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ORIGINAL ARTICLE

The investigation of different particle size magnesium-doped zinc oxide ($Zn_{0.92}Mg_{0.08}O$) nanoparticles on the lubrication behavior of paraffin oil

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Abstract Magnesium-doped zinc oxide ($Zn_{0.92}Mg_{0.08}O$) (ZMO) nanoparticles of 23 nm particle size have been synthesized by auto-combustion method. The variation in particle size of these nanoparticles has been performed by their further calcination at 800 and 1000 °C for 2 h and the corresponding calcined particles are designated as ZMO-1 and ZMO-2, respectively. The nanoparticles have been characterized by powder-XRD, scanning electron microscopy (SEM), energy dispersive X-ray and transmission electron microscope. The effect of particle size on the antiwear lubrication behavior of paraffin base oil has been investigated on four-ball lubricant tester. The tribological tests of these nanoparticles as antiwear additives have been studied at an optimized concentration (0.5 %w/v) by varying load for 30 min test duration and by varying the test durations at 392 N load. Various tribological parameters such as mean wear scar diameter, friction coefficient (μ), mean wear volume, running-in and steady-state wear rates show that these nanoparticles act as efficient antiwear additives and possess high load-carrying ability. From these tribological tests it has been observed that the lubrication behavior of studied nanoparticles is strongly size-dependent. The best tribological behavior is shown by nanoparticles of the smallest size, ZMO. Being sulfur, halogen and phosphorous free, ZMO nanoparticles have potential to be used as low SAPS lubricant additives. The SEM and atomic force microscopy analysis of the worn surfaces lubricated with ZMO nanoparticles at 392 N applied load for 60 min test duration show drastic decrease in surface roughness. The values of surface roughness of different additives are in good agreement with their observed tribological behavior.

Keywords Four-ball tester · Antiwear lubricant additives · $Zn_{0.92}Mg_{0.08}O$ nanoparticles · Material characterization · Surface analysis: AFM, SEM

Introduction

Lubricants play an important role in reducing friction and wear and thus increasing the life of contact interfaces. According to literature survey, a lot of organic compounds have been used as antiwear and extreme pressure lubrication additives. These additive molecules basically contain active elements such as phosphorous, sulfur, halogens, nitrogen and oxygen as well as polar groups for strong adsorption (He et al. 2002). Additives with these active elements get adsorbed on the contacting metal surface and form a tribochemical film under lubricating conditions. This enhances machine efficiency by reducing wear and friction. Besides this, tribological performance of zinc, molybdenum and lanthanum complexes of dithiohydrazodicarbonamides, dialkyldithiophosphates, dithiocarbamates, tricresylphosphates, etc., has also been investigated (Spikes 2004). Modern engine oils contain a large number of additives, but the most influential compounds on the tribological performance of the lubricants are antiwear zinc dialkyldithiophosphates (ZDDPs). ZDDPs have been used in engine oils as multifunctional additives for more than 70 years and are probably the most successful antiwear additives ever discovered. However, the excessive use of

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ZDDPs has been limited due to their adverse impact on environment caused by poisoning of the catalytic converters since these contain high amount of sulfated ash, phosphrous and sulfur (SAPS) (Isaksson et al. 2002). Besides this, ZDDPs are also health hazardous and responsible for eye irritation, allergic contact dermatitis and mutagenicity (McFall 2004). Several norms are available which strictly limit the SAPS (sulfated ash, phosphorous and sulfur) contents of additives. According to ILSAC GF-5, the acceptable limits of phosphorous and sulfur are 0.08 and 0.5 %, respectively (Kalyani et al. 2014). Therefore, a lot of efforts have been made to develop new antiwear additives which have low SAPS contents.

