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RESEARCH

Effect of Nano and Micro Friction Modifier Based Lubricants on Wear behavior between Steel-Steel Contacts

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A B S T R A C T

The wear and surface morphology between steel (EN24, 22-24Rc)-steel (EN 31, 58-60Rc) contacts was investigated in presence of friction modifiers based (micro-graphite/nano particles- multi wall carbon nano tubes and zinc oxide) mineral oil. Though a decrease in wear was observed (upto a certain concentration of nano friction modifiers) but a weight-gain in pins after the tests was observed for all tests with ZnO nanoparticles while weight loss was observed in tests with multi wall carbon nano tubes and graphite particles based oil samples. Surface characterization of the worn surfaces showed more surface deteriorations in case of mineral oil (no friction modifiers) and mineral oil with graphite as compared with nano particles/tubes based lubricants. The occurrence of a tribo film due to the deposition of nano particle and the formation of a modified layer on the pin surfaces are likely to be responsible for the reduction of coefficient of friction and better surface roughness. Apart from investigating the wear behaviour between two steel surfaces under micro and nano particles based lubricant and analysing the surfaces of the samples a part of the work was also focussed on the weight gain after tribo tests with ZnO nano particle additions.

1. INTRODUCTION

Lubrication is one of the major concerns in all process industries and mineral oils of various viscosity grades are used for gear boxes. With the advancement in technologies and awareness of environmental pollutions many friction modifiers such as sulphur and phosphorous have been discontinued. Nowadays, researchers are trying to reduce the content of friction modifiers in both mineral and synthetic oils to achieve “minimum quantity additivation”. In order to achieve “minimum quantity additivation” one of the main parameters of friction modifiers is their size. Nano sized friction modifiers have smaller diameter and higher aspect ratio as compared to a micro sized particles and so the nano friction modifiers can penetrate into intrinsic parts very easily. This is likely to enhance the anti-wear and load carrying capacity of the lubricant. Researchers have proposed various mechanisms which are responsible for improving the tribological behaviour of nanolubricants viz. ball bearing effect [1-4], protective film [5-8], mending and polishing effect [9,10]. Various nano particles such as LaF3 [11], carbon nano onions [12], copper oxide [13,14] also showed good effects.

Although some work [15-17] has been reported using nanolubricants but no systematic representation of the gain in weight of the samples after the tribo test has been reported. The present work aimed at investigating the wear between two steel surfaces under micro and nano particles based lubricant and analysing the surfaces of the samples and also focussed on the weight gain after tribo tests with ZnO nano particle additions.

