Applied Nanoscience
https://doi.org/10.1007/s13204-020-01458-z

ORIGINAL ARTICLE

Friction-reduction and anti-wear properties of polyalphaolefin oil with Mo-DTC additive enhanced by nano-carbon materials

Dingshun She[1,2,3] · Peixuan Gong[1] · Yanyan Wang[1] · Jiajie Kang[1,2] · Lina Zhu[1,2] · Guozheng Ma[4] · Li Zhong[5] · Haipeng Huang[6] · Haidou Wang[1,4] · Wen Yue[1,2,3]

Received: 15 March 2020 / Accepted: 20 May 2020

Abstract

Polyalphaolefin (PAO) oil is one of the most commonly-used based oil to decrease the fuel energy consumption of mechanical systems, like vehicles. Nevertheless, it heavily relies on environmental toxic organic additives with sulfur, phosphorus, and/or chlorine. Accordingly, nano-carbon materials, such as nano-diamond (ND), onion-like-carbon (OLC) and graphene (Gr.), was adopted to develop a novel kind of environmentally-friendly PAO-based lubricants with low toxic additives. Synergetic effects between nano-carbon materials and MoDTC additives were investigated to enhance friction-reduction and anti-wear performances of PAO oil with molybdenum di-thiocarbamate (MoDTC) additive. Experimental results show that ND and OLC additives are effective in the enhancement of friction-reduction and anti-wear performances of self-mated AISI 52100 steels lubricated under poly-alpha-olefin (PAO) oil with Mo-DTC additive, due to the formation of tribo-film consist of MoSx, polishing, ball-bearing and reinforcement effects of nano-particles. Via the addition of ND or OLC additive with a content of 0.05 wt.%, the optimized dosage of MoDTC additive can be significantly decreased from 1 to 0.1 wt.%. Friction coefficient of self-mated AISI 52100 steels lubricated under PAO oil with 0.1 wt.% Mo-DTC and 0.05 wt.% ND additive is about 0.05, approximately equal to that lubricated under PAO oil with 1 wt.% Mo-DTC additives. Moreover, ND additive resulted in a lower friction coefficient, better wear resistance (about 2.3×10^{-16} m^3/N m) and shorter duration of run-in period than OLC additive in PAO oil with MoDTC additive. Graphene is not helpful to enhance the friction-reduction and anti-wear performance of PAO oil with or without MoDTC, due to the absence of polishing, ball-bearing and reinforcement of nano-particles effects. Although, individual addition of OLC additive in PAO oil also caused friction-reduction effectiveness, serious wear damage occurred attributed to the abrasive of nano-particles.

Keywords Nano-diamond · Onion-like-carbon · Graphene · MoDTC · Friction · Wear

✉ Jiajie Kang
kangjiajie@cugb.edu.cn

✉ Haidou Wang
wanghaidou@aliyun.com

1 School of Engineering and Technology, China University of Geosciences (Beijing), Beijing 100083, People's Republic of China

2 Zhengzhou Research Institute, China University of Geosciences (Beijing), Zhengzhou 451283, People's Republic of China

3 Key Laboratory On Deep Geo-Drilling Technology of the Ministry of Land and Resources, China University of Geosciences (Beijing), Beijing 100083, People's Republic of China

4 National Key Lab for Remanufacturing, Army Academy of Armored Forces, Beijing 100072, People's Republic of China

5 SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing 2100096, People's Republic of China

6 Beijing Research Institute, Sinopec Lubricant Co., LTD, Beijing 100085, People's Republic of China

Published online: 28 May 2020

Introduction

Polyalphaolefin (PAO) oil is one of the most effective lubricants to protect engines and other mechanical systems operated under low friction and wear which means higher fuel savings and longer durability (Berman et al. 2014; Kenneth et al. 2014). However, PAO-based lubricants still rely heavily on the environmental toxic organic additives with sulfur, phosphors and/or chlorine (Du et al. 2016; Morina et al. 2006; Wang et al. 2014; Wei et al. 2016). Among that, molybdenum di-thiocarbamate (Mo-DTC), as one of the essential additives of current engine lubricant, are widely used, since it is a promising organic additive to be promoted by synergistic or antagonistic effects from the interactions with other additives (Morina et al. 2006). A great number of investigations indicate that Mo-DTC additive is not merely a high-efficiency friction modifier which can give a very low friction coefficient of around 0.05 (Du et al. 2016; Morina et al. 2006; Wang et al. 2014); even, the tribo-film with MoS_2 resulted from the tribo-action of Mo-DTC also is one of the possible ways to achieve super-lubricity, due to its catalytic roles on carbon materials (Berman et al. 2018). Therefore, decreasing the use of traditional poisonous organic additives, like MoDTC, via the synergistic effects of eco-friendly materials deserves in-depth investigations.

The nano-materials additive has been proved as an excellent additive to enhance the thermal, hydrodynamic and tribological performances of nano-fluids which are vital to lubricant (Ewen et al. 2016; Nunn et al. 2015; Peña-Parás et al. 2019; Reinert et al. 2018; Salari et al. 2017; Sarafraz and Arjomandi 2018; Sarafraz et al. 2017; Sarafraz and Safaei 2019). Of them, nano-carbon materials, including nano-diamond (ND), onion-like carbon (OLC), graphene (Gr.), are being considered as promising additives in liquid lubricants, due to their excellent friction-reduction and anti-wear potential accompanied with outstanding thermal stability and biocompatibility. (Berman et al. 2014; Cai et al. 2016; Ewen et al. 2016; Nunn et al. 2015; Peña-Parás et al. 2019; Wei et al. 2016; Zhao et al. 2016). ND additive is effective to enhance the friction-reduction and anti-wear resistance of lubricants resulted from the rolling and polishing effects and formation of reinforced tribo-film (Ivanov and Shenderova 2017; Karami and Shojaei 2017; Lee et al. 2017; Novak et al. 2014; Nunn et al. 2015; Raina and Anand 2017, 2018; Reinert et al. 2018; Tortora and Veeregowda 2017; Zhai et al. 2019). OLC shown as one of an effective mechanism to achieve macro-superlubricity (with a friction coefficient lower than 0.001) is also proven as a friction modifier and anti-wear additive, attributed to its mechanical and tribo-chemical action of core–shell structure (Berman et al. 2019, 2018; Ewen et al. 2016; Nunn et al. 2015; Peña-Parás et al. 2019). As an additive, graphene with intra-planar and weak inter-planar bonds structure is capable to form a sheet-like lubricious film absorbed on contact surfaces, of which delamination and exfoliation finally results in low friction, especially under high contact loads (Berman et al. 2014; Cai et al. 2016; Zhao et al. 2016). Nevertheless, the application of solid nano-carbon additives is restricted by their inferior dispersion, blockage, abrasive wear performances.

Accordingly, lubricant with nano-carbon additives often requires enhancements by means of chemically-modifying nano-carbon materials via the incorporation of polar groups or the aid of surfactants (Li et al. 2008; Lin et al. 2011; Mustafa et al. 2009; Xiao and Liu 2017), preparing surface textures on contact surface for spanabfuhr and particles stockpile (Cai et al. 2016), or/and introducing synergistic effects of additives (Nunn et al. 2015). Among those solutions, introducing synergistic effects of additives is the convenient, direct, ubiquitous, and efficient one to further improve the lubricating performances of nano-carbon additives. Ankush R et al. (Raina and Anand 2017, 2018) revealed that the addition of CuO, h-BN, MoS2 and WS2 nanoparticles in PAO (poly-alpha-olefin) based oil with ND particles caused more excellent lubrication performances, comparing with the oil with individual nanoparticles. Shenderova O et al. (Ivanov and Shenderova 2017) demonstrated that synergetic effects between metallic nanoparticle (Cu, Mo etc.) and nano-carbon nanoparticle is effective to improve the friction-reduction and anti-wear resistance of oil-based lubricants. Nunn et al. (Nunn et al. 2015) found that synergic actions between nano-carbon additives and organic liquid additives (molybdenum dialkyldithiophosphate, MoDDP) resulted in an ultra-low friction coefficient of ~ 0.013. Unfortunately, synergistic effects between organic additives and nano-carbon materials remain relatively unexplored.

Here, nano-carbon materials, such as ND, OLC and graphene, were added to PAO based oil with molybdenum dithiocarbamate (MoDTC, a kind of conventional organic lubricant additive), to enhance the friction-reduction and anti-wear performances. The effects of nano-carbon additives on the lubricating properties of oil with Mo-DTC additive were investigated to reveal synergetic mechanism between nano-carbon and Mo-DTC. Finally, a novel kind of lubricants with a relatively low dosage of organic lubricant additive (means less harmful emissions and low toxicity), excellent dispersity and outstanding friction-reduction and anti-wear performances was developed.

