

Anti-wear and friction-reduction mechanism of Sn and Fe nanoparticles as additives of multialkylated cyclopentanes under vacuum condition

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ABSTRACT

The effect of Sn and Fe nanoparticles as additives of multialkylated cyclopentanes (MACs) was investigated in vacuum ($\sim 10^{-4}$ Pa) by a vacuum four-ball tribometer. Results showed that the steel balls exhibited the transient seizure-like high friction when lubricated with MACs base oil in vacuum, while introducing Sn and Fe nanoparticles could effectively eliminate it. Moreover, Sn nanoparticles were more effective on friction-reduction and frictional heat reduction, but less effective on anti-wear ability in comparison with Fe nanoparticles. Confirmed by the surface analysis, the improved tribological performances should be ascribed to a protective film with low shear stress and hardness formed on the worn surface.

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1. Introduction

To aerospace mechanical components, although solid lubricants are still the most important choice for the complex and harsh space environments [1–4], liquid lubricants are increasingly used in space mechanisms due to their low mechanical noise, no wear in the elastohydrodynamic (EHL) regime, ease of replenishment, ability to remove wear debris, and insensitivity to environmental factors [5]. However, the application of liquid lubrication under high vacuum conditions has been a technical challenge for many years [6–8]. The high vacuum environment induces rapid evaporation of the liquid lubricants employed, and undoubtedly, the loss of liquid lubricants could result in failure of the mechanism.

In recent years, multialkylated cyclopentanes (MACs) have received increasing attention as a kind of space lubricants. MACs possess many excellent properties, such as extremely low volatility, high viscosity index, low pour point and good solubility with many commercial additives [9]. Under vacuum conditions, it was found that MACs and perfluoropolyether (PFPE) showed initial seizure-like high friction under the boundary lubrication condition, and correspondingly they would also suffer the initial high wear volume [10–12]. High friction and severe surface damage under vacuum

condition, which is caused by high contact pressure and flash temperature, could be reduced by applying friction-reduction (FR) and anti-wear (AW) additives. These traditional additives, which are sulfur-, chlorine- and phosphorous-containing compounds, react chemically with the metal surfaces, forming low-shearing layers of sulphides, chlorides or phosphides, and thereby preventing severe wear and seizure. Unfortunately, in high vacuum environments, high vapor pressure of the traditional additives leads to the decrease in the effective lifetime of the system due to the volatilization and loss of anti-wear additives.

Researches about nanoparticles used as oil additives have been extensively conducted in recent years [13–28]. Results showed that the tribological properties of the base oil could be improved by means of reducing the friction and avoiding the severe wear even at very low nanoparticle concentrations. The FR and AW mechanisms of nanoparticle additives can be summarized as four different processes: nanoparticles may be melted and welded on the shearing surface, reacted with the specimen to form a protective layer, tribo-sintered on the surface or act as nano-bearings on the rubbing surfaces [18,22,26,27].

Along with the rapid development of nanotechnology, lubricating oil with metallic additives has also been studied [13–26]. Table 1 shows a summary of the main metallic nanoparticles tested as lubricating oil additives. Many soft metallic nanoparticles [16–19], such as Cu, Ag, Sn and Pb, have been investigated and the main mechanism of the improved tribological properties was

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Table 1
Summary of the main metallic nanoparticles as lubricating oil additives.

Nanoparticles	Size (nm)	Base oil	Concentration (wt.%)	References
Cu	5	Liquid paraffin	0.5	[18]
		HVI WH150	0.1–1	
Cu	25	PAO6	0.5–2	[26]
Cu	10–20	Motor oil	0.3–0.6	[14]
Cu	20	50CC oil	0.2	[20]
Cu	8	Liquid paraffin	4	[13]
Cu	25,60	Raw oil	0.1	[21]
Cu	66	Hydrorafinat oil	0.02–0.25	[17]
Mo	54			
Ag	4–7	MACs oil	2	[22,29]
Ag	20	PEG300	0.25–5	[23]
Ag	15	Liquid paraffin	0.5	[15]
	8–10		0.05–0.4	[25]
Pb	40	Liquid paraffin	0.06–1	[16]
Sn	50–3500	Liquid paraffin	0.8	[19]
Ni	20	PAO6	0.5–2	[24]

reported to be a soft protective film with low shearing stress formed on the rubbing surfaces. However, few researchers have studied the tribological characteristics of the Fe nanoparticles, which were the main composition of the most widely used friction pairs.