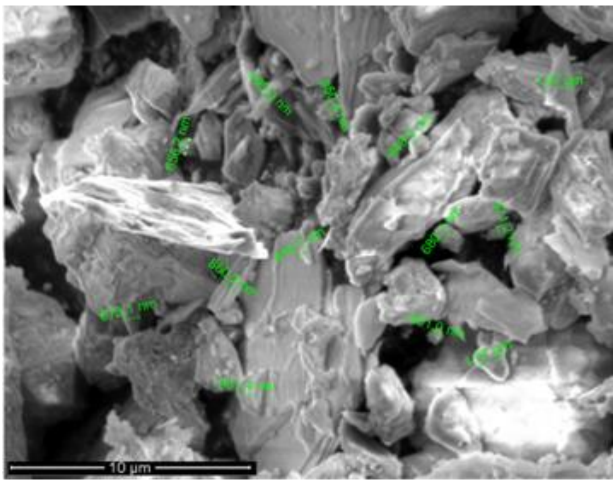
2. EXPERIMENTAL DETAILS

2.1 Base Oil

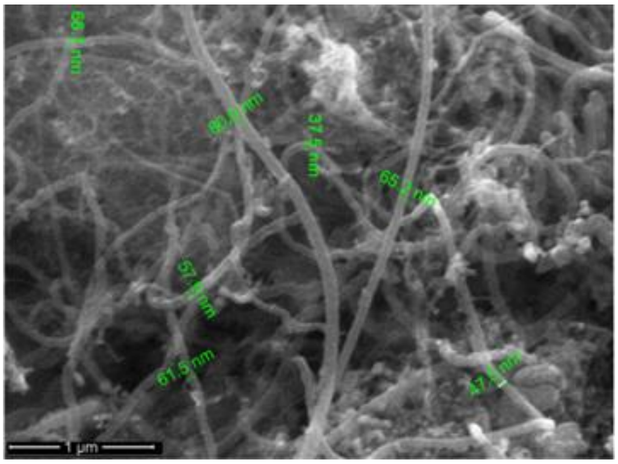
Commercially available industrial gear mineral oil (MCO) of viscosity 460cSt was procured locally. Mineral oil of viscosity 460cSt was chosen as it is commonly used in gear boxes of process plants.

2.2 Friction modifiers:

Commercially available graphite micro powders by weight percentage (0.2%wt.) , multi wall carbon nano tube (MWCNT) and zinc oxide (ZnO)nano particles were added to mineral oil in weight percentage basis (0.05%wt., 0.1%wt., 0.15%wt., 0.2%wt.) to formulate the lubricant which was used during tribo testing.



a)



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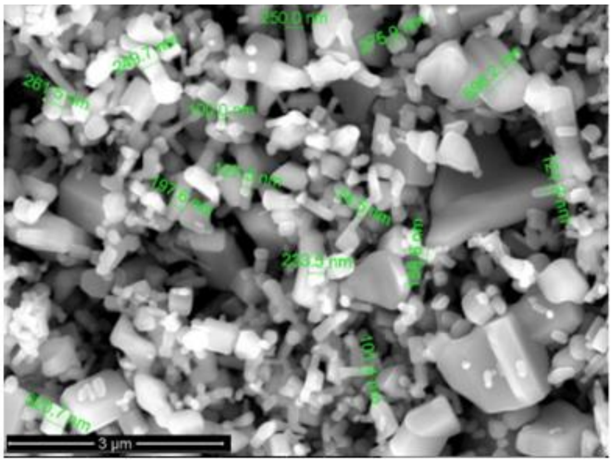


c)

Fig. 1. SEM images of (a) Graphite particles, (b) Multi wall carbon nano tubes, (c) Zinc oxide nanoparticle.

Figure 1 shows the scanning electron microscope (SEM) images of graphite micro particles, MWCNTs, ZnO nanoparticles. In order to find the optimal concentration and hence, the weight percentages were selected from a lower value of 0.05%wt. Since, the maximum concentration of friction modifiers chosen was 0.2%wt. so the same was considered in case of graphite so as to know the reduction capacity at the maximum %wt. concentration.

2.3 Preparation of nano friction modifiers based lubricants

Graphite micro-particles, MWCNT and ZnO nano-particles were added to 460cSt industrial gear mineral oil. For each %wt. of friction modifiers, 1000 ml mineral oil was used. Sonication was done for 45-50 minutes using a probe sonicator and was followed by homogeneous stirring for 30 minutes using a magnetic stirrer. It was taken care that the particles do not settle down during the experiments and hence, the dispersion was stirred intermittently every 10-15 minutes.

2.4 Antiwear test

The anti-wear tests were carried out using a pin-on-disk tribometer (Make: Ducom, Model TR20) according to ASTM G-99.The pin was EN24 (hardness 24Rc) as it is used in gear manufacturing. The disc is of EN 31 (hardness 58-60 Rc). The pins were of 10 mm in diameter and 25 mm in length. All pins were cleaned with acetone and dried before and after tests. Oil was supplied drop by drop at the interface in order to maintain thin film lubrication/boundary lubrication [18]. Each test was performed three times and the average value of the test has been shown in this work. Each pin was polished using emery papers of various grades (220, 600, 800, 1000, 1200). The roughness of each pin for the tribo tests was maintained in between (0.80-0.89 microns). The roughnesses of the pins at optimum concentration of friction modifiers were recorded before and after tribo test using a surface roughness tester (Make: Surfcom). The specific wear rate (ΔW) (m^2/N) was calculated using Archard equation as:

