of the produced CuO nanoparticles has been investigated. Microstructure analysis shows that as the current intensity increases from 100 to 250 to 500 A, the mean size of the nanoparticles reduces from 53.4 to 47.3 to 23.15 nm. FESEM images are presented in Figs. 2c and 3a-b for samples S4 and S4 respectively.



(a)



(b)

Fig.3 The FESEM images of samples a) S4 and b) S5.

The summarized synthesis conditions and properties of samples S1 to S5 are listed in Table 2.

Table 2

The synthesis conditions and properties of the samples S1, S2, S3, S4 and S5

sample	Current Intensity (A)	Wire diameter (mm)	Mean particle size (nm)	Percentage of the metallic phase
S1	500	0.5	73.50	80
S2	500	0.3	34.17	59
S3	500	0.2	23.15	46
S4	250	0.2	47.30	[redacted]
S5	100	0.2	53.40	[redacted]

3.3. Pin-on-disc test results

Tribological behavior of the calcium based grease was evaluated using a horizontal pin-on-disc wear test machine, and lubricant was applied between the pin and the disc, so that its wear and friction could be determined.Table 3 presents the experimental conditions related to the wear tests and coefficient of friction of the reinforced greases.

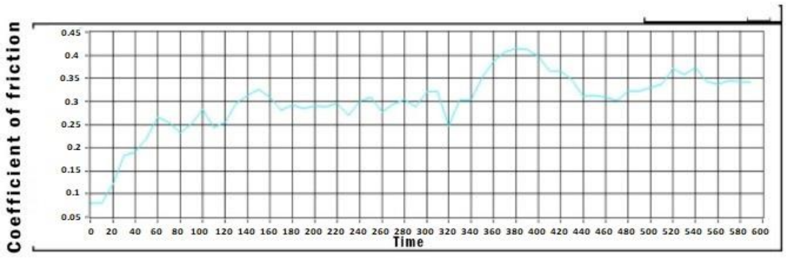
Table 3.

The experimental conditions related to the wear tests

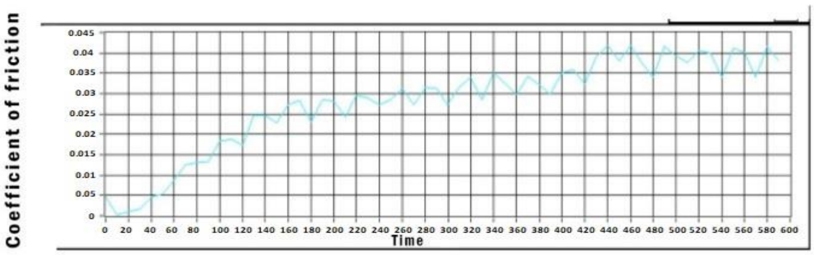
Row	Pin Pressure on Disk	Coefficient of Friction
1	Single pin	0.299
2	Pin and grease without any additives	0.028
3 (S1)	Pin and grease blended with CuO nanoparticles (wire diameter: 0.5 mm,	0.023

	current density: 500 A)	
4 (S2)	Pin and grease blended with CuO nanoparticles (wire diameter: 0.3 mm, current density: 500 A)	0.0068
5 (S3)	Pin and grease blended with CuO nanoparticles (wire diameter: 0.2 mm, current density: 500 A)	0.0016
6 (S4)	Pin and grease blended with CuO nanoparticles (wire diameter: 0.2 mm, current density: 250 A)	0.0052
7 (S5)	Pin and grease blended with CuO nanoparticles (wire diameter: 0.2 mm, current density: 100 A)	0.0177

Table 3 clearly reveals the effect of CuO nanoparticles on the coefficient of friction between the pin and the disc. All samples (S1 to S5) contained 2 wt% CuO nanoparticles. As it can be seen from row 2 and 3, adding nanoparticles have caused the coefficient of friction to decrease from 0.028 to 0.023. This result is in coincidence with other works as well[24-27].Moreover, in a constant current density of 500 A, diminishing the wire diameter results in the coefficient of friction to reduce from 0.023 to 0.0016 (row 3 to 5). In addition, in a constant wire diameter of 0.2 mm, decreasing the current intensity has an increasing effect on the coefficient of friction (row 5 to 7). In conclusion, the best result happens at row 5, which is related to sample S3, when the current density and wire diameter are at their highest and lowest values respectively (500 A and 0.2 mm). Wear test diagrams are represented in Fig. 4a-c and 5a-d for rows 1 to 7 respectively.