Reduction in frictional heat and extremely low volatility are the two important characteristics of nanoparticle additives. However, they were always liable to be ignored by researchers when using nanoparticle as additives in base oil. Temperature rise caused by frictional heat could strongly influence the friction-reduction and anti-wear properties in fluid lubrication condition. Another advantage of nanoparticles as the potential additives in space liquid lubricants was their extremely low volatility, which satisfies the high vacuum environment of the space application.

This paper now studies the friction-reduction, anti-wear and frictional heat reduction properties of Sn and Fe nanoparticles as additives in MACs oil. Through scanning electron microscopy (SEM) and energy dispersive X-ray analyzer attachment (EDX) analysis of the wear scar surfaces, the mechanisms of improved tribological properties was discussed.

2. Experimental details

2.1. Nanoparticles and lubricant

MACs were synthesized in our laboratory with the method reported in literature [9]. The main properties of the nanoparticles, lubricant and specimens used in the experiments are listed in Table 2. Sn and Fe nanoparticles were separately dispersed in MACs oil with the concentrations of 0.1–0.5–1.0 wt.% using an ultrasonic probe for 5 min.

2.2. Friction and wear test

To study the friction-reduction, anti-wear and frictional heat reduction properties of these nanoparticles, a vacuum four-ball tribometer was employed, which was designed and manufactured based on the configuration of a traditional four-ball tribometer by the State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. As shown schematically in Fig. 1, the vacuum chamber was evacuated by a series of a turbo molecular pump and a mechanical pump. The tribological characteristics of liquid lubricants for space applications were evaluated by this tribometer under the pressure of 2.0×10^{-4} Pa. The apparatus can also be operated at low vacuum

Table 2
Material properties.

Material	Properties				
Nanoparticles	Morphology	Size (nm)	Shear modulus (GPa)	Melting point (°C)	Brinell hardness (N/mm ²)
Sn	Spherical	30–60	15.6	232	51
Fe	Spherical	20–70	77.5	1535	490
Base oil Physical properties					
MACs	Average molecular weight: 630 Surface tension: 24.5 mN m ⁻¹ Kinematic viscosity: 56 cSt (40 °C), 9.3 cSt (100 °C) Viscosity index: 148 Vapor pressure (20 °C): 5.6×10^{-6} Pa				
Specimens	Properties				
Test ball	Steel: AISI 52100 Brinell hardness: 705 N/mm ² $d = 12.7$ mm $R_a = 0.025$ μm Chemical composition: 0.95–1.05%C, 0.25–0.45%Mn, 0.15–0.35%Si, 1.40–1.65%Cr, ~0.30%Ni, ~0.25%Cu, ~0.025% S, ~0.025%P				

(about 10 Pa) and at atmospheric pressure with air or other atmosphere.

Different additive concentrations were adopted to examine the effect of nanoparticles on friction-reduction, anti-wear and frictional heat reduction performances of MACs base oil under high vacuum ($\sim 10^{-4}$ Pa). All tests were performed under the load of 300 N with a rotating speed of 1450 rpm at 25 °C for 30 min. Before and after each test, test specimens were ultrasonically cleaned in petroleum ether (normal alkane with a boiling point of 60–90 °C). For each sample, three tests were conducted to minimize data scattering. At the end of each test, the wear scar diameters of the three lower balls were measured with an optical microscope with an accuracy of 0.01 mm, and then the average wear scar diameter of the three identical tests was calculated as the wear scar diameter (WSD) in this paper.

2.3. Analysis instruments

The crystal structure of nanoparticles was measured by the X'Pert PRO polycrystalline powder X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. To learn about detailed information on contact surfaces, the topography of the wear scar surfaces was examined with the SEM (JSM-5600LV). The Kevex EDX was employed to analyze the composition of chemical elements on the worn surfaces.