Experiential details

Materials and lubricant preparation

The base oil used in the present work selected synthetic oil PAO-4 widely applied in automotive. Its rheological performances are as follow: the density of 800 kg/m^3, the viscosity of 16.8 cSt (mm^2/s) at 40 °C and 3.26 cSt (mm^2/s) at 100 °C, the viscosity–pressure coefficient of 3.53×10^{-8} Pa^{-1} at 100 °C, pour point of – 60 °C, flesh point of 236 °C and fire point of 253 °C. Incorporating relatively low concentration of additives, negligible changes of thermal, hydrodynamic performances of nano-fluids are not able to cause a decisive effect on lubricated performances of PAO oil.

MoDTC used in this work shows a microstructure of the alkyl chains are C8 (2-ethylhexyl) and C13 and a density of 850 kg/m^3. The chemical compositions of MoDTC are Mo 10.0 wt.% and S 11.0 wt.%.

Nano-carbon materials including ND, OLC, and graphene was adopted as the solid additives added to PAO oil with MoDTC, respectively. ND (manufactured by Nanjing Xianfeng nano-science and Technology) used in the present work was synthesized via the detonation of high-energy explosives. Prior to use as an additive, ND was purified. the purity of ND used in this work is about 97 wt.%. OLC in the present work show was prepared via heat treatments of purified ND at 1100 °C with a duration of 2 h. Graphene platelets manufactured by Shenzhen Zhong Seng Ling Hang Science and Technology Ltd. were adopted, which were prepared by mechanical exfoliation.

The concentrations of nano-carbon and MoDTC additives are 0.05 wt.% and 0.1 wt.%, respectively. The detailed concentrations and sample ID of lubricants used in present study are shown in Table 1. To prepare PAO oil with suspended nano-carbon materials, PAO base oil was firstly mixed with Mo-DTC additive via a magnetic stirring for 30 min; and then, probe model ultrasonic generator was used for ultrasonic oscillation under 75 °C for 30 min to ensure the complete mixing of nanocarbon additives.

Table 1 Detailed content and ID of PAO oil and additives in lubricants

Lubricants ID	Content (wt.%)				
	PAO oil	MoDTC	Graphene	OLC	ND
PAO	100	0	0	0	0
PAO + Gr	99.95	0	0.05	0	0
PAO + OLC	99.95	0	0	0.05	0
PAO + ND	99.95	0	0	0	0.05
PAO + MoDTC	99.85	0.1	0	0	0
PAO + MoDTC + Gr	99.85	0.1	0.05	0	0
PAO + MoDTC + OLC	99.85	0.1	0	0.05	0
PAO + MoDTC + ND	99.85	0.1	0	0	0.05

Sedimentation experiment

After preparation, the effects of MoDTC on the dispersion of nanocarbon additives were investigated by Turbiscan Lab Expert (Formulaction Co., France) via a sedimentation experiment. The dispersion of PAO oil with suspended nano-carbon and MoDTC additives was observed 15 days with a frequency of 2 times per day.

Tribo-tests of lubricants

To test the lubricating performances of PAO oil with nanocarbon and MoDTC additives, tribological tests were carried out using a ball-on-disc configuration of CSM macroscale tribo-meter, in accordance to the ASTM G-99 standards. Self-mated AISI 52,100 steel ball with a diameter of 6 mm and disc with a thickness of 8 mm was adopted in this work. The surface roughness of ball and disc is Ra = ~250 nm. The Young's modulus of the ball and disc is about 208 GPa. After performing zero calibration of the tribo-meter was, lubricants were dropped on the disc. Prior to tribo-tests, the heating device of tribo-meter was started to achieve and keep at the test temperature of 100 °C. During tribo-tests, the upper ball was fixed; while the lower disc was rotated with a revolving velocity of 200 rpm (equivalent to 83.73 mm/s). The normal load during the tribo-tests was kept at 5 N (equivalent to an initial Herzian contact pressure of 0.62 GPa), to ensure the boundary lubrication regime. Frictional force was measured by a sensor with a frequency of 50 Hz; and then, it was converted into friction coefficient. The duration of tribo-tests is 3600 s. For proposing of confirming the reproducibility, all tests were repeated more than five times.

Minimum film thickness ($T_{\min}$) was obtained via the calculation of the Hamrock and Dowson's Eq. (1) (Du et al. 2016; Wang et al. 2014), as follows:

$$T_{\min} = 3.63r(U^*)^{0.68} \times (G^*)^{0.49} \times \left(1 - e^{-0.68k}\right)/(W^*)^{0.073} \quad (1)$$

where $U^* = \eta_0 V/E^* r$, $G^* = \alpha/E^*$, $W^* = L/E^* r^2$, and η_0 is the dynamic viscosity at 100 °C, α is the viscosity–pressure coefficient at 100 °C, r is the radius of the ball, V is the average linear speed, L is the normal load, E^* is the effective Young's modulus (228.6 GPa), and k is an elliptical parameter. The calculated $T_{\min}$ value was about 4.8 nm.

The lambda ratio (λ) was calculated using Eq. (2) (Du et al. 2016; Wang et al. 2014):

$$\lambda = T_{\min}/\left[\left(R_{\text{ball}}\right)^2 + \left(R_{\text{disc}}\right)^2\right]^{0.5} \quad (2)$$

where R_{ball} and R_{disc} is surface roughness of the ball and discs. Via calculation, the lambda ratio λ-ratio value is obtained as 0.68 (less than 1), which indicated that tribo-tests was carried out under the boundary lubrication regime.

Worn volume on the discs is tested by a ZYGONex View model 3D surface profilometer. The worn volume of the ball is represented via the diameter of wear scar tested by Olympus BX51M optic microscope (Sarafraz and Arjomandi). Wear rates (k) used to evaluate the wear performance of lubricants was calculated according to Achard Eq. (3) (Du et al. 2016; Wang et al. 2014):

$$k = V \times L^{-1} \times D^{-1} \quad (3)$$

where V is worn volume. L also is the normal load, D is sliding distance.

Characterizations

The phase structure was detected by D/max-2500 X-ray diffractometer with a Cu–Kα radiation source (wavelength λ = 0.15406 nm). During detections, a continuous scan mode was selected. The scanning speed was 5°/min. 2θ ranges are ranging from 20 to 80°.

Raman spectra of nanocarbon materials were analyzed by the confocal Raman spectrometer (LabRam HR800 Jobin Yvon, 532 nm argon-ion laser). It also was employed to analyze the composition of worn surface after friction.

The morphology of nano-carbon materials was observed by JSM-7001f field emission scanning electron microscope. For proposes of analyzing wear mechanism, this SEM and its appendant energy disperse X-ray spectroscopy (EDS) were applied to analyze the morphology and elemental composition of the worn surface, respectively. During observation, the accelerating voltage was 15 kV, and, a secondary electron image system was used.

The morphology and microstructure of nano-carbon materials are imaged via a JEOL 2100F model transmission electron microscopy (equipped with a Gatan imaging filter (GIF) system.

PHI Quantera X-ray photoelectron spectroscopy (XPS) with a monochromatized Al-Ka radiation source of (hv = 1486.6 eV) was use to conducted chemical analysis of tribo-films. Sputtering clean by Ar ions was carried out before detections to remove the adsorption on the top worn surface. The binding energy of 284.8 eV for C 1 s was considered as a reference for charge correction.

Results and discussion

Micro-structure and morphology of nano-carbon additives

X-ray diffraction (XRD) patterns of ND, OLC and graphene were shown in Fig. 1. The diffracted peaks of ND additive at two-theta of 43.9°and 75.3° which are the diffracted peaks of diamond of (111) and (220), respectively. The average diameter (d) of ND can be calculated by the Scherrer–Wilson Eq. (4) (She et al. 2015, 2013):

$$d = 0.89\lambda / \left(\beta_{hkl} \times \cos\theta\right) \quad (4)$$

where λ is the wavelength of X-ray produced by Cu–Kα radiation source, β_{hkl} is full width at half maximum of diffracted peaks of (hkl), θ is the half of the diffraction angle. Via estimation of the diffracted peaks of (111), the average diameter (d) is about 4.2 nm. The pattern of nano-sized OLC additive demonstrates that it exhibits a compound structure with combined P6m2 graphene and diamond phase. Graphene additive shows a broad peak with low intensity and two-theta ranging from 20 to 30°.