In order to meet the aforesaid objectives, several substituted Schiff bases and thiosemicarbazones as antiwear additives were explored by our research group. Their synergistic action with organoborates show better tribological properties as compared to ZDDP. Besides this, β-lactam antibiotics and stearic acid-modified zinc-doped calcium copper titanate nanoparticles have been recently reported as efficient low/zero SAPS antiwear additives in paraffin base oil (Kalyani et al. 2014, Jaiswal et al. 2014a, b). With continuous efforts in the field of development of nanoscience and nanotechnology, nanoparticles have attracted much attention due to their unique properties and applications in electronics, photonics, magnetism, tribology (Astruc et al. 2010), nanorefrigerants (Saidur et al. 2011 and Bi et al. 2008), conductor (Robert 2007), semiconductor (Katz et al. 2004) and sensors (Luo et al. 2006). The use of nanoparticles in the field of medicines (Sanvicens et al. 2008) and cosmetics (Guix et al. 2008) is well acknowledged. In tribology, several types of inorganic nanoparticles such as fullerene-like (IF) supramolecules of metal dichalcogenides MX_2 (M = Mo, W, etc.; X = S, Se) CaO, CuO, ZnO, TiO_2, CeO_2, lanthanum borate, etc. (Battez et al. 2008 and Rapoport et al. 2003), have been used. The blends of these particles with lubricating oils improve the extreme pressure, antiwear and friction reducing properties of the lubricating base oil. Magnesium metal, in general, has been used as metal-self-repairing additives (Wang et al. 2010). Magnesium palmitate and magnesium stearate-based detergents show oxidation stability (Mohammed et al. 2013). On the other hand, magnesium borate nanoparticles have been used as antiwear and friction modifying additives in lubricating oils (Hu et al. 2002). This is a general observation that the size of the nanoparticles reduces upon doping. Reduction in size of nanoparticles is known to increase lubrication properties of a lubricant. Therefore, ZnO nanoparticles have been selected as a parent material and magnesium as a dopant in the present communication.

The objective of the current study is, therefore, to synthesize magnesium-doped zinc oxide nanoparticles ($Zn_{0.92}Mg_{0.08}O$; ZMO) of different sizes and explore the effect of particle size on the tribological behavior of paraffin base oil under boundary conditions. To accomplish this objective, various techniques have been employed to study the particle size, shape (morphology), chemical composition, tribological properties (friction and wear) and surface morphology of worn track (SEM and AFM) during present investigation.

Experimental section

Synthesis and characterization

Aqueous solutions of metal nitrates were mixed with an aqueous solution of citric acid maintaining at constant citrate to nitrate ratio of 0.3. The mixed solution was evaporated with continuous stirring at 200 ± 5 °C until it gelled and finally burnt. Within a few seconds, the combustion reaction completed giving blackish porous ash filling the container. The ash was calcined at 600 °C in air for 4 h. Thus prepared magnesium-doped zinc oxide nanoparticles ($Zn_{0.92}Mg_{0.08}O$), named as Mg-doped-ZnO (ZMO), were further calcined at 800 and 1000 °C and designated as ZMO-1 and ZMO-2, respectively. The phase, composition and morphology of synthesized ZMO nanoparticles have been characterized by powder-XRD, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and transmission electron microscope (TEM).

X-ray diffraction data were indexed on the basis of a cubic unit cell similar to undoped ZnO (JCPDS 36-1451) (Fig. 1), which confirms the formation of single phase. The average crystallite size of the ZMO nanoparticles was estimated as 23, 34 and 39 nm prepared at 600, 800 and 1000 °C, respectively, using the Debye–Scherrer formula:

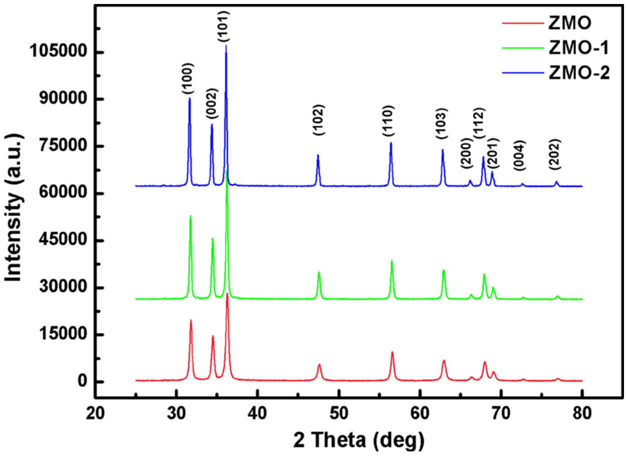


Fig. 1 X-ray diffraction pattern of different sized ZMO nanoparticles

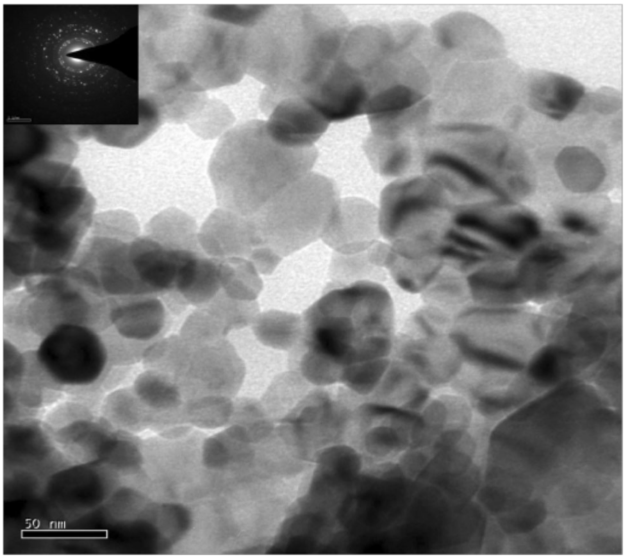
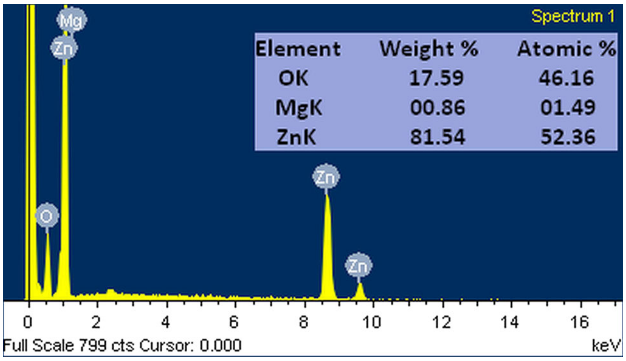


Fig. 2 TEM-image with SAED pattern of ZMO nanoparticles



Element	Weight %	Atomic %
OK	17.59	46.16
MgK	00.86	01.49
ZnK	81.54	52.36

Fig. 3 Energy dispersive X-ray spectrum showing constituents and chemical composition of ZMO nanoparticles

$$D = k\lambda/\beta\cos\theta,$$

where λ is the wavelength of the X-ray, k is a constant taken as 0.89, θ is the diffraction angle and β is the full width at half maxima (FWHM). The crystallite size was derived from the XRD data. It is clearly observed from the XRD data that the average crystalline size increased with increasing temperature. The increase in crystallite size with increase in temperature is mainly due to over grown grains resulting from the destruction of the grain boundaries at higher temperature.

A TEM was used to investigate the size of ZMO nanoparticles. The TEM observation reveals that the ZMO nanoparticles possess almost a spherical shape (Fig. 2). Further, it can be seen from TEM-image that the average particle size of ZMO nanoparticles is 22 nm which supports the XRD data.

The EDX spectrum of the ZMO nanoparticles (Fig. 3), comprises Zn, O and Mg. Elemental analysis reveals the atomic percentages of Zn, O and Mg as 52.4, 46.2 and 1.5 %, respectively.

Tribological characterization

All the tribological testing was performed according to ASTM D4172 standard using neutral paraffin oil on four-ball lubricant testing machine. Paraffin oil blends of ZMO nanoparticles having concentration 0.00, 0.25, 0.5 and 1.0 % (w/v) were made by stirring for 2 h on magnetic stirrer. The blends were further sonicated for 1 h. The entire tests were carried out at an optimized concentration, i.e., 0.5 % w/v.