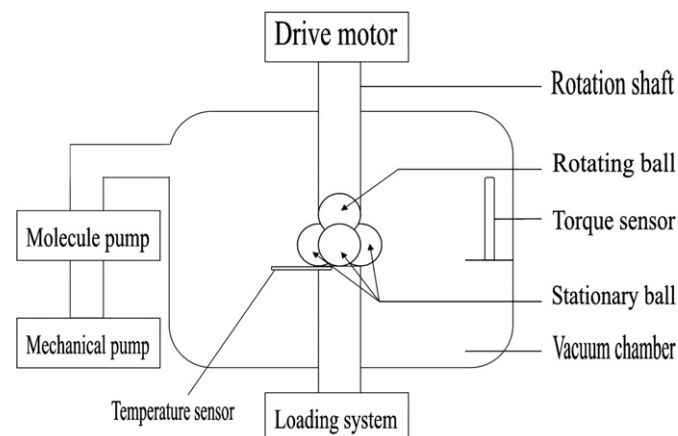


Fig. 1. Schematic illustration of the vacuum four-ball tribometer.

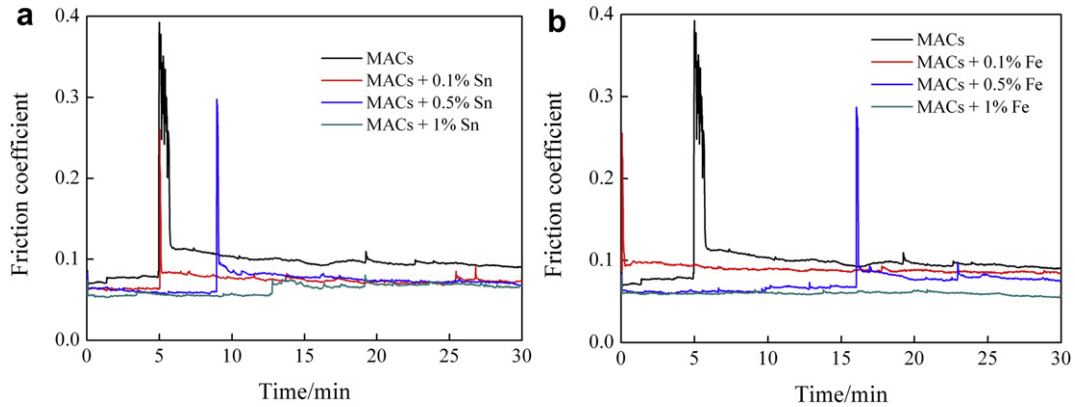


Fig. 2. Friction coefficient as a function of rotating time for MACs with nanoparticles under vacuum condition: (a) Sn; (b) Fe.

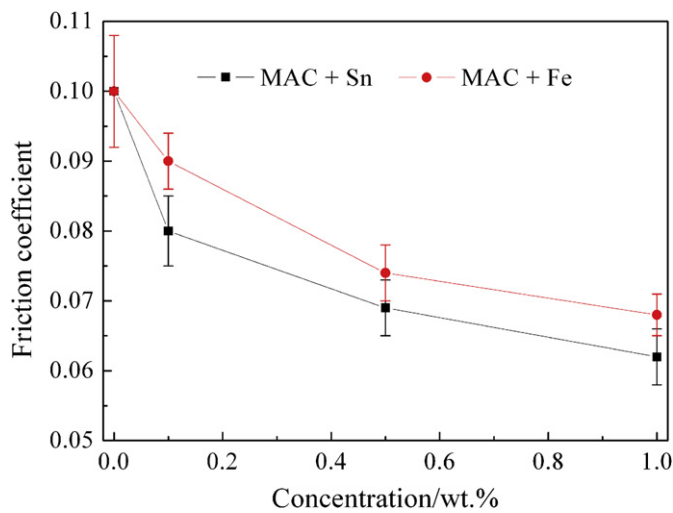


Fig. 3. Friction coefficient as a function of nanoparticle concentration for all tested oil samples.