(a)



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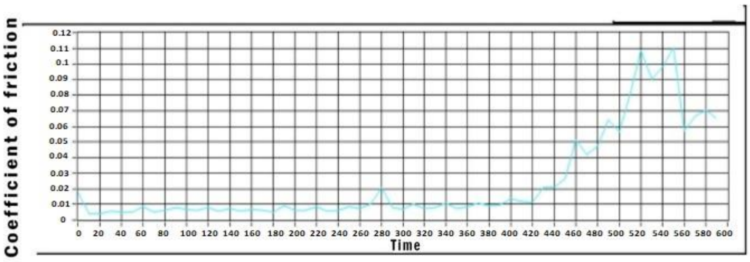
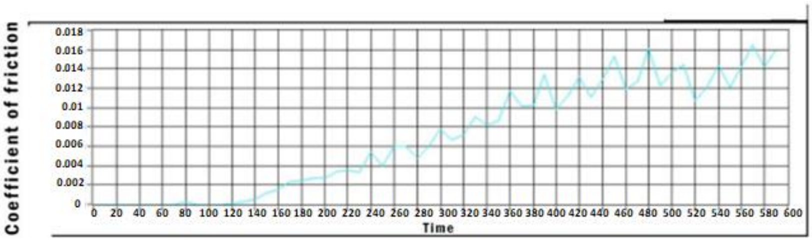
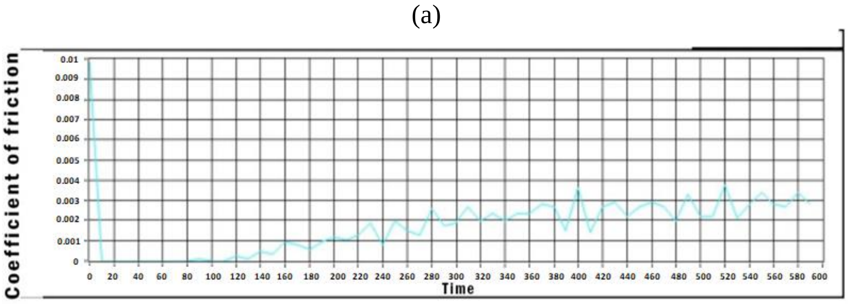


(c)

Fig.4 The plots of friction coefficient with time for different wear tests of table 3: a) row 1, b) row 2 and c) row 3.



(a)



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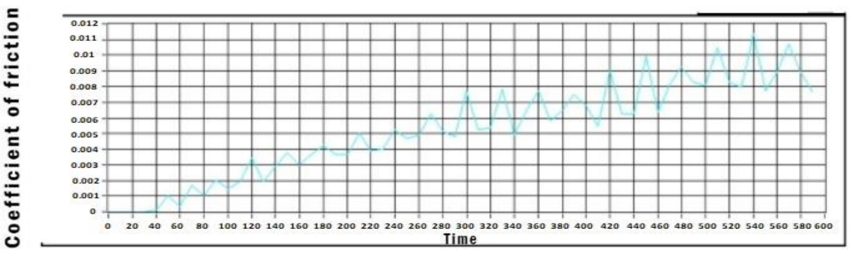

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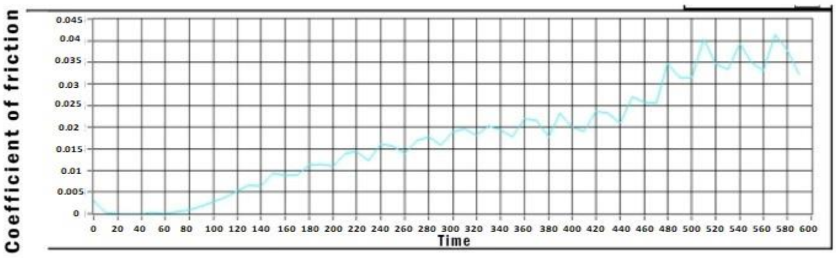

(d)

Fig.5. The plots of friction coefficient with time for different wear tests of table 3: a) row 4, b) row 5, c) row 6 and d) row 7.