Results and discussion

The lubrication properties of these different sized ZMO nanoparticles in paraffin oil have been evaluated on four-ball tester machine. Figure 4 demonstrates the optimization result for the ZMO nanoparticles with different additive concentrations at 392 N load; 1200 rpm and for 60 min test duration. In absence of additives in the base oil, the mean wear scar diameter (MWD) was found to be very large, but in presence of ZMO nanoparticles it was fairly reduced at each concentration. As the concentration of ZMO nanoparticles in the base oil increases, the reduction in the

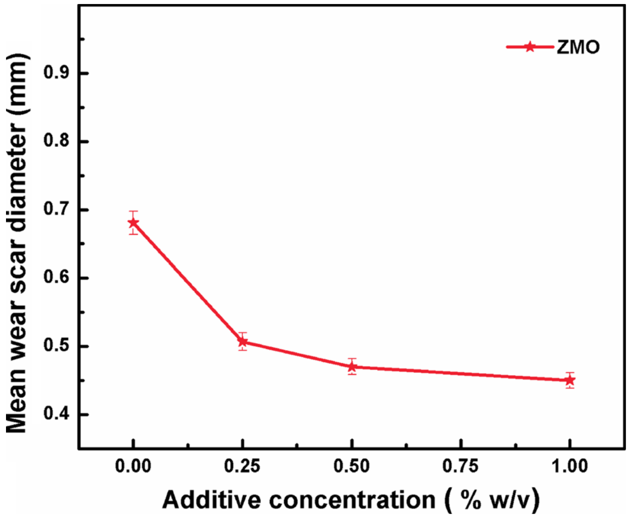


Fig. 4 Variation of MWD for the paraffin oil as a function of increasing ZMO concentrations at 392 N applied load for 60 min duration

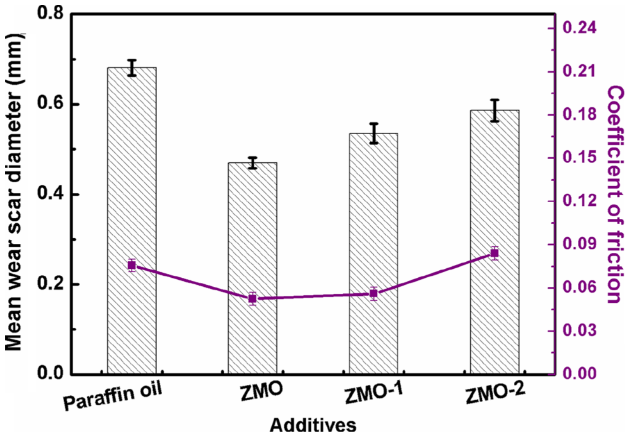


Fig. 5 Comparison of MWD and COF of steel balls lubricated with 0.5 w/v % of ZMOs in paraffin oil at 392 N; rotating speed, 1200 rpm; temperature, 75 °C; test duration, 1 h

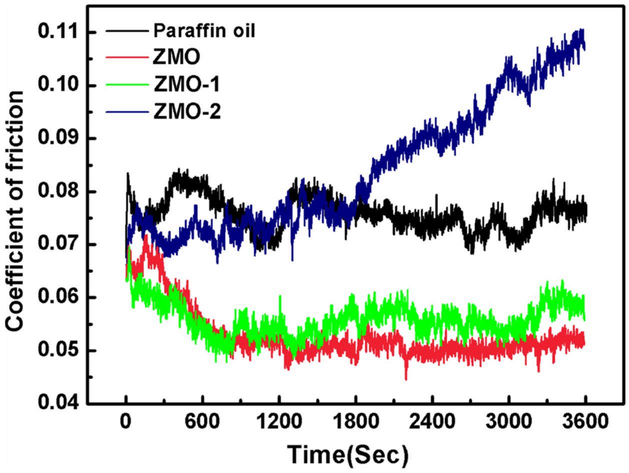


Fig. 6 Variation of COF with sliding time in presence and absence of ZMO additives (0.5 w/v %) in paraffin oil at 392 N; rotating speed, 1200 rpm; temperature, 75 °C; test duration, 1 h

value of MWD also increases and it was found to be lowest at 1.0 % w/v. However, there is marginal increase in reduction of MWD at 1.0 % than that of 0.5 % w/v. Therefore, 0.5 % w/v was taken as optimized concentration and all the tribological tests were performed at 0.5 % w/v concentration of ZMO nanoparticles.