3. Results and discussion

Fig. 2 shows the influence of nanoparticle concentrations in MACs on the friction coefficient under vacuum condition. It can be seen that the steel balls showed transient seizure-like high friction under vacuum condition lubricated with MACs oil. Then, a low friction coefficient around 0.1 was obtained that is

indicative of good lubrication. The result could be explained as that some species, such as carbon coating, might be produced during the high friction period to lubricate surfaces and to facilitate return to a low friction condition [10]. Adding Sn and Fe nanoparticles could effectively reduce the transient seizure-like high friction. The steel balls exhibited stable friction coefficients without any transient high friction when lubricated by the MACs with 1% Sn or 1% Fe nanoparticles, comparing with other additive concentrations. The transient seizure-like high friction was also observed when lubricated by the MACs with 0.1% and 0.5% nanoparticles, but their magnitudes are lower, and the durations are shorter than MACs oil. Fig. 3 illustrates that the lowest friction coefficient of all tested oil samples was found for a content of 1% for the both kind of nanoparticles. It is worth noting that Sn nanoparticles exhibited more effective friction-reduction ability than Fe nanoparticles for each additive concentration.

Fig. 4 shows the influence of additive concentrations on the temperature of oil samples under vacuum condition. The temperature rise caused by frictional heat for each oil sample differed depending on nanoparticle concentration. As shown in Fig. 4, the smoothest temperature–time curves were found for a nanoparticle content of 1% for Sn and Fe. For each nanoparticle concentration, the temperature rise of these oil samples appeared the similar variation tendency with the friction coefficient. Fig. 5 shows that the lowest temperature rise of all the tested oil samples was also found for a content of 1%. In addition, Sn nanoparticles were more effective in temperature rise reduction than Fe nanoparticles for each additive concentration.

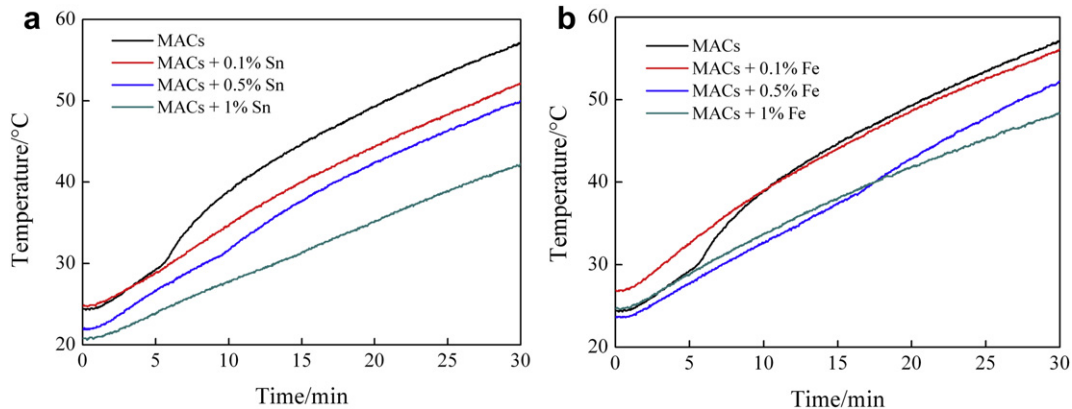


Fig. 4. Temperature as a function of rotating time for MACs with nanoparticles under vacuum condition: (a) Sn; (b) Fe.

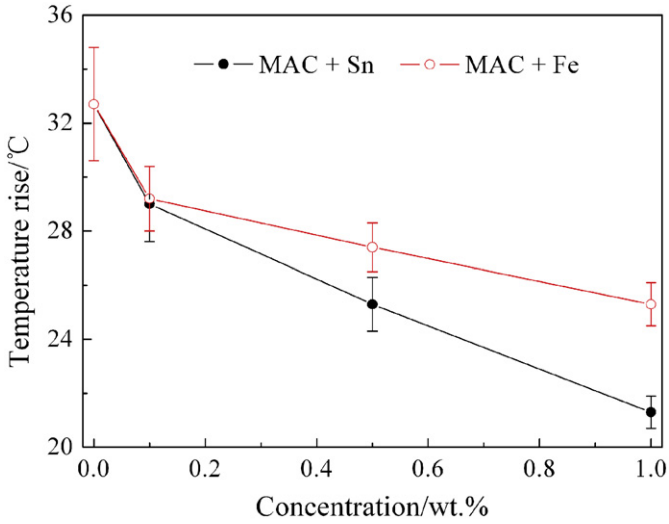


Fig. 5. Temperature rise as a function of nanoparticle concentration for all tested oil samples.