Figure 2 shows the Raman spectra of ND, OLC and graphene additives. For ND, no obvious G peak at 1580 cm^{-1} is found, and the predominant peak is only D peak at ~ 1340 cm^{-1}, which corresponds to the sp^3 hybrid structures (tetrahedron structure) of ND. For both graphene and OLC additives, Raman spectra contain intense features of D and G peaks. Raman spectra taken from OLC is revealed by the characteristic peaks of OLCs; specifically, the position of the G peak shifted from 1580 to 1572 cm^{-1}, which is associated with bending graphene sheets of OLC. G

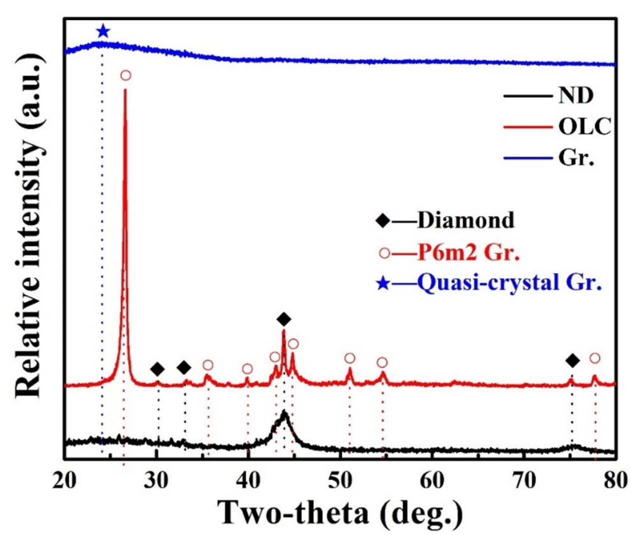

Fig. 1 XRD patterns of ND, OLC and graphene additives

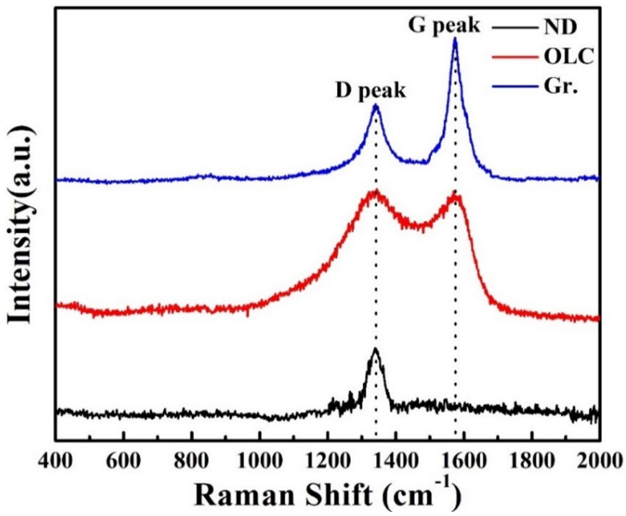

Fig. 2 Raman spectra of ND, OLC and graphene additives

peaks of graphene and OLC additives is due to the breathing modes of sp^2 atoms in rings. D peak found on graphene is attributed to the defects of sp^2 carbon. The ratio of the intensity of D and G (I_d/I_g) for OLC is about 1.02, and for graphene, the additive is about 0.55, respectively.

Figure 3 are SEM images showing the mophology of ND, OLC, and graphene. ND is shown as nano-particles with an average diameter of ~ 5 nm. OLC is the agglomerate of nanoparticles and nano-sized sheets. The dimension of OLC is a little larger than that of ND. Graphene exhibits lamellar morphology.

High-resolution transmission electron microscope (HR-TEM) images and selective area electron diffraction (SAED) patterns of the ND, OLC and graphene additives are shown in Fig. 4. Via HR-TEM observation and SAED analysis, it can be seen that ND shows as crystalline nanoparticles with a diameter of ~ 5 nm, which is consistent with the calculation results of XRD. The structure of OLC is a core–shell structure with ND particle core and graphene shell (3 ~ 5). The lamellar monocrystalline microstructure is observed via the HR-TEM images and SAED patterns of graphene.

Dispersibility of nano-carbon additives

Figure 5 shows the results of sediment observations showing the dispersibility of ND, OLC and graphene in PAO oil with MoDTC additives. Evidently, solid–liquid separation occurred in the PAO oil with individual nano-carbon additives after sediment for 15 days, indicated that nano-carbon additives exhibit relatively poor dispersibility in PAO oil.

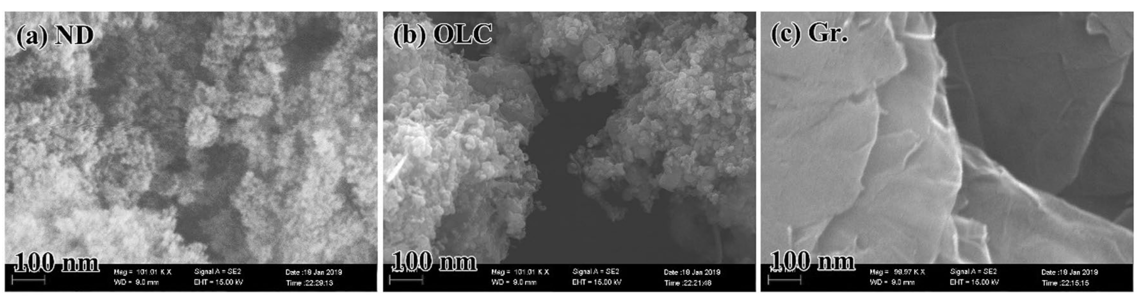

Fig. 3 SEM images showing the morphologies of **a** ND, **b** OLC and **c** graphene additives

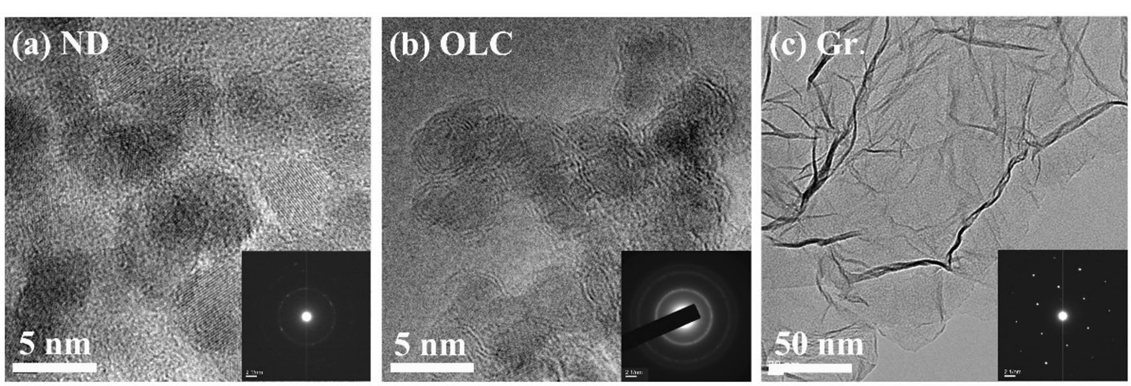

Fig. 4 HR-TEM images and SAED patterns of **a** ND, **b** OLC and **c** graphene additives

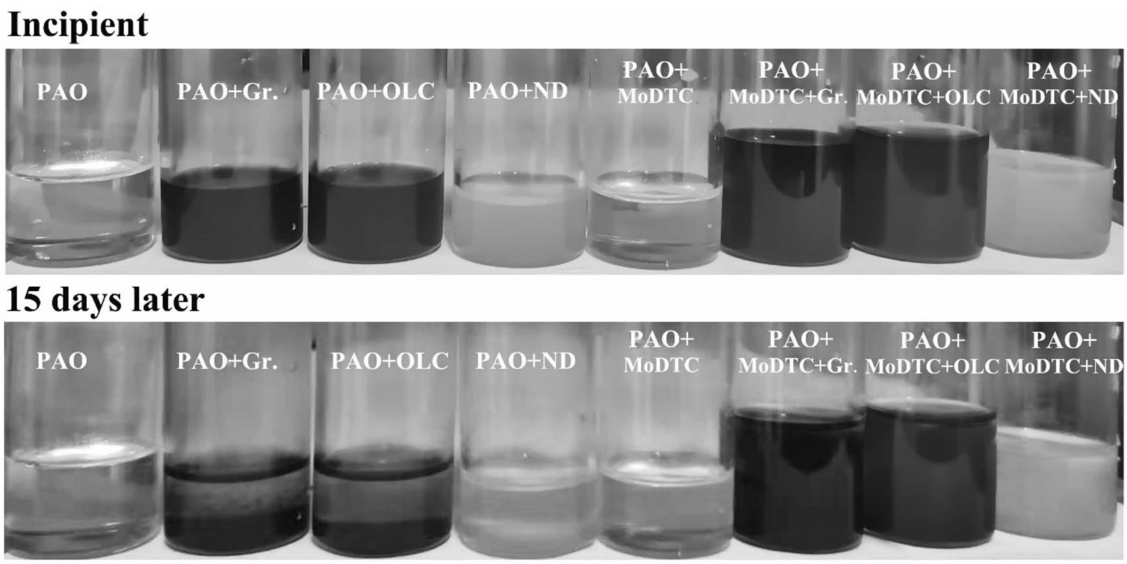

Fig. 5 Results of settlement observations showing the dispersion of PAO oil with suspended nano-carbon and MoDTC additives