Figure 5 shows the changes in MWD and average coefficient of friction (COF) in presence and absence of ZMO nanoparticles in paraffin oil. The value of MWD is much large in case of paraffin oil alone, but in presence of different ZMO nanoparticles it fairly reduces. In general, on addition of ZMO nanoparticles to the paraffin oil both the friction coefficient and the MWD were significantly reduced. From the Fig. 5, it can be clearly seen that the value of MWD and COF significantly decreases for ZMO (23 nm), ZMO-1 (34 nm) and ZMO-2 (39 nm), but in case of ZMO-2 small increase in COF is observed. The ZMO-2 having 39 nm particle size shows the increasing behavior in COF values with time (Fig. 6). The smallest MWD and lowest COF were found in case of surface lubricated with blend of ZMO nanoparticles (23 nm) in base oil. This reveals that ZMO nanoparticles, used as additives, played a positive role in remarkably improving the tribological properties of paraffin oil.

Figure 6 shows the variation of COF with sliding time at 392 N applied load. The blends of ZMO nanoparticles in paraffin oil show lower COF values than the paraffin oil except ZMO-2. In general, COF initially increases with time in all cases. After some time duration, the value of COF reduces and it remains stabilized in case of ZMO and ZMO-1. However, the unusual trend of ZMO-2 may be due to its larger particles size and/or agglomeration. It was noted that ZMO-2 dispersed in paraffin oil tends to settle down after couple of hours, which reveals its poor dispersion stability. Under tribological conditions, the high pressure and temperature probably facilitate the agglomeration of ZMO-2 nanoparticles, resulting in high COF values. This phenomenon is found to increase with the contact time.

The antiwear mechanism of the investigated additives may follow three different processes: the nanoparticles may melt, get welded on the shearing surfaces and react with sliding surfaces to form tribofilm, or these may act as nanobearings or get tribosintered on the surfaces (Battez et al. 2010). The ZMO nanoparticles follow antiwear mechanism through nanobearings and/or tribosinterisation where nanoparticles get deposited in the valleys form more compact tribofilm. Therefore, the additives with smaller size as expected show excellent tribological behavior (Jaiswal et al. 2014a).

$$\mathrm{ZMO} \; > \; \mathrm{ZMO}-1 > \; \mathrm{ZMO}-2 > \; \text{Paraffin oil}$$

For determining wear rate, mean wear volume (MWV) was calculated using Archard's equation based on elastic recovery (Sethuramiah 2003). The running-in and steady-state wear rates have been determined using linear

Table 1 Wear rates of paraffin oil in absence and presence of ZMO nanoparticles as antiwear additives at 392 N applied load for 90 min test duration

S. no.	Additives	Wear rate (10^{-4} × mm^3/h)	
		Running-in	Steady-state
1.	ZMO	39.60	06.88
2.	ZMO-1	40.80	15.56
3.	ZMO-2	54.58	21.16
4.	Paraffin oil	69.99	38.88

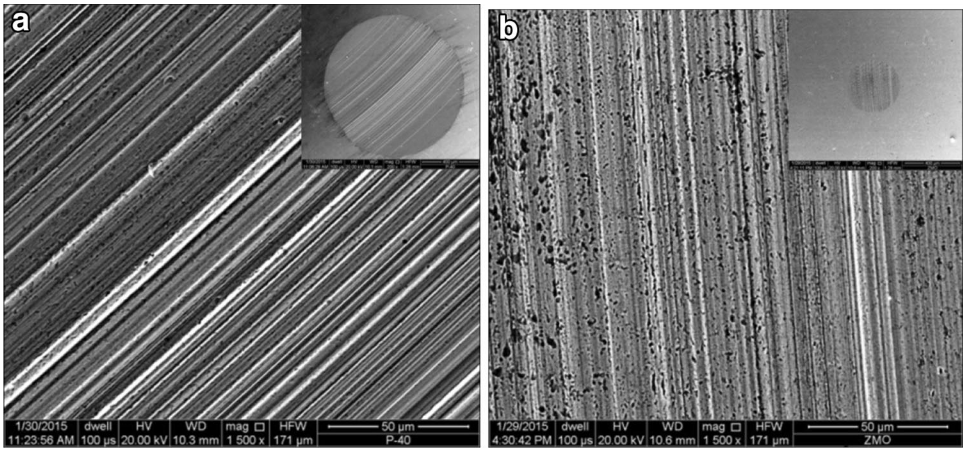


Fig. 7 SEM micrographs of the worn steel surface lubricated with **a** paraffin oil and (**b**) ZMO nanoparticles (0.5 % w/v) in paraffin oil for 60 min test duration at 392 N applied load