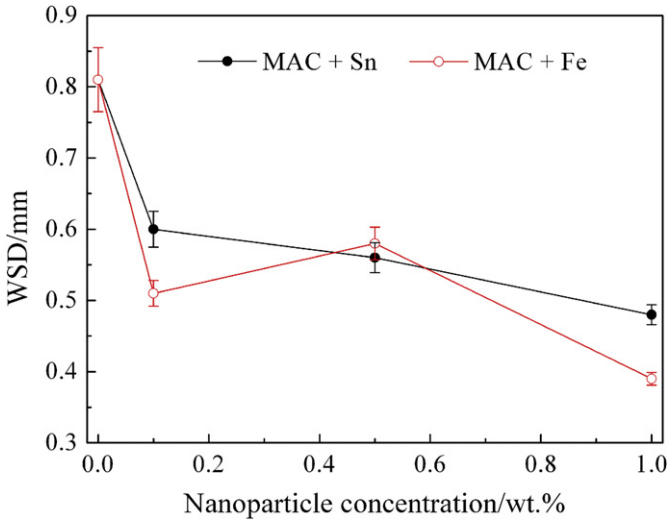


Fig. 6. WSD values as a function of nanoparticle concentration for all tested oil samples.

In Fig. 6, it could be found that both kind of nanoparticles exhibited good anti-wear behavior. The lowest WSD value was obtained by the 1% additive concentration for the both nanoparticles. Moreover, Fe nanoparticles exhibited more effective

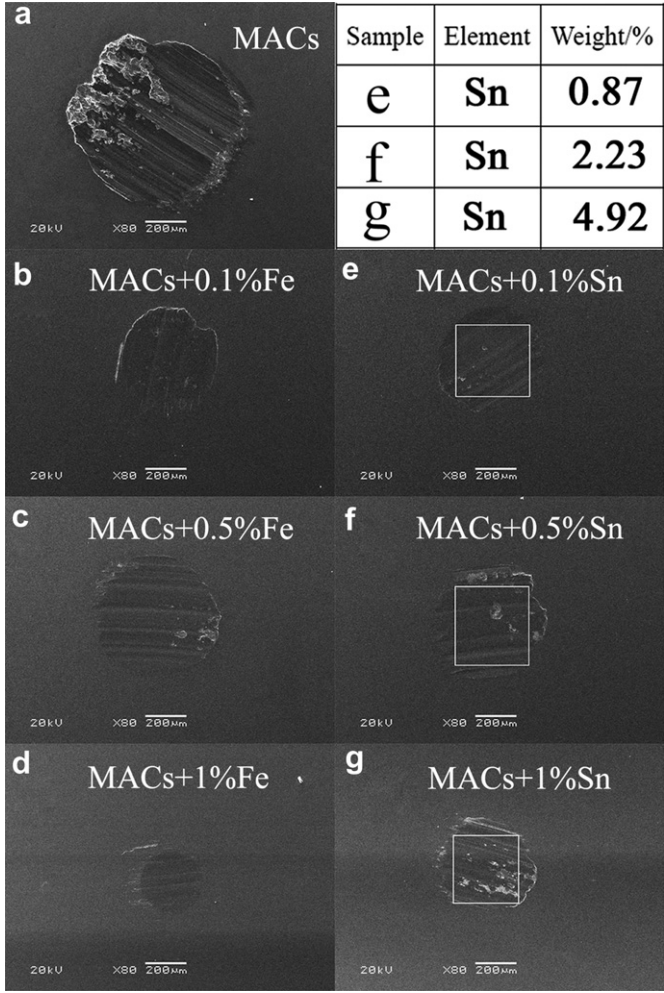


Fig. 8. SEM micrographs and elemental analysis of the wear scar surfaces lubricated by the different nanoparticle concentration MACs oil: (a) MACs oil; (b–d) Fe nanoparticle oil samples; (e–g) Sn nanoparticle oil sample; the table list the Sn elements content of the marked area of (e–g).

anti-wear ability than Sn nanoparticles for all additive concentration except for 0.5%. The further research works are needed for such unexpected difference caused by 0.5% nanoparticle concentration. In conclusion, the steel ball showed lower friction coefficient, lower temperature rise and larger WSD value when lubricated by MACs with Sn nanoparticle additives in comparison with those by MACs with Fe nanoparticle additives.