Nevertheless, PAO oil with both nano-carbon and MoDTC additives keeps as a stable suspension liquid without solid–liquid separation, which demonstrated the dispersion of nano-carbon materials in PAO oil is enhanced by MoDTC additive. This enhancement may result from the chemically modifying caused functional groups absorbed on the surface of ND (Berman et al. 2014; Lee et al. 2017; Li et al. 2008; Lin et al. 2011; Mustafa et al. 2009).

Friction coefficient

Figure 6 shows the effects of nano-carbon materials on friction coefficient of self-mated AISI52100 steel lubricated under PAO oil with Mo-DTC additives. The individual addition of OLC or graphene at a concentration of 0.05 wt.% does not affect the friction-reduction of PAO oil. Nonetheless, the individual addition of ND the is effective to reduce the friction coefficient (from ~ 0.15 to ~ 0.12). The individual addition of Mo-DTC in PAO oil at a concentration of 0.1 wt.% is not enough to cause a low friction coefficient. Whereas, ND or OLC can further drive down the friction coefficient of PAO oil with MoDTC additive. PAO + MoDTC + ND lubricant causes a friction coefficient of ~ 0.05, and PAO oil with OLC and MoDTC additives (PAO + MoDTC + OLC) also results in a lower friction coefficient (~ 0.6). In comparison to the results shown in Ref (Du et al. 2016; Wang et al. 2014) that AISI 52100 steel ball lubricated under PAO with 1 wt.% MoDTC is also

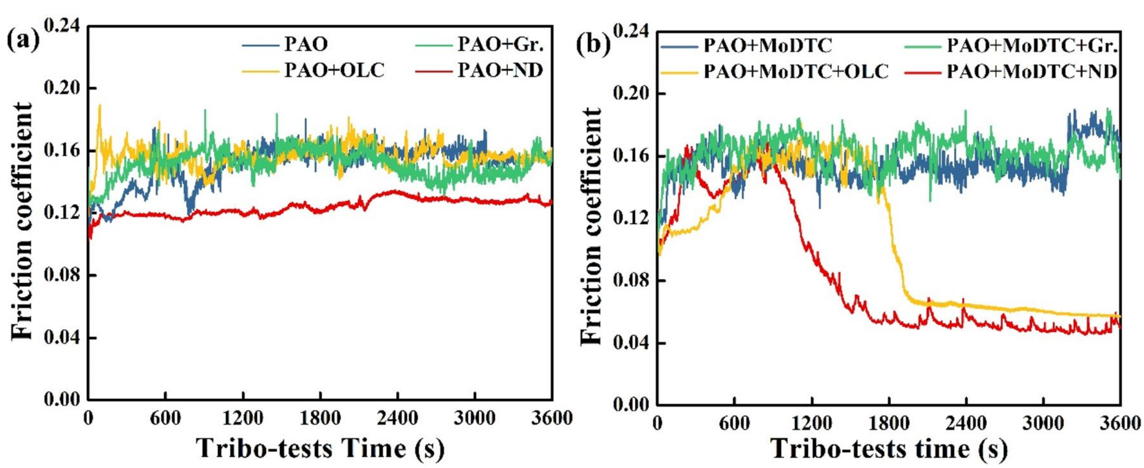

Fig. 6 Effects of nano-carbon materials on friction coefficient of self-mated AISI52100 steels lubricated under PAO oil **a** without and **b** with Mo-DTC additive

around 0.055, it can be concluded that ND and OLC is effective additives to reduce the dosage of MoDTC. The run-in period of steel lubricated under PAO + MoDTC + ND is 20 min, shorter than that in PAO + MoDTC + OLC lubricant for 30 min. Besides, the additions of 0.05 wt.% Gr. cannot reduce the friction coefficient for both PAO oil and PAO oil with Mo-DTC additive.

Wear behaviors

Wear rates and 3D morphologies of AISI52100 steel discs lubricated under PAO oil with nano-carbon and MoDTC additives are shown in Fig. 7. It can be seen that the AISI52100 steel discs lubricated under PAO oil with ND additive (PAO + ND) show a lower wear rate (about $2.3 \times 10^{-16} m^3/Nm$) than that under PAO, PAO + MoDTC, PAO + Gr. or PAO + OLC lubricant demonstrated ND is an effective anti-wear additive. Especially, PAO + MoDTC + ND lubricant causes a further lower wear rate (about $1.92 \times 10^{-16} m^3/Nm$) comparing with PAO with individual ND or MoDTC additive, which means that ND is effective to improve the anti-wear performances of PAO + MoDTC lubricant. In other words, MoDTC, as a well-known friction modifier, plays its anti-wear roles on PAO oil with ND additive. Interestingly, the individual addition of OLC in PAO results in a high wear rate (about $11.8 \times 10^{-16} m^3/Nm$); whereas a low wear rate (about $2.8 \times 10^{-16} m^3/Nm$) for that in PAO with MoDTC additives. This reduction means that the MoDTC also can enhance the anti-wear performance of PAO + OLC lubricant. Graphene cannot play any positive roles on the anti-wear performances of PAO or PAO + MoDTC lubricants.

Figure 8 shows the surface morphology and diameter of wear scar on the balls lubricated under PAO oil with nano-carbon and MoDTC additives. Visibly, the surfaces of wear scars of the balls lubricated under PAO oil with nano-carbon and MoDTC additives are all covered with micro-plowing, indicated the occurrence of abrasive wear. Wear scars of the balls lubricated under PAO + ND, PAO + MoDTC + ND, and PAO + MoDTC + OLC exhibit as a locally colorful surface that may relate the formation of tribo-films. The diameter of wear scar on the ball lubricated under PAO + ND is smaller than that with individual graphene, OLC, or MoDTC additive. The ball lubricated under PAO + MoDTC + ND shows the smallest wear scar among that in all PAO oils with ND and MoDTC additives. The enhancement of the anti-wear performance is not observed in PAO + OLC and PAO + MoDTC. Nonetheless, the diameter of wear scar of the ball lubricated under PAO + MoDTC + OLC is effectively decreased. Graphene is not effective to decrease wear performances of the PAO + Gr. or PAO + MoDTC + Gr. lubricants.

Worn surface analysis

Figure 9 is typical SEM images showing the morphology of worn surface on the discs lubricated under PAO oil with nano-carbon and MoDTC additives. All worn surfaces on the discs lubricated under PAO oil with nano-carbon and MoDTC additives also exhibit the features of plowing