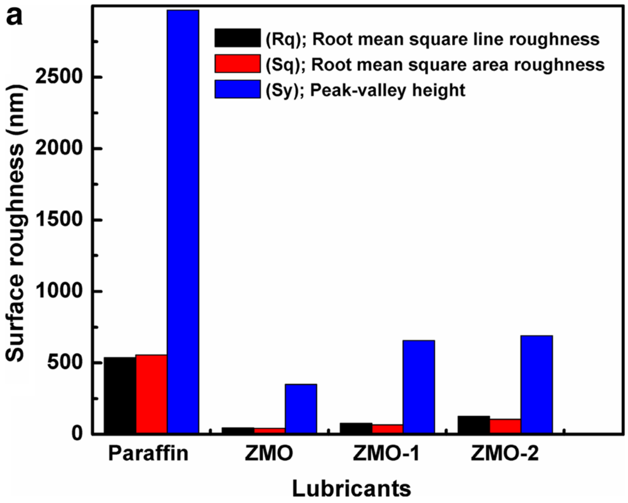


Fig. 8 Surface roughness parameters obtained from digital processing software of Nanosurf basic Scan 2 for different additives at 392 N load for 60 min test duration. *2D* and *3D* AFM images of the worn steel surface with and without ZMO nanoparticles (0.5 % w/v) in paraffin oil for 60 min test duration at 392 N applied load: **a** paraffin oil, **b** ZMO, **c** ZMO-1 and **d** ZMO-2

regression model and their values are mentioned in Table 1. The lowest running-in and steady-state wear rate has been found in case of ZMO followed by ZMO-1 and ZMO-2.