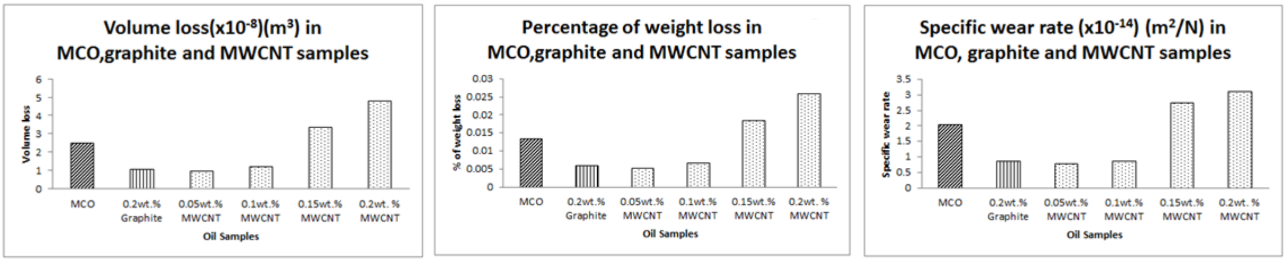
$$\Delta W = \frac{\Delta V}{L.d} \tag{1}$$

where ΔV (m^3) is volume loss, L is load (N) and d is sliding distance (m).

2.5 Analysis of wear property

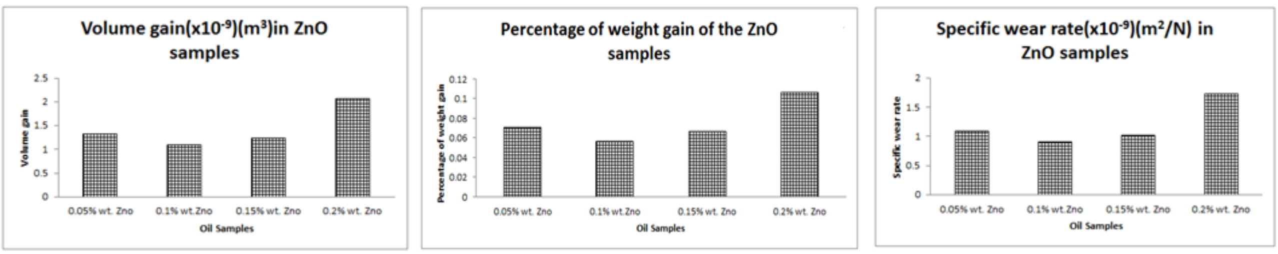
From Fig. 2, it was observed that wear was less in additive based mineral oil samples as compared with MCO up to a certain concentration (0.05%wt. MWCNT and 0.1%wt. ZnO). Both graphite and MWCNT based samples showed lesser specific wear rate than MCO (up to a certain concentration of the particles) but the quantity of graphite (0.2%wt.) used as an additive was higher than the next best result (0.05%wt. MWCNT) of nanotube.

As observed from Fig. 3, an increase in weight of the pins after the tests was observed in ZnO samples which have been discussed in later stage. As observed from Fig. 4, the coefficients of friction (COF) in case of nanoparticles based lubricants were lesser than MCO and also with graphite based MCO but there exists an optimum concentration of nanoparticles viz. 0.05%wt. in case of MWCNT and 0.1%wt. in case of ZnO where COF is least and the COF increased as the concentration of the particles increased. Since, surface roughness is an important parameter in evaluating the film stability, hence, the surface roughness of the pins which were tested in MCO, graphite and optimal concentrations of nano friction modifiers (0.05%wt. MWCNT and 0.1%wt. ZnO) were measured as shown in Table 1. The surface roughness of the pins after the tests was compared with the roughness of the virgin pins.