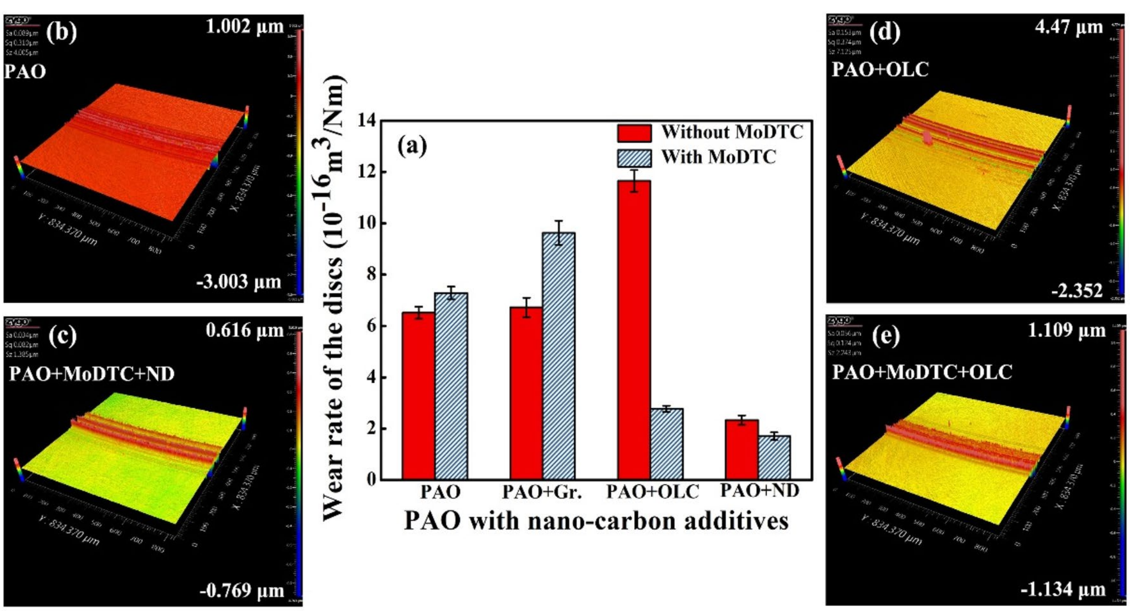

Fig. 7 Anti-wear performances of PAO oil with nano-carbon and MoDTC additives shown via **a** wear rates and **b–e** worn surface 3D morphologies of AISI52100 discs

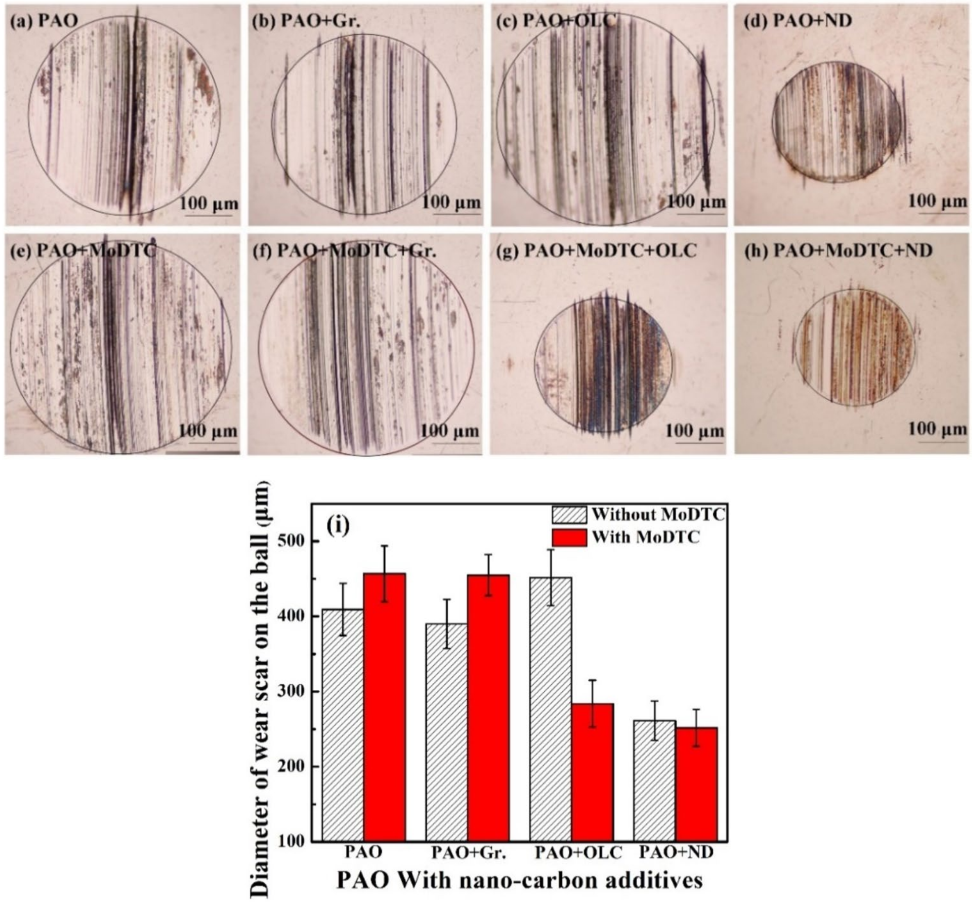

Fig. 8 Wear behaviors of the AISI52100 steel lubricated under PAO oil with nano-carbon and MoDTC additives shown via **a–h** surface morphology and **i** diameter of wear scar

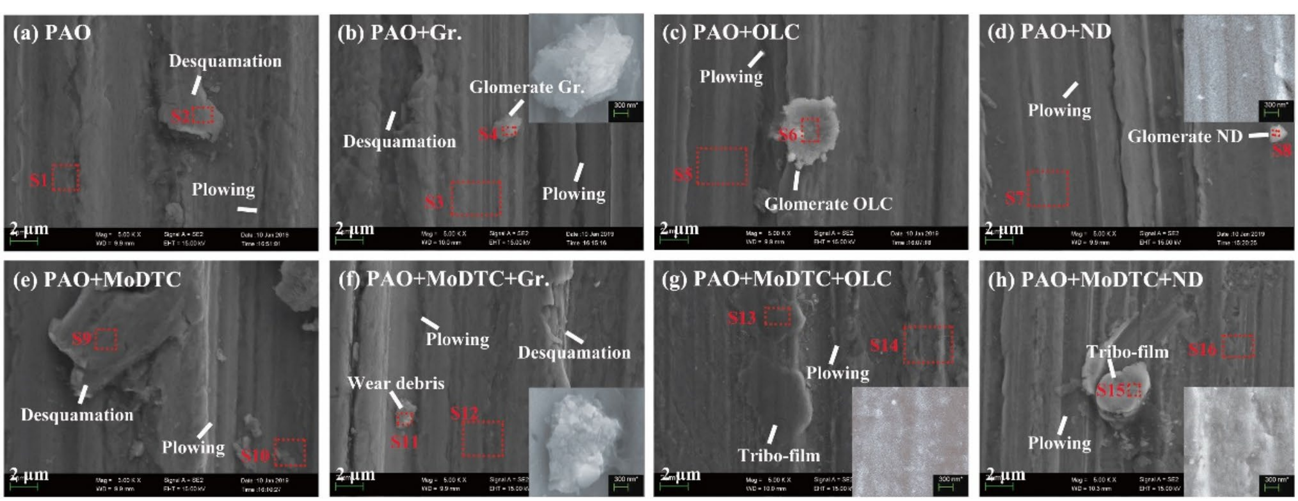

Fig. 9 Typical SEM images showing the morphology of worn surface on the discs lubricated under PAO oil with nano-carbon and MoDTC additives

indicated the occurrence of abrasive wear. Besides, the characteristics of desquamation can be found on the worn surface of the discs lubricated under PAO, PAO + MoDTC, PAO + Gr. or PAO + MoDTC + Gr., which demonstrated that their wear damages are attributed to the coaction of abrasive wear and fatigue wear. No desquamation features can be seen on the worn surface of the disc lubricated under PAO + OLC, and PAO + ND, PAO + MoDTC + OLC or PAO + MoDTC + ND; and wear mechanism is dominated by abrasive wear.

Combined with SEM observation, EDS analysis was used to further reveal wear mechanism. The results of EDS analysis are shown in Table 2 and Fig. 10. wear debris with a laminated morphology (inset of Fig. 9b) and a content of 57 wt.% C (Table 2) can be observed on the worn surface of the discs lubricated PAO + Gr. which may relate to its poor dispersibility of Graphene. Nevertheless, wear debris on the worn surface of discs lubricated under PAO + MoDTC + Gr. are nano-particles with a content of 63 wt.% Fe and 29 wt.% O. Similarly, there are glomerate wear debris with high content carbon (72 wt.%) on the worn surface of the disc lubricated under PAO + OLC. Unlike that under PAO + OLC, worn surface of the disc lubricated under PAO + MoDTC + OLC shows no glomerate wear debris but a great number of embedded nano-carbon particles. Such embedded nano-carbon particles also can be found on the worn surface of the discs lubricated under PAO + ND and PAO + MoDTC + ND. The embedded nano-carbon particles on the worn surface play a positive role on the enhancement of anti-wear performance and load capacity due to reinforcement (Zhai et al. 2019). Additionally, EDS surface spectrum for distribution maps of Fe, O, Mo, S, and C shown in Fig. 10 demonstrated that local tribo-film with high content of Mo and S (Table 2; Fig. 10) can be detected on the worn