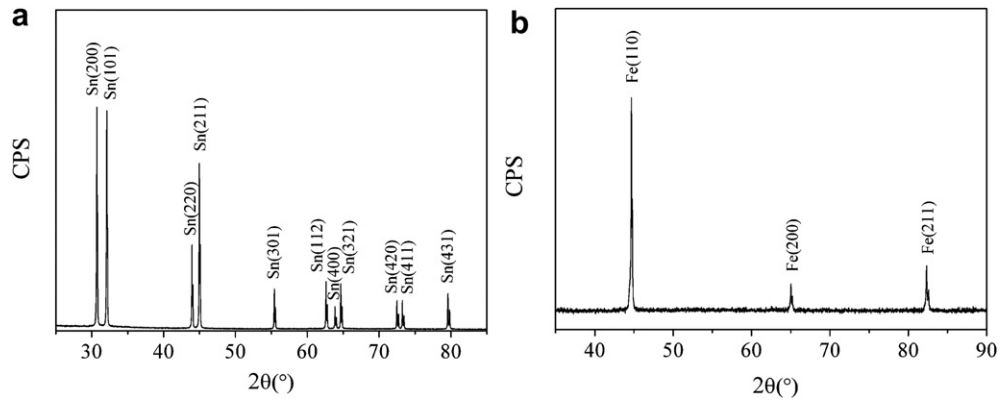


Fig. 7. X-ray diffraction pattern of nanoparticles: (a) Sn; (b) Fe.

Friction coefficient, wear and temperature rise variations of oil samples as a function of nanoparticle content are related to hardness, shear modulus and crystal structure of nanoparticles on wear surfaces. As shown in Table 2, Sn and Fe have lower hardness than the steel balls. Therefore, it is possible for Sn and Fe nanoparticles to form Sn or Fe metallic films on the surfaces of the steel ball under high pressure. The metallic films with relatively low shear modulus could separate the steel friction pairs from each other and effectively inhibit the transient high friction under vacuum condition. Furthermore, the hardness and shear modulus of Sn nanoparticles are lower than these of Fe nanoparticles. As a result, it would be easier for Sn to form a metallic film with lower shear stress on the steel balls. Therefore, Sn nanoparticles could be more effective in friction-reduction and temperature rise reduction than Fe nanoparticles.