(a) (b) (c)

Fig. 2. (a) Volume loss, (b) weight loss, (c) Specififc wear rate in MCO, graphite and MWCNT sample.



(a) (b) (c)

Fig. 3. (a) Volume gain, (b) Percentage of weight gain, (c) Specific wear rate in pins tested with ZnO based MCO.

Table 1. Surface roughness of pin.

Oil Samples	Roughness of virgin before testing (μm)	Roughness of pins after testing (μm)	%Increase in roughness
Mineral oil	0.813	2.386	65.92
Mineral oil + 0.2%wt. graphite	0.801	1.435	44.18
Mineral oil + 0.05%wt. MWCNT	0.898	1.282	29.95
Mineral oil + 0.1%wt. ZnO	0.898	1.450	38.06

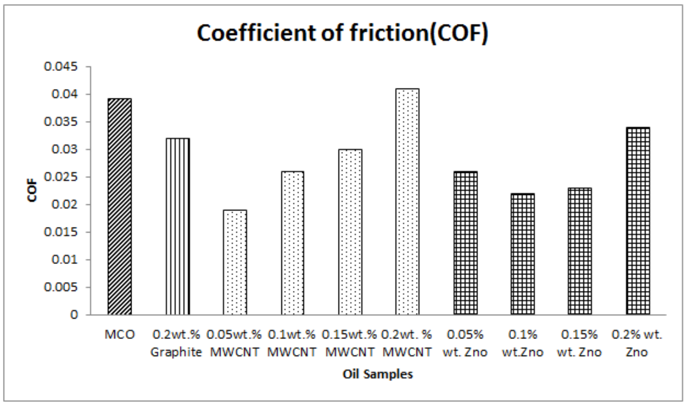
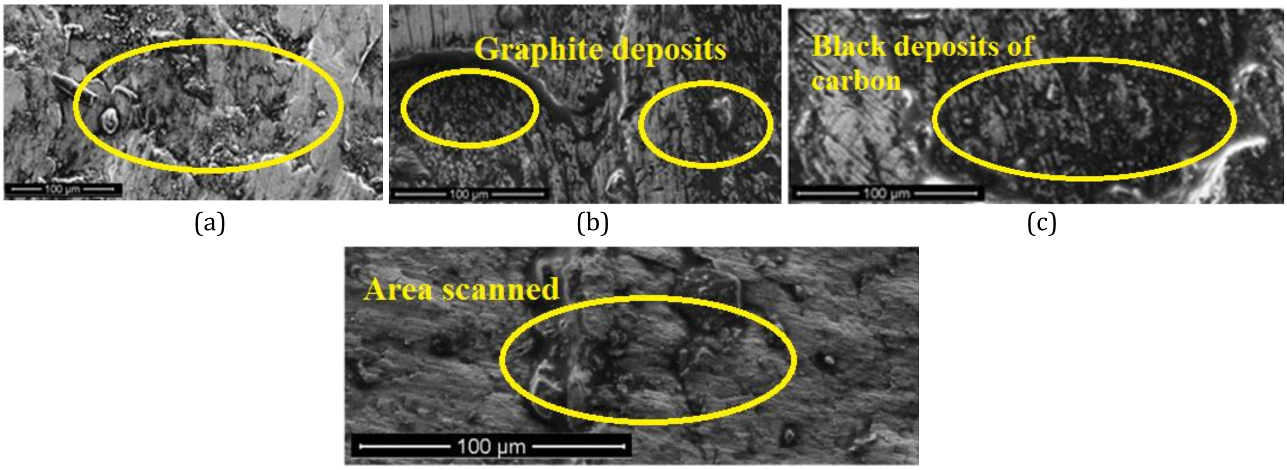


Fig. 4. Co-efficient of friction.

