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ORIGINAL PAPER

Study on the Synthesis and Tribological Property of Fe_3O_4 Based Magnetic Fluids

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Abstract In this paper, Fe_3O_4 based magnetic fluids with different particle concentrations were prepared by the co-precipitation technique. The size of the Fe_3O_4 nanoparticles is about 13 nm and their shape is spherical. The tribological performances of the fluids with different concentration Fe_3O_4 nanoparticles were evaluated in a MMW-1A four-ball machine. The results show that the tribological performance of magnetic fluids with proper Fe_3O_4 nanoparticles can be improved significantly. The maximum nonseized load (P_B) has been increased by 38.4% compared with carrier liquid. The wear scar diameter has been reduced from 0.68 mm to 0.53 mm and the relative percentage in friction coefficient has decreased to 31.3%. The optimal concentration of the Fe_3O_4 nanoparticles in the carrier liquid is about 4 wt.%.

Keywords Magnetic fluid · Fe_3O_4 nanoparticles · Tribological properties · Wear reduction

1 Introduction

Lubrications are widely utilized in the industry, especially in machine industry. The proper use of the lubrications can improve the efficiency of the engine, economize on energy as well as prolong the machine life. In the past few decades, putting oil-soluble additives into oil to reduce friction coefficient and improve anti-wear ability or to mend a worn surface have been widely applied in lubrication engineering [1–3]. However, the use of these additives has brought about some problems, such as toxicity, waste disposal, pollution, etc.

With the development of nanomaterials, nanoparticles were added into lubricating oils to improve extreme pressure, anti-wear, and friction reducing properties. Joly-Pottuz et al. [4] studied the anti-wear and friction reducing mechanisms of carbon nano-onions as lubricant additives. Proper concentration of graphite nanosheets as additive in oil shows better tribological properties than pure paraffin oil [5] and the wear resistance of the paraffin oil was also improved by the addition of the MoS_2 nanoparticles [6, 7]. Wu et al. [8] have reported that CuO nanoparticles added to standard oils exhibit good friction–reduction and anti-wear properties. All the nanomaterials mentioned above are nonmagnetic and there are few reports on tribological properties of magnetic nanoparticles as an oil additive.

Magnetic fluid is a stable colloidal suspension of single domain ferromagnetic nanoparticles dispersed in base oil and stabilized by means of a suitable organic surfactant [9]. Brownian motion keeps the magnetic particles from settling under gravity, and surfactant is placed around each particle to provide short range steric repulsion between particles to prevent particle agglomeration. Stable suspensions of this kind were first synthesized in 1964 by Papell and have meanwhile reached even technical importance in everyday life [10]. As mentioned above, magnetic fluids are homogeneous fluids which can be magnetized by applying an external magnetic field, but still retaining the properties of the fluid. These fluids show unusual properties, e.g., they can be confined, positioned, shaped, and controlled at desired places by applying an external magnetic field. This leads to important applications of magnetic fluid lubrication in liquid seals, roller bearing, and so on.

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In this paper, Fe_3O_4 based magnetic fluids with different concentrations were prepared by the co-precipitation technique. The tribological properties of the Fe_3O_4 based magnetic fluids were investigated by a four-ball machine. The results show that the Fe_3O_4 based magnetic fluids with proper concentration exhibit good performance in anti-wear and friction–reduction.

2 Experimental Details

2.1 Sample Preparation and Characterization

In a first step, Fe_3O_4 nanoparticles coated with a primary surfactant (oleic acid) were obtained by chemical co-precipitation from an aqueous solution of Fe(II) and Fe(III) salts in the presence of 25% $NH_3 \cdot H_2O$ solution at room temperature. Then the Fe_3O_4 nanoparticles coated with oleic acid was washed four times with distilled water so as to remove impurity. Then water in the particles was removed by washing with acetone. The resulting particles coated with a secondary surfactant (T161) were dispersed in α-olefinic hydrocarbon synthetic oil (PAO4) by ultrasonic method. The final fluid was centrifuged at 12,000 rpm for 10 min. The detailed synthetic procedures can be found elsewhere [11].

After synthesized, X'Pert PRO (Panalytical) X-ray diffractometer was used to analyze the phase composition of magnetic particles. The diffraction was performed with $Co_{k\alpha_1}$ ($\lambda = 1.7889$ Å) and the ray was filtered by the graphite. The experimental parameters used were: 40 mA, 35 kV, continuous scan, and a scan speed of 2°/min. The transmission electron microphotographs of the nanoparticles were obtained using a 2100fx transmission electron microscope (TEM) operated at 200 keV. Samples were prepared by air-drying drops of diluted solutions of the preparations on carbon films supported by copper grids. The stability of the magnetic fluids prepared was roughly estimated from the percent of particle suspending percentage [12].