The reducing effect of copper oxide nanoparticles on the wear and coefficient of friction of the grease could be due the rolling of soft spherical CuO nanoparticles between the rubbing surfaces. Moreover, the anti-wear mechanism can be attributed to precipitation of CuO nanoparticles on the worn surface and filling the grooves and pores of the disc surface[28]. In fact, the nanoparticles create tribo-films that are the result of complex mechanochemical interactions between the nanoparticles and the lubricant[29],and tribo-films play a significant role in reducing friction and wear in lubricated wear systems[30, 31]. Furthermore, according to table 2 and 3, increasing the percentage of the metal phase in the sample can have a reversed effect on the tribological properties of the grease and cause COF to increase. This lies in the fact that the crushing of copper particles between the sliding surfaces increases the adhesion of the surface; thus, results in an increase in COF. Finally, as the size of the particles diminishes, COF and wear reduces. This is due the fact that the smaller the particles, the higher the surface to volume ratio of particles; hence nanoparticles tend to be more active and make stronger bonds with the rubbing surface. This results in a better capability of nanoparticles to create tribo-films and reduce the wear between sliding surfaces.

4. Conclusion

In this work, the effect of copper oxide nanoparticles, produced via electric discharge method, on the tribological behavior of Ca^{2+} grease has been investigated. The coefficient of friction of the grease and antiwear properties of the CuO nanoparticles were examined via a horizontal pin on disc wear testing machine under.

1. All experiments showed a decrease in the coefficient of friction. However, those nanoparticles which were produced via the explosion of a 0.2 mm copper wire in the current density of 500 A had the most effect on the decrease in the friction; thus, making them the best candidate for CuO nano-lubricants and enhancing wear resistance.

2. Anti-friction and anti-wear behavior of the nanoparticles is due the fact that the soft CuO nano powders are precipitated on the worn surface and cause the friction between sliding surfaces to decrease.
3. CuO nanoparticles have been synthesized via the process of electric arc discharge in the distilled water and with no impurities. This can be observed regarding the results of X-ray diffraction.
4. By increasing the ampere from 100 to 500, the mean particle size diminishes from 54.40 to 23.15 nm. Better tribological performances in terms of friction and wear are related to those nanoparticles which were synthesized in higher current densities and lower wire diameters.
5. Because of quick and uniform cooling from a high temperature resulted from electric discharge process, the particles are nanometer-sized and spherical in shape.
6. According to X-ray diffraction results, as the wire diameter increases, the ratio of the oxide phase to the copper itself decreases.

R E F E R E N C E S

[1] Henrich VE, Cox PA. The surface science of metal oxides. Cambridge university press, 1996.
[2] Kung HH. Transition metal oxides: Surface chemistry and catalysis. Elsevier, 1989.
[3] Ahmadi R, Razaghian A, Eivazi Z, et al. Synthesis of cu-cuo and cu-cu2o nanoparticles via electro-explosion of wire method. Int J Nanosci, 2018, 14: 93-99.
[4] Noguera C. Physics and chemistry at oxide surfaces. Cambridge University Press, 1996.
[5] Jan T, Iqbal J, Ismail M, et al. Synthesis, physical properties and antibacterial activity of metal oxides nanostructures. Mater Sci Semicond Process, 2014, 21: 154-160.
[6] Harrison WA. Electronic structure and the properties of solids: The physics of the chemical bond. Courier Corporation, 2012.
[7] Wells AF. Structural inorganic chemistry. Oxford university press, 2012.
[8] Tu Z, Hu E, Wang B, et al. Tribological behaviors of ni-modified citric acid carbon quantum dot particles as a green additive in polyethylene glycol. Friction, 2020, 8: 182-197.
[9] Liu L, Zhou M, Jin L, et al. Recent advances in friction and lubrication of graphene and other 2d materials: Mechanisms and applications. Friction, 2019, 7: 199-216.
[10] Jia X, Huang J, Li Y, et al. Monodisperse cu nanoparticles @ mos2 nanosheets as a lubricant additive for improved tribological properties. Applied Surface Science, 2019, 494: 430-439.
[11] Song W, Yan J, Ji H. Fabrication of gns/mos2 composite with different morphology and its tribological performance as a lubricant additive. Applied Surface Science, 2019, 469: 226-235.
[12] Deepika. Nanotechnology implications for high performance lubricants. SN Applied Sciences, 2020, 2: 1128.
[13] Zhao J, Huang Y, He Y, et al. Nanolubricant additives: A review. Friction, 2021, 9: 891-917.
[14] Uflyand IE, Zhinzhilo VA, Burlakova VE. Metal-containing nanomaterials as lubricant additives: State-of-the-art and future development. Friction, 2019, 7: 93-116.