Surface characterization

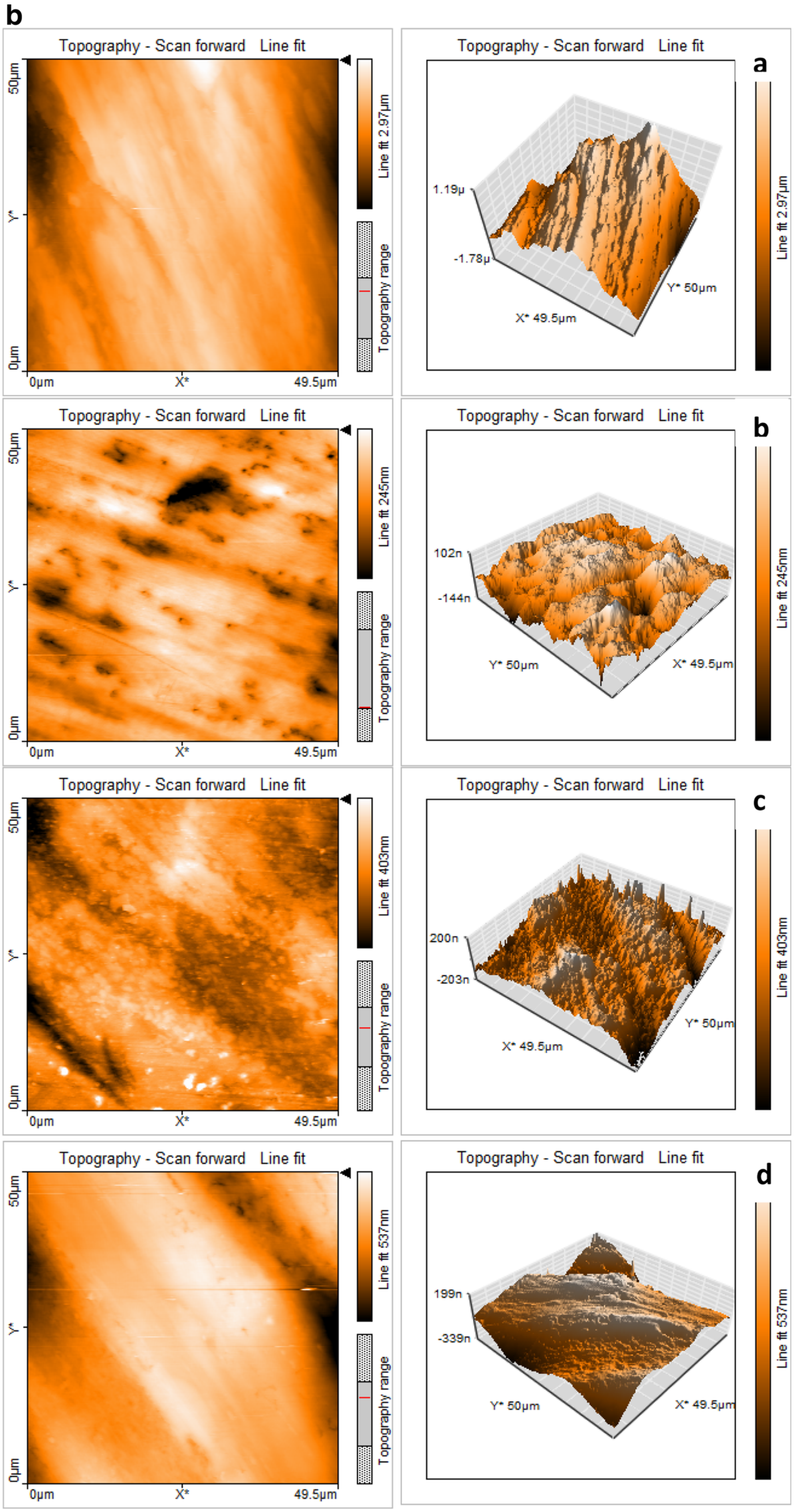
The topography of the wear track has been studied by SEM and atomic force microscopy (AFM). Here for comparison of SEM images, ZMO nanoparticle is chosen which is the best among all nanoparticles and paraffin oil. Figure 7 shows the SEM images of worn surface of steel balls under the lubrication of paraffin oil alone and ZMO nanoparticles at a load of 392 N for 60 min time duration. The MWD of steel ball lubricated with ZMO nanoparticles is notably smaller than the steel ball lubricated with base oil alone. The worn area lubricated with paraffin oil shows very deep scratches and groves illustrating metal-to-metal contact because of poor lubrication. The presence of ZMO in paraffin oil, improved the antiwear property by reducing MWD compared to the surface lubricated with paraffin. The presence of shallow scratches and grooves on worn area indicates the role of ZMO nanoparticles as antiwear additive. The extent of surface smoothening in case of surface lubricated with ZMO nanoparticles is found to be much increased which filled the surface irregularities. Therefore, the new additives possess significant antiwear properties.

On comparing the plots in Fig. 8, it has been found that the area as well as line roughness are extremely large in case of paraffin oil, whereas these have magnificently reduced in the presence ZMO additives. A large difference in the average peak–valley height (2.97 μm) is observed for the surface lubricated with paraffin oil alone, whereas very small surface undulations are found in case of ZMOs (350–690 nm) (Fig. 8). Beside this, the value of area roughness as well as line roughness has been found to be maximum for the base oil; however, these values are much lower in presence of ZMO nanoparticles. Thus, the AFM images also support the observed results of tribological tests.

Conclusion

Magnesium-doped zinc oxide ($Zn_{0.92}Mg_{0.08}O$; ZMO) nanoparticles were synthesized by auto-combustion method and variation in particle size was made by increasing temperature. Formation of single phase was confirmed from the powder-XRD data of the different sized ZMO nanoparticles. The average crystalline size of these nanoparticles was found to be 23, 35 and 39 nm for ZMO,

Fig. 8 continued



ZMO-1 and ZMO-2, respectively. These blends effectively enhance the antiwear properties in base oil in order of decreasing particles size. ZMO nanoparticles as additives in paraffin oil exhibited excellent friction-reduction and antiwear behavior. The running-in and steady-state wear rates of ZMO nanoparticles have been found to be much lower than paraffin base oil. On the basis of observed tribological parameters, SEM and AFM results, it was inferred that addition of ZMO nanoparticles significantly improved tribological characteristics of the paraffin oil by acting as nanobearing and/or tribosintering. Surface analysis by SEM and AFM also supports the observed tribological behavior of ZMO nanoparticles.

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