2.2 Tribological Experiments

The friction and wear tests were carried out at ambient temperature on a MMW-1A four-ball machine made in Jinan Yihua Tribology Testing Technology Co. Ltd of China. The friction and wear tests were conducted at a rotating speed of 1,450 rpm and load of 588 N, for 30 min. The maximum nonseized loads (P_B value) were tested. The P_B values were recorded at room temperature for a duration of 10 s. All the balls used in the test were 12.7 mm diameter made of GCr15 bearing steel (C, 0.95–1.05%; Si, 0.15–0.35%; Mn, 0.20–0.40%; P, <0.027%; S, <0.020%; Cr, 1.30–1.65%; Ni, <0.30%; Cu, <0.25%) with an HRC 59–61. Before each test, the steel balls were cleaned in petroleum ether and dried. The balls after testing were cleaned using ultrasonic bath in ligroin and then in distilled water for 10 min, respectively. The wear scar diameters on the steel balls were measured using an optical microscope to an accuracy of ±0.01 mm. The friction coefficients were automatically measured and recorded. Duplicate tests were run with each oil sample and, if the wear scar diameters showed a relative error above 10%, additional tests would be run until at least two of the results agreed within 10%. The worn surfaces of the balls were examined by scanning electron microscope (SEM JSM-6480LV); and energy dispersive spectrometry (EDS) was used to detect to elements present on wear scar surfaces.

3 Results and Discussion

3.1 Characterization of the Particles

Figure 1 shows the X-ray diffraction pattern of the nanoparticles. It was indicated that the synthesized samples consisted of cubic phase Fe_3O_4 (JCPDS 19-629), i.e., magnetite. The broadening Bragg peaks for the as-prepared Fe_3O_4 are due to their small particle size. The average grain size perpendicular to (3 1 1) of 12.5 nm was calculated from X-ray line broadening analysis by Scherer formula [13]. Besides, the unit-cell parameter calculated was $a = 8.370$ (Å), which are approximate to the results of $a = 8.396$ (Å) reported in JCPDS 19-629.

Figure 2 shows the transmission electron micrograph of the Fe_3O_4 powder and the shape of the particles is nearly spherical. It can be seen from Fig. 2 that the particles have an average size of about 14 ± 2 nm which is higher than the value determined by XRD. The reason may come from the overlap of the nanoparticles during the TEM analysis.

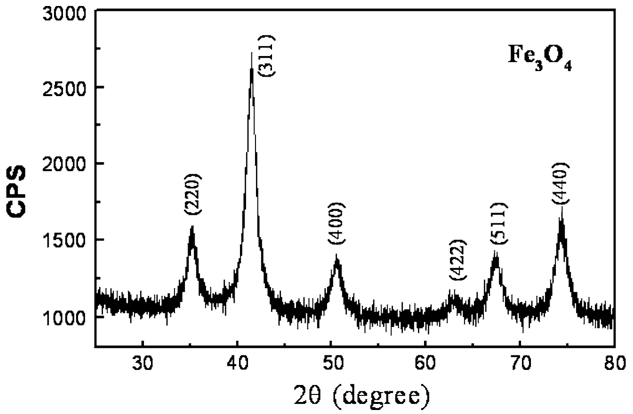

Fig. 1 X-ray diffraction pattern of Fe_3O_4 magnetic nanoparticles ($Co_{k\alpha_1}$)

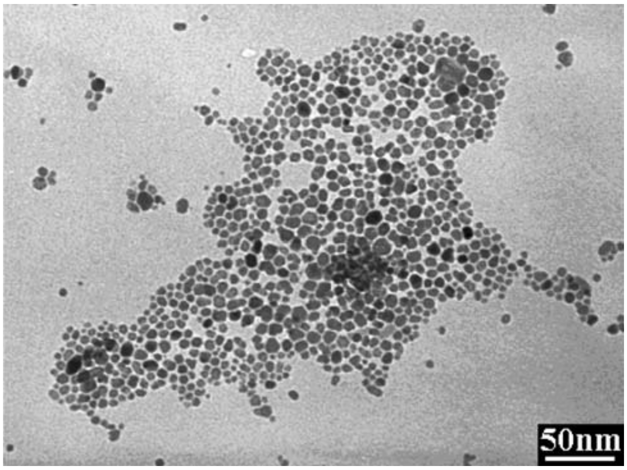

Fig. 2 TEM image of Fe_3O_4 particles

According to reference [12] the stability of the magnetic fluids was estimated. After resting for 10 days, the particle suspension percentage of all the magnetic fluid samples are keeping above 98%. And it means that the magnetic particles can be coated completely by the surfactant and dispersed in the carrier liquid homogeneously.