3. Surface morphologies and wear mechanisms

The surfaces of the pins were analysed using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The decrease in the coefficient of friction in case of nano particles/tubes based samples may be due to the fact that the nano particles/tubes behaved as third bodies and were responsible for the formation of protective layer which in turn reduced friction, but as the concentration of nanoparticles increased, an increase in co-efficient of friction was observed which was also more than MCO. Furthermore, the results showed that 0.2%wt. MWCNTs were having least anti wear properties and was much inferior than MCO. This may be due to the excessive absorbance of MWCNTs (physically and chemically) on the surface and thus, the further addition of the nanotubes led to an increase in coefficient of friction and wear rate [19]. As observed from Table 1, surface roughness increased in all the tests but was higher in case of MCO and MCO+0.2%wt. graphite sample. This may be due to the formation of better tribo film in case of nano particles based lubricants as compared to graphite based MCO and MCO and thus, prevented metal to metal friction. Furthermore, graphite being micro in size could not enter the intrinsic grooves and form a stable lubricant film as compared to MWCNTs. Though ZnO could not be detected in EDS, ZnO nano particles might have acted as third bodies on the surface and may have formed modified protective layers on the pin surfaces [24] and thus, prevented metal to metal contact, due to which roughness did not increase much as seen in Table 1. Furthermore, the presence of oxygen as detected by EDS (Fig. 6) also shows the possibility of formation of oxides which contributed to the reduction of coefficient of friction. As observed from Fig. 5, the pin surface in case of MCO was more deteriorated than the friction modifiers based samples. Among the friction modifiers based samples, the surfaces of MWCNTs (except 0.2%wt.) and graphite samples were better as compared to that of ZnO based samples. This shows that the carbonaceous friction modifiers performed better in maintaining a stable tribo film than zinc oxide nano particles within optimal concentration.

The pin surfaces (Fig. 5) were also characterized using EDS (Fig. 6) to identify the mechanisms of wear involved which resulted in enhancing the antiwear property of MCO. Figure 7(a) shows the SEM of EN24 pin under lubricated condition of MWCNT nanoparticles samples. It was observed that carbon nano tubes (dark patches) were deposited in the crevices and thus, acted as a protective layer. An increase in concentration of carbon atom and high peak values in the wear area as detected by EDS (Fig. 6) also indicated the formation of protective layer(presence of carbon) of MWCNT and graphite [22].



(d)

Fig. 5. SEM images of pin surfaces in (a) MCO, (b) MCO+0.2%wt. graphite, (c) MCO+0.05%wt. MWCNT (d)MCO +0.1%wt. ZnO.