Table 2 EDS analysis results of wear debris and worn surface on the discs lubricated under PAO oil with nano-carbon and MoDTC additives

Lubricants	Spectrum No	Element content (wt.%)						Lubricants	Spectrum No	Element content (wt.%)					
		Fe	Cr	O	C	Mo	S			Fe	Cr	O	C	Mo	S
PAO	S1	58	0	33	9	–	–	PAO + MoDTC	S9	53	0	28	18	1	0
PAO	S2	58	1	31	10	–	–	PAO + MoDTC	S10	64	1	17	17	1	0
PAO + Gr	S3	63	1	29	7	–	–	PAO + MoDTC + Gr	S11	61	1	23	11	3	1
PAO + Gr	S4	14	0	29	57	–	–	PAO + MoDTC + Gr	S12	65	1	15	18	1	0
PAO + OLC	S5	69	1	23	7	–	–	PAO + MoDTC + OLC	S13	60	0	15	16	7	2
PAO + OLC	S6	11	0	17	72	–	–	PAO + MoDTC + OLC	S14	57	1	17	22	2	1
PAO + ND	S7	62	0	9	29	–	–	PAO + MoDTC + ND	S15	62	1	12	15	8	2
PAO + ND	S8	13	0	12	75	–	–	PAO + MoDTC + ND	S16	53	0	18	26	3	1

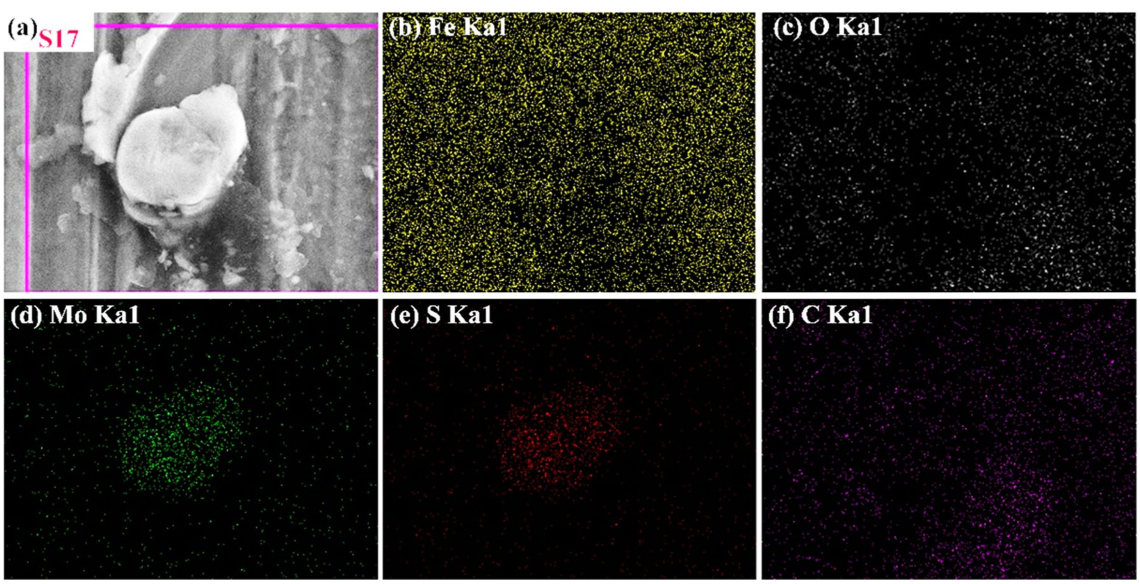

Fig. 10 EDS surface spectrum showing the distribution of elements on worn surface of the disc lubricated under PAO oil with MoDTC and ND additives: **a** SEM image showing the spectrum area via pink rectangle and **b**–**f** the distribution maps of Fe, O, Mo, S and C

surface of the discs lubricated under PAO + MoDTC + OLC and PAO + MoDTC + ND. Undoubtedly, the formation of such tribo-film is one of the main reasons for the low friction coefficient caused by PAO + MoDTC + OLC and PAO + MoDTC + ND.

Figures 11a, b are Raman spectra of worn surfaces of the disc lubricated under PAO oil with MoDTC and nano-carbon additives. D carbon peak with a position of ~ 1340 cm^{-1}), G carbon peak with a position of ~ 1580 cm^{-1} and peaks for FeOx at 225, 290, 405, 495, 611, 658, 825, 1081 and 1322 cm^{-1} indicate carbon and FeOx on the worn surface. Moreover, E_{2g} peak at ~ 383 and A_{1g} peak at ~ 408 for MoS_2 shown in Fig. 11b suggests that the addition of MoDTC additive results in the formation of MoS_2 on worn surface. Obviously, PAO + OLC lubricant causes a lower intensity of peaks for iron oxides and D and G peaks for carbon than PAO, PAO + Gr. and PAO + ND lubricants, which is related to the occurrence of serious abrasive wear (Figs. 7 and 9c).

The ratios of D peak intensity to G peak intensity (I_D/I_G) of Raman spectra for the disc lubricated under PAO oil with MoDTC and nano-carbon additives were plotted in Fig. 12. Comparing with individually added ND additive, the addition of both MoDTC and ND additive leads to a low value of I_D/I_G, resulted from the catalytic action of MoS_2 promoted phase transition of sp3 to sp2 carbon (Berman et al. 2019; 2018). Similarly, PAO + MoDTC and PAO + MoDTC + Gr. lubricants also cause a lower value of I_D/I_G than PAO and PAO + Gr. lubricants, respectively. It is interesting that the value of I_D/I_G for the disc lubricated under PAO + MoDTC + OLC is closed to that under PAO + MoDTC + ND (~ 1.5); however, it is higher than that under PAO + OLC due to the formation of nano-particles wear debris on the worn surface (as shown in Fig. 9g and its inset).

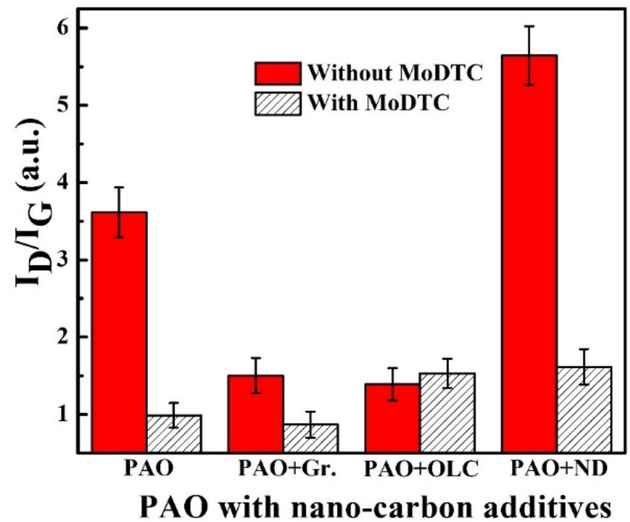

Fig. 12 The ratios of D peak intensity to G peak intensity (I_D/I_G) of Raman spectra for the disc lubricated under PAO oil with MoDTC and nano-carbon additives

XPS spectra of the worn surfaces of the disc lubricated under PAO oils with MoDTC and ND additives were shown in Fig. 13. The XPS peaks of Fe 2p, Fe 3p, C 1 s, O 1 s, and O KLL can be detected on the worn surfaces of the disc lubricated under all the PAO oils with MoDTC and/or nano-carbon additives. Nonetheless, only the addition of MoDTC additive in PAO oil (such as PAO + MoDTC, PAO + MoDTC + Gr., PAO + MoDTC + OLC, and PAO + MoDTC + ND) results in the formation of Mo 3d and S 2p on the worn surfaces.