3.2 Effect of Fe_3O_4 Concentration on Maximum Nonseized Load

Maximum nonseized load (P_B) represents the load-carrying capacity of the lubricant. Figure 3 gives the P_B values of different concentration Fe_3O_4 based magnetic fluids and the carrier liquid (PAO4 + 6 wt.%T161) examined on a MMW-1A four-ball machine.

It can be seen that Fe_3O_4 based magnetic fluids exhibit good load-carrying capacity, but the lubricating effect depends on the concentration of Fe_3O_4 nanoparticles. The P_B rises as the concentration of Fe_3O_4 nanoparticles increases below 4 wt.%, and when the concentration is higher than 4 wt.%, the P_B decreases on the contrary. This result means that excessive Fe_3O_4 nanoparticles in the fluid leads to a decrease in maximum nonseized load of the magnetic fluids. It is known that the Fe_3O_4 nanoparticles can be treated as single domain particles and each of them is a small permanent magnet in the carrier liquid [10]. The magnetic moment of each of the particles is of the order of about 10^4 μ_B. In a diluted magnetic fluid the magnetic particles can be thought of as noninteraction but at higher concentrations, the dipolar interactions between particles have to be taken into account [14]. Owing to the dipolar–dipolar interaction, a particle tends to attract the neighboring particles in the direction of its magnetic moment and some coagulations or chain-like clusters may be formed [15] which made the friction unstable or caused vibration and the maximum nonseized load decreases.

3.3 Effect of Fe_3O_4 Concentration on Anti-wear Properties

From Fig. 4 it is obvious that wear scar diameters increase with friction time in the four cases. And the wear scar diameter lubricated with 4 wt.% concentration Fe_3O_4 fluid is the smallest. The result further indicates that magnetic fluid with 4 wt.% Fe_3O_4 nanoparticles has the best wear resistance compared with the carrier liquid. The mechanisms of anti-wear can be explained as follows: (a) the spherical shape Fe_3O_4 nanoparticles opens the possibility for an effective rolling friction mechanism which will decrease the shearing stress between the steel balls; (b) the Fe_3O_4 nanoparticles serve as spacer, which eliminate metal to metal contact between steel balls.

Figure 5 gives the wear scar diameters on the ball running in magnetic fluids containing 4 wt.% Fe_3O_4 nanoparticles and in carrier liquid (PAO4 + 6 wt.%T161) after 30 min. It can be seen from Fig. 5 that the wear scar diameter reduced from 0.68 mm to 0.53 mm compared

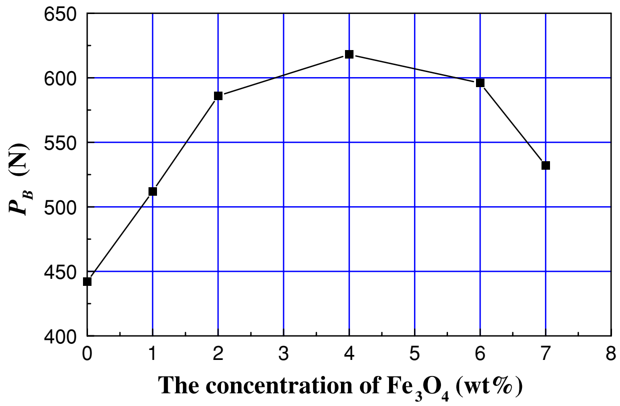

Fig. 3 Variation of maximum nonseized load (P_B) with the concentration of Fe_3O_4 nanoparticles

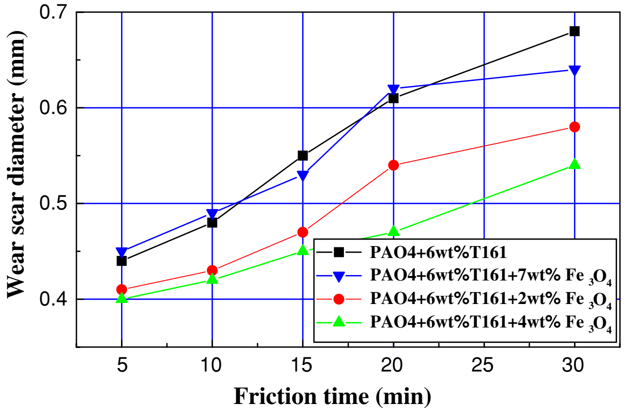

Fig. 4 Dependence of wear scar diameter on friction time (four-ball, 1,450 rpm, 588 N)