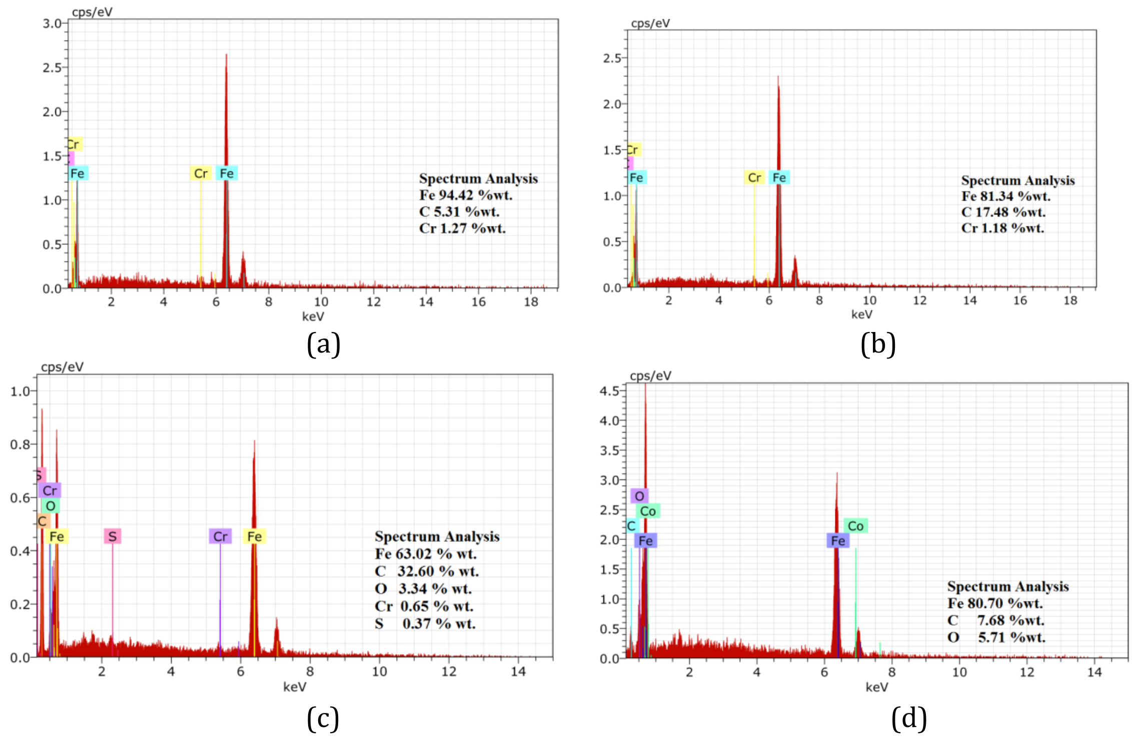
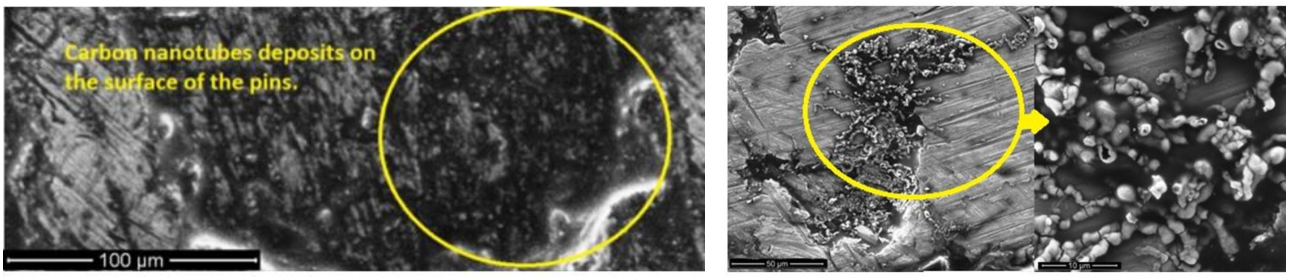
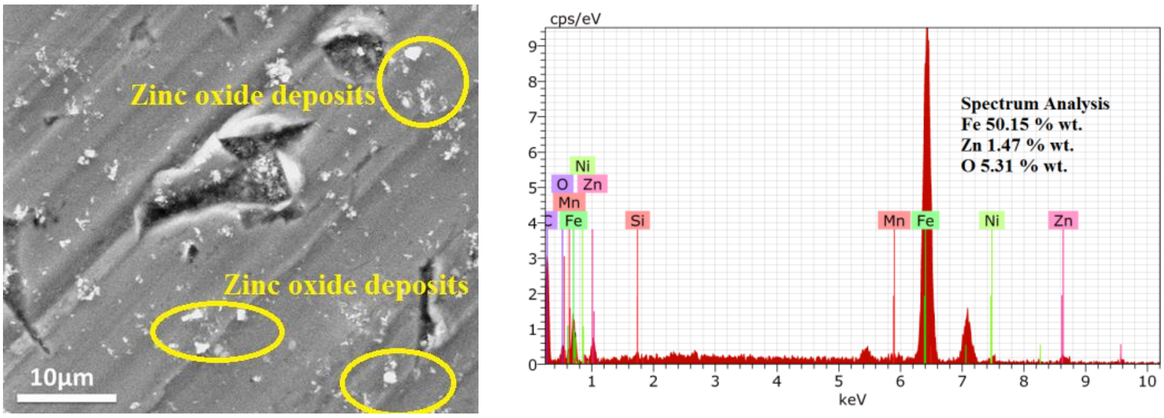


Fig. 6. EDS results of (a) MCO (b) MCO+0.2 %wt. Graphite (c) MCO+0.05%wt. MWCNT (d) MCO + 0.1%wt. ZnO.