Chemical elemental composition of worn surface on the discs lubricated under PAO oil with MoDTC and ND additives was further analyzed using XPS spectra, as shown

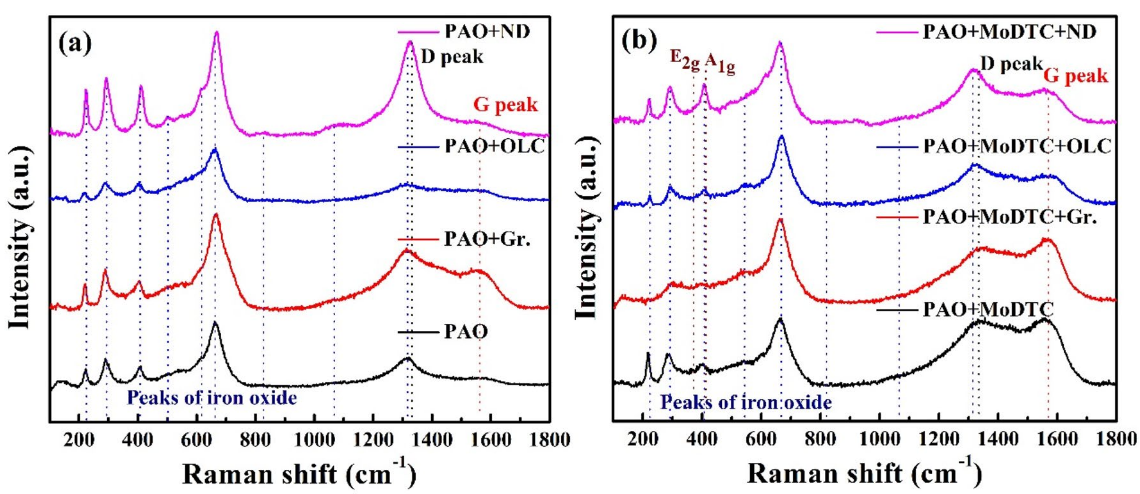

Fig. 11 Raman spectra of worn surfaces of the disc lubricated under PAO oil with **a** individual nano-carbon and **b** both MoDTC and nano-carbon additives

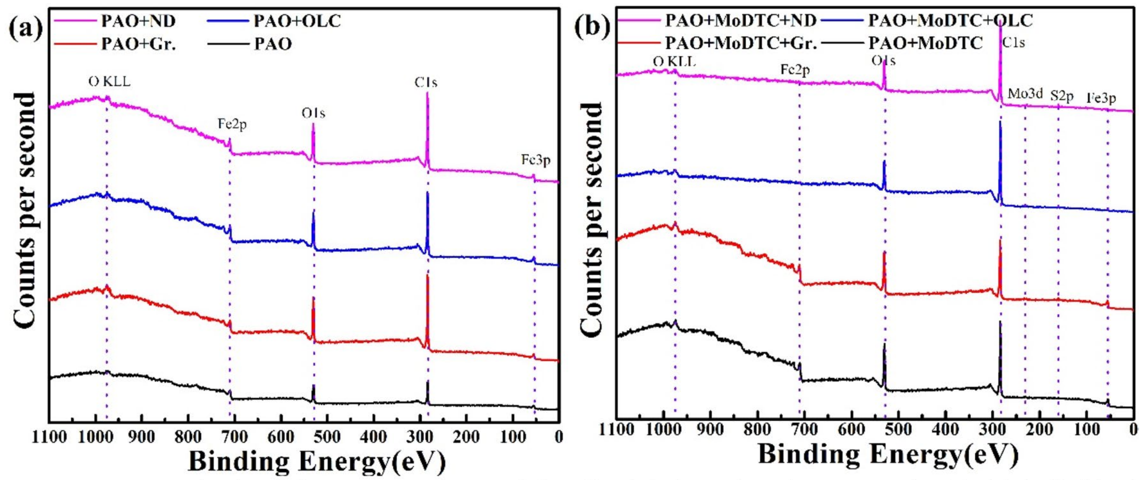

Fig. 13 XPS analysis of the worn surfaces of the disc lubricated under PAO oil with **a** individual nano-carbon and **b** both MoDTC and nano-carbon additives

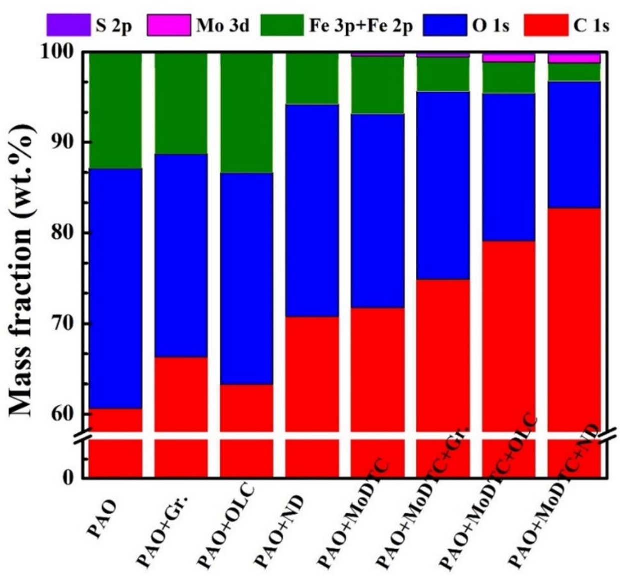

Fig. 14 Chemical elemental composition of worn surface on the discs lubricated under PAO oil with MoDTC and ND additives

in Fig. 14. Distinctly, the addition of nano-carbon additive resulted in high content of C1s. ND additive causes the highest content of C1s (~70 wt.%), and OLC additive resulted in the lowest content of C1s (~65 wt.%) on the worn surface among the PAO oils with individual nano-carbon additives, which may be related to the embedded nano-carbon particles on the worn surface (Fig. 9d and its inset) for PAO + ND and the occurrence of serious abrasive wear consequent as PAO + OLC. Worn surface the disc lubricated under PAO + MoDTC + ND also shows a higher content of C1s (~80 wt.%), compared with that under the other PAO oils with MoDTC and nano-carbon additives. Additionally, ND and OLC additives is also helpful to increase the content of Mo 3d and S 2p on the worn surfaces of the discs lubricated under PAO oil with MoDTC and ND additives (promote the formation of MoS_x). From another perspective, it can be concluded that MoDTC also plays a positive role on increasing the content of C1s on the worn surface of the discs lubricated under PAO oil with nano-carbon additives.

Similar with the results shown in Ref (Ivanov and Shenderova 2017; Karami and Shojaei 2017; Novak et al. 2014; Nunn et al. 2015; Raina and Anand 2017, 2018; Zhai et al. 2019), ND has been demonstrated as an effective additive to enhance the friction-reduction and anti-wear performances of PAO oil. Friction-reduction effects is attributed to the rolling and polishing of the abrasive (nano-particles) (Ivanov and Shenderova 2017; Karami and Shojaei 2017; Raina and Anand 2017, 2018; Tortora and Veeregowda 2017; Zhai et al. 2019). Besides, the anti-wear effects is due to the formation of reinforced tribo-film (Zhai et al. 2019), which are demonstrated by the worn surface embedded with a great number of ND particles proved by the SEM images (Fig. 9d), EDS (Table 2), Raman (Fig. 11) and XPS (Fig. 12) results in the formation of tribo-film. Nevertheless, no embedded particles (Fig. 9c and its inset) are on the worn surface lubricated under PAO + OLC, manifested as the low intensity of D and G peak in Fig. 11, and low intensity for C 1 s XPS spectra in Fig. 13. The glomerate OLC wears debris (Fig. 9c and its inset) caused even serious abrasive wear, resulted from the graphene shell of OLC and its poor dispersion stability which are passive to the formation of reinforced tribo-film. As a consequence, the dominated effect of OLC additives is abrasive of the hardcore, which finally resulted in a high wear rate. Micro-scaled glomerate OLC on the worn surface is also the main reason for its less friction-reduction effect. Similarly, graphene exhibits poor friction-reduction and anti-wear effects, due to the micro-scaled glomerate graphene on the worn surface.

The addition of MoDTC additive remarkably enhances the dispersion stability of nano-carbon materials in PAO oil (Fig. 5), which causes no micro-size glomerate nano-carbon to wear debris on the worn surface (Fig. 9f–h). The enhancement of the dispersion stability of ND is also able to promote nano-sized ND particles embed into the worn surface (the reinforcement of ND). Besides the synergistic effects between ND and MoDTC additives is helpful to the formation of a film with a high content of MoS_2 (as shown in Figs. 10, 12 and 13). Accordingly, PAO oil with both ND and MoDTC additives exhibits excellent friction-reduction and anti-wear effectiveness. PAO with 0.1 wt.% MoDTC and 0.05 wt.% ND additives even shows an equivalent friction-reduction effects to PAO with 0.1 wt.% MoDTC additive. It can be concluded that ND is not only capable to decrease the optimized dosage of MoDTC, but also to enhance the anti-wear effects of PAO oil with MoDTC. As a result of a similar mechanism, the addition of 0.05 wt.% OLC is also able to enhance the friction-reduction and anti-wear performances of PAO with 0.1 wt.% MoDTC additive. Whereas, the core–shell structure (nano-diamond core and graphene shell shown in Fig. 4) of OLC may the essential reason for the long duration of the run-in period. Similar with the results shown in Ref (Nunn et al. 2015), competing mechanisms for the formation of tribo-film between sp^2 layers and MoDTC leads to antagonistic effects between the graphene and MoDTC additives, which finally resulted in the addition of graphene exhibits nearly no friction-reduction effectiveness on PAO oil with MoDTC additive. Moreover, graphene cannot reinforce the worn surface; as a consequence, graphene shows no help for the enhancement of friction-reduction and anti-wear resistance of PAO with MoDTC additive.