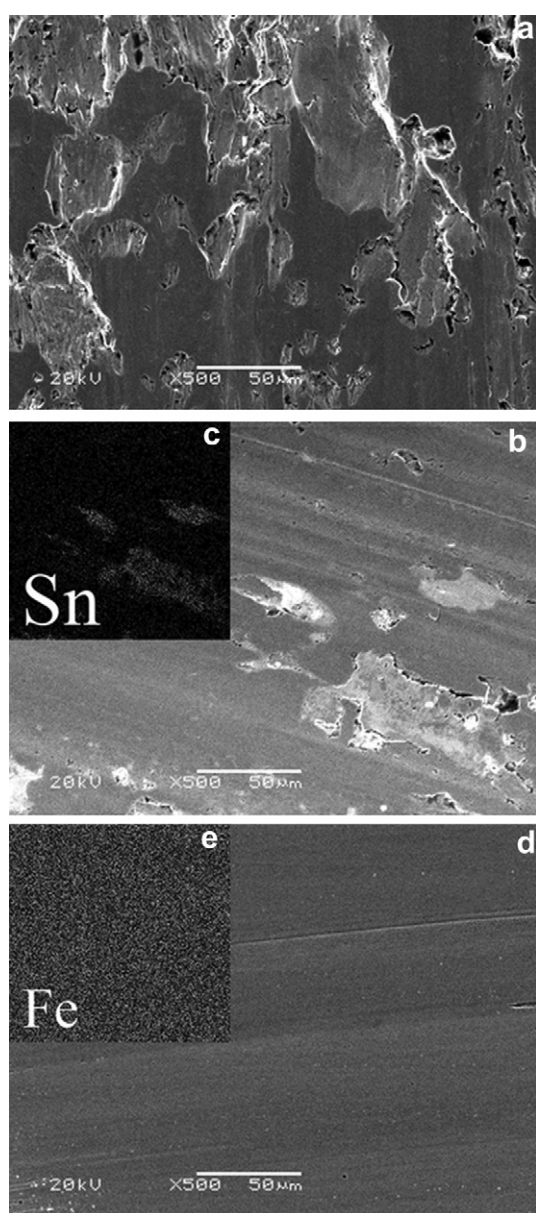


Fig. 9. High-magnification SEM micrographs and elements mapping of the wear scar surfaces for the oil samples: (a) MACs oil; (b) MACs + 1% Sn; (c) Sn elements mapping of (b); (d) MACs + 1% Fe; (e) Fe elements mapping of (d).

Besides the temperature rise reduction and friction-reduction abilities, the both kind of nanoparticles also exhibited good anti-wear ability via the deposition of nanoparticles to repair the worn surfaces. From Fig. 7, it can be observed that crystal structure of Sn nanoparticles is tetragonal and the crystal structure of Fe nanoparticles is body-centered cubic. As the main composition of the tested steel balls is Fe, Fe nanoparticles may have much higher solubility in the ball surfaces than Sn nanoparticles. As a result, Sn metallic films formed on the steel ball surfaces will be less steady and more easily to be removed in comparison with Fe metallic films. Therefore, Fe nanoparticles could be more effective on anti-wear ability than Sn nanoparticles.

After tribological tests, the wear scar surfaces of the steel balls were analyzed by SEM and EDX. The results are shown in Fig. 8. It can be observed that only the chemical elements presented in steel could be found when lubricated by MACs. In the tests with Sn nanoparticle oil samples, Sn appeared on the wear scar surfaces, while for Fe nanoparticle oil samples, it cannot differentiate the deposited Fe and the Fe element existed in the steel ball. It is also suggested that the higher the nanoparticle concentration is in the MACs oil, the higher deposition on the wear scar surfaces will be obtained, and higher nanoparticle concentration is beneficial for improving the tribological properties of the MACs oil.

More detailed analysis about the wear scar surfaces was done by SEM and EDX in order to study the formation of the protective metallic films. As shown in Fig. 9, without the nanoparticles additives, severe plastic deformation and adhesive wear could be found on the rough and worn steel ball surfaces. Sn nanoparticles were bogged down along the wear scar direction to repair the worn surface, and therefore smoother worn surface was obtained in comparison with that by pure MACs oil. As discussed above, due to higher solubility in the steel ball surfaces, Fe nanoparticles should exhibit better anti-wear ability, which was confirmed in Fig. 9. The smoother wear scar surface was found for Fe nanoparticle oil sample in comparison with Sn nanoparticle oil sample.

4. Conclusions

The following conclusions can be drawn from the results and discussions above:

- 1) Under vacuum condition, the steel balls exhibited the transient seizure-like high friction and severe surface damage when lubricated by MACs oil.
- 2) Both the Sn and Fe nanoparticles exhibited friction, wear and frictional heat reduction in comparison with MACs oil. The higher Sn nanoparticle concentration is in MACs oil, the more deposition of Sn is on the worn surfaces, and the better tribological behavior would be got, which was similar with Fe nanoparticles.
- 3) The tribological mechanism of the metallic nanoparticle additives was that a protective film with low shear stress and hardness was formed on the worn surface during friction tests.
- 4) With higher hardness, higher shear modulus and higher solubility with the frictional pair, Fe nanoparticles are more effective in anti-wear, but less effective in friction-reduction and temperature rise reduction in comparison with Sn nanoparticles.

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