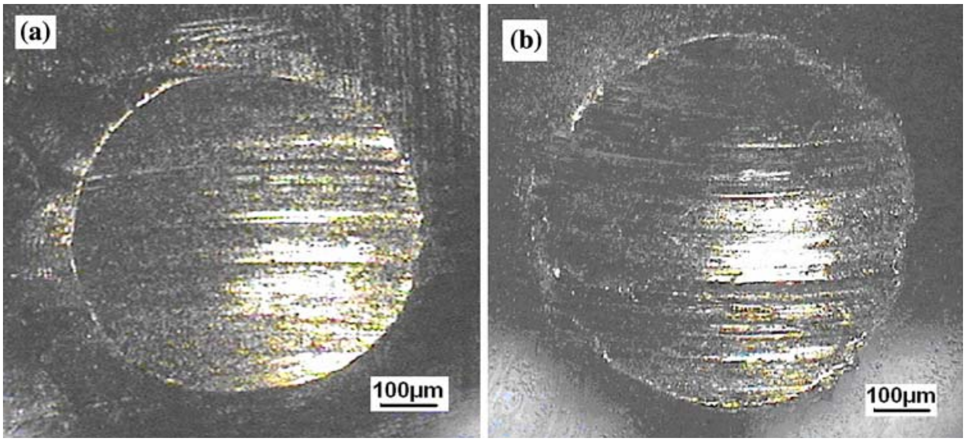

Fig. 5 Images of wear scar diameter (**a**) lubricated with 4% magnetic fluid; and (**b**) lubricated with carrier liquid (four-ball, 1,450 rpm, 588 N, 30 min)

with the carrier liquid (PAO4 + 6 wt.%T161). Nevertheless, when the concentration of Fe_3O_4 nanoparticle is above 4 wt.%, the wear scar diameter increased quickly. The result is coincident with the maximum nonseized load at the particle concentration of 4 wt.%.

3.4 Effect of Fe_3O_4 Concentration on Friction Coefficient

Figure 6 shows the dependence of the friction coefficient on friction time lubricated with different concentration magnetic fluids and the carrier liquid (PAO4 + 6 wt.% T161). Figure 7 gives the SEM images of the rubbing surface lubricated by carrier liquid, 4 wt.% and 7 wt.% concentration Fe_3O_4 magnetic fluids after tribo-testing for 30 min, respectively. And the corresponding elemental components are also shown in Fig. 7.

From Fig. 6 we can see that the magnetic fluids with 2 wt.% and 4 wt. % particle concentrations gave smaller and more stable friction coefficients than carrier liquid. It was reported [16] that hard enough wear particles may even act like rollers between two surfaces. The Fe_3O_4 nanoparticles in the fluids may play as the rollers and the relative percentage in friction coefficient has decreased 32.1% between 4 wt.% concentration of magnetic fluid and carrier liquid. Experimental results indicate that 4 wt.% concentration magnetic fluid lubrication is located in mixed-film lubrication regime. From Fig. 6 we can also see that the friction coefficient of 7 wt.% magnetic fluid increases with friction time. A possible explanation is that some coagulation was formed for the ferromagnetism of the particles and high particle concentration which will reduce the ball effect.

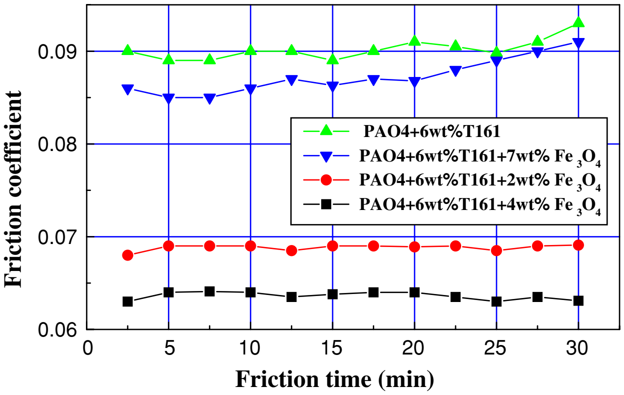

Fig. 6 Dependence of the friction coefficient on friction time (four-ball, 1,450 rpm, 588 N)

The evidence of reducing the friction and wear of proper concentration Fe_3O_4 nanoparticles in magnetic fluid can be confirmed by the results of SEM. It can be found that the worn surface lubricated by carrier liquid shown in Fig. 7a is evidently rough with many thick and deep furrows, but the rubbing surface lubricated by 4 wt.% particle concentration magnetic fluid is rather smoother and the furrows are rather shallower (Fig. 7b). The worn surface (Fig. 7c) lubricated by 7 wt.% particle concentration magnetic fluid is also rough but the furrows are shallower compared to Fig. 7a. EDS in Fig. 7 shows