In the present work, by adding nano-carbon materials into PAO oil with MoDTC additive, a new kind of eco-friendly lubricant with low-concentration organic additive was developed. Synergetic effects between nano-carbon and MoDTC additive were unraveled, which finally resulted in excellent friction-reduction and anti-wear performance of PAO-based oil. Additionally, a new lubricated mechanism shown as co-actions of polishing, ball-bearing and reinforcement effects of nano-carbon materials revealed, which could serve as a paradigm for lubricant development.

Conclusions

1. The addition of ND or OLC in PAO oil with MoDTC additive are effective to promote the formation of tribo-film consist of MoSx, which finally decreases friction coefficient from 0.15 to about 0.05 and the optimized dosage of MoDTC from 1 to 0.1 wt.%.
2. The addition of ND or OLC in PAO oil with MoDTC additive result in the enhancement of its anti-wear effectiveness, due to the formation of ND embedded worn surface. Lubricant with dosages of 0.1 wt.% MoDTC and 0.05 wt.% ND additives results in the wear rate of self-mated steel ball decrease from 6.5×10^{-16} to about 2.3×10^{-16} m^3/N m.
3. Graphene shows no help for the friction-reduction and anti-wear performances of PAO with MoDTC additive.
4. MoDTC can enhance the dispersion stability of nano-carbon materials in PAO oil, the friction-reduction and anti-wear performances of PAO oils with ND or OLC additives.

Acknowledgements We would like to thank the Natural Science Foundation of China (41902319, 51875537), Beijing Natural Science Foundation (3194056), Pre-Research Program in National 13th Five-Year Plan (61409230603), China Postdoctoral Science Foundation (2018M641429 and 2019T120122), Fundamental Research Funds for the Central Universities (2652018088 and 2242D19K40184) and Research Foundation of Key Laboratory of Deep Geodrilling Technology, Ministry of Land and Resources (No.KF201804) for the financial support.

References

Berman D, Erdemir A, Sumant AV (2014) Graphene: a new emerging lubricant. Mater Today 17:31–42

Berman D, Narayanan B, Cherukara M, Sankaranarayanan SKRS, Erdemir A, Zinovev A, Sumant AV (2018) Operando tribochemical formation of onion-like-carbon leads to macroscale superlubricity. Nat Com 9:1164

Berman D, Mutyala KC, Srinivasan S, Sankaranarayanan SKRS, Sumant AV (2019) Iron-nanoparticle driven tribochemistry leading to superlubric sliding interfaces. Adv Mater Interfaces 6:1901416

Cai Z, Zhao L, Zhang X, Yue W, Zhu M, Dedkov Y (2016) Combined effect of textured patterns and graphene flake additives on tribological behavior under boundary lubrication. PLoS ONE 11:e0152143

Du S, Yue W, Wang Y, She D, Huang H, Fu Z (2016) Synergistic effects between sulfurized-nanocrystallized 316L steel and MoDTC lubricating oil additive for improvement of tribological performances. Tribol Int 94:530–540

Ewen JP, Gattinoni C, Thakkar FM, Morgan N, Spikes HA, Dini D (2016) Nonequilibrium molecular dynamics investigation of the reduction in friction and wear by carbon nanoparticles between iron surfaces. Tribol Lett 63:38

Ivanov M, Shenderova O (2017) Nanodiamond-based nanolubricants for motor oils. Curr Opin Solid St M 21:17–24

Karami P, Shojaei A (2017) Improvement of dry sliding tribological properties of polyamide 6 using diamond nanoparticles. Tribol Int 115:370–377

Kenneth H, Peter A, NilsOlof N, Kari M, Ali E (2014) Global energy consumption due to friction in trucks and buses. Tribol Int 78:94–114

Lee GJ, Park JJ, Lee MK, Rhee CK (2017) Stable dispersion of nanodiamonds in oil and their tribological properties as lubricant additives. Appl Surf Sci 415:24–27

Li D, Müller MB, Gilje S, Kaner RB, Wallace GG (2008) Processable aqueous dispersion of graphene nanosheets. Nat Nanotechnol 3:101–105

Lin J, Wang L, Chen G (2011) Modification of graphene platelets and their tribological properties as a lubricant additive. Tribol Lett 41:209–215

Morina A, Neville A, Priest M, Green I (2006) ZDDP and MoDTC interactions in boundary lubrication—the effect of temperature and ZDDP/MoDTC ratio. Tribol Int 39:1545–1557

Mustafa L et al (2009) Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. J Am Chem Soc 131:3611–3620

Novak C, Kingman D, Stern K, Zou Q, Gara L (2014) Tribological properties of paraffinic oil with nanodiamond particles. Tribol Trans 57:831–837

Nunn N, Mahbooba Z, Ivanov M, Ivanov D, Brenner D, Shenderova O (2015) Tribological properties of polyalphaolefin oil modified with nanocarbon additives. Dia Relat Mater 54:97–102

Peña-Parás L, Maldonado-Cortés D, Kharissova OV, Saldívar KI, Contreras L, Arquieta P, Castaños B (2019) Novel carbon nanotori additives for lubricants with superior anti-wear and extreme pressure properties. Tribol Int 131:488–495

Raina A, Anand A (2017) Tribological investigation of diamond nanoparticles for steel/steel contacts in boundary lubrication regime. Appl Nanosci 7:371–388

Raina A, Anand A (2018) Effect of nanodiamond on friction and wear behavior of metal dichalcogenides in synthetic oil. Appl Nanosci 8:581–5911

Reinert L, Green I, Gimmler S, Lechthaler B, Mücklich F, Suárez S (2018) Tribological behavior of self-lubricating carbon nanoparticle reinforced metal matrix composites. Wear 408–409:72–85

Salari E, Peyghambarzadeh SM, Sarafraz MM, Hormozi F, Nikkhah V (2017) Thermal behavior of aqueous iron oxide nano-fluid as a coolant on a flat disc heater under the pool boiling condition. Heat Mass Transfer 53:265–275

Sarafraz MM, Arjomandi M (2018) Thermal performance analysis of a microchannel heat sink cooling with copper oxide-indium (CuO/In) nano-suspensions at high-temperatures. Appl Therm Eng 137:700–709

Sarafraz MM, Safaei MR (2019) Diurnal thermal evaluation of an evacuated tube solar collector (ETSC) charged with graphene nanoplatelets-methanol nano-suspension. Renew Energ 142:364–372

Sarafraz MM, Arya A, Nikkhah V, Hormozi F (2017) Thermal Performance and Viscosity of Biologically Produced Silver/Coconut Oil Nanofluids. Chem Biochem Eng Q 30:489–500

She D, Wen Y, Fu Z, Gu Y, Wang C, Liu J (2013) The effect of nitriding temperature on hardness and microstructure of die steel pre-treated by ultrasonic cold forging technology. Mater Des 49:392–399

She D, Wen Y, Du Y, Fu Z, Wang C, Liu J (2015) Vacuum tribological properties of titanium with a nanocrystalline surface layer. Tribol Lett 57:1

Tortora A, Veeregowda D (2017) Effects of two sliding motions on the superlubricity and wear of self-mated bearing steel lubricated by aqueous glycerol with and without nanodiamonds. Wear 386–387:173–178

Wang Y, Yue W, She D, Fu Z, Huang H, Liu J (2014) Effects of surface nanocrystallization on tribological properties of 316L stainless steel under MoDTC/ZDDP lubrications. Tribol Int 79:42–51

Wei D, Bassem K, Hong G, Hong L (2016) Roles of nanoparticles in oil lubrication. Tribol Int 102:88–98

Xiao H, Liu S (2017) 2D nanomaterials as lubricant additive: a review. Mater Des 135:319–332

Zhai W, Lu W, Liu X, Zhou L (2019) Nanodiamond as an effective additive in oil to dramatically reduce friction and wear for fretting steel/copper interfaces. Tribol Int 129:75–81

Zhao J, He Y, Wang Y, Wang W, Yan L (2016) An investigation on the tribological properties of multilayer graphene and MoS2 nanosheets as additives used in hydraulic applications. Tribol Int 97:14–20