(a) (b)

Fig. 7. (a) Protective layer formations by MWCNT (dark patches), (b) Adhered particles on the pins in case of ZnO based MCO.



(a) (b)

Fig. 8. (a) SEM image and (b) EDS spectrum of zinc oxide nano particles (1.0%wt.) based pin samples.

In case of ZnO based samples, no Zn nano particles were detected by EDS but still there was a decrease in COF and roughness in case of ZnO based samples (0.1% wt. being the optimal concentration). This behaviour predicted that ZnO particles passed through the contact area reducing the friction [24] and acted as a third body between the mating parts, thus prevented metal to metal frictional wear. It may be due to the lesser quantity of ZnO that EDS analysis was not able to detect ZnO on the worn surface. The wear scar was further assessed qualitatively using SEM. As observed from Fig. 7 (b) some particles were seen adhered on the surfaces of the pins which were tested with ZnO nanoparticles based MCO. This debris that adhered to the surface may have resulted in the weight gain of the pins after the test. Even though there is an increase in weight gain in ZnO based samples, the ZnO based lubricant tested samples have also shown a decrease in COF (Fig. 4). The decrease in the coefficient of friction in ZnO based samples may be due to the formation of the adhered layers or the formation of a mechanically modified mixed layer due to the presence of metallic oxide particles as friction modifiers [24] or might have acted as a solid lubricant [21,24] along with ZnO particles thus, reducing the COF and wear rate. Similar results of adhered wear particles in fretting wear at 24 ^{0}C were also reported by Pearson et al. [20]. Furthermore, it was also outlined by Godet [23], the importance of “third body approach” that when two contacting bodies are separated by debris, then the debris layer can act as a protective tribo film. Thus, in the present work these adhered particles might have acted as third body along with ZnO nano particles which resulted in the decrease in COF and wear rate.

Since, the EDS analysis could not detect ZnO (due to lesser concentrations) the tests were conducted with higher concentrations of zinc oxide nano particles (2%wt., 2.5%wt. and 3%wt.) to confirm the weight gain. In all the samples the weight gain was observed again similar to earlier tests. EDS analysis of the pin surfaces (Fig. 8) now detected zinc on the tested areas. Thus, it was confirmed that metallic protective films are formed at the areas of contact which led to an increase in weight in all the pins that were tested with ZnO based lubricant. The presence of zinc may have resulted in the formation of a mixed modified layer [24] which may have helped in avoiding metal to metal contact, thus reducing friction up to the optimal friction modifiers concentration. Thus, the formation of modified protective layers is most likely being the reason for the increase in weight of the pin samples and reduction of wear. But at higher concentrations of the metallic nano particles, the interaction of the lubricant/particle and the steel surface may have increased which led to higher oxidative wear, thus increasing the coefficient of friction and specific wear rate.

4. CONCLUSIONS

The following can be concluded from the present work:

1. Volume loss and specific wear rate were minimum in case of 0.05%wt. MWCNT. An increasing trend in both volume loss and specific wear rate were observed with the increase in concentration of nano friction modifiers.

2. An increase in weight gain in the pins (after tribo test) was observed in case of all ZnO nanoparticles based lubricant tested pins.
3. The pin surface in case of MCO indicated more deterioration than the friction modifiers based samples.
4. Formation of modified mixed layer is possible when metallic oxides friction modifiers are used.
5. Thus, it can be concluded that the friction modifiers exhibited mechanisms such as tribo films, modified layers and adhered particles (third body) which were responsible for reducing frictional wear.

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