[15] Lee C-G, Hwang Y-J, Choi Y-M, et al. A study on the tribological characteristics of graphite nano lubricants. INT J PR ENG MAN, 2009, 10: 85-90.

[16] Wang L, Gong P, Li W, et al. Mono-dispersed ag/graphene nanocomposite as lubricant additive to reduce friction and wear. Tribology International, 2020, 146: 106228.

[17] Chen G, Zhao J, Chen K, et al. Ultrastable lubricating properties of robust self-repairing tribofilms enabled by in situ-assembled polydopamine nanoparticles. Langmuir, 2020, 36: 852-861.

[18] Pena-Paras L, Taha-Tijerina J, Garza L, et al. Effect of cuo and al2o3 nanoparticle additives on the tribological behavior of fully formulated oils. Wear, 2015, 332: 1256-1261.

[19] Battez AH, González R, Viesca J, et al. Cuo, zro2 and zno nanoparticles as antiwear additive in oil lubricants. Wear, 2008, 265: 422-428.

[20] Gupta H, Rai SK, Satya Krishna N, et al. The effect of copper oxide nanoparticle additives on the rheological and tribological properties of engine oil. Journal of Dispersion Science and Technology, 2021, 42: 622-632.

[21] Petcharoen K, Sirivat A. Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. MAT SCI ENG B-ADV, 2012, 177: 421-427.

[22] Alwan RM, Kadhim QA, Sahan KM, et al. Synthesis of zinc oxide nanoparticles via sol–gel route and their characterization. J NANOSCI NANOTECHNO, 2015, 5: 1-6.

[23] Yatsu S, Takahashi H, Sasaki H, et al. Fabrication of nanoparticles by electric discharge plasma in liquid. ARCH METALL MATER, 2013, 58: 425-429.

[24] Bao Y, Sun J, Kong L. Tribological properties and lubricating mechanism of SiO2 nanoparticles in water-based fluid. In: Proceedings of the IOP Conference Series: Materials Science and Engineering, 2017. IOP Publishing:

[25] He Q, Li A, Wang Z, et al. Tribological behavior of zno-Si3N4 nanoparticles-based lubricating grease. J Exp Nanosci, 2018, 13: 231-244.

[26] He Q, Li A, Guo Y, et al. Effect of nanometer silicon dioxide on the frictional behavior of lubricating grease. NANOMATER NANOTECHNO, 2017, 7: 1847980417725933.

[27] Chang H, Lan C-W, Chen C-H, et al. Anti-wear and friction properties of nanoparticles as additives in the lithium grease. INT J PR ENG MAN, 2014, 15: 2059-2063.

[28] Laad M, Jatti VKS. Titanium oxide nanoparticles as additives in engine oil. JKSUES, 2018, 30: 116-122.

[29] Biswas S. Some mechanisms of tribofilm formation in metal/metal and ceramic/metal sliding interactions. Wear, 2000, 245: 178-189.

[30] Hansen J, Björling M, Minami I, et al. Performance and mechanisms of silicate tribofilm in heavily loaded rolling/sliding non-conformal contacts. Tribol Int, 2018, 123: 130-141.

[31] Hsu SM, Gates RS. Boundary lubricating films: Formation and lubrication mechanism. Tribol Int, 2005, 38: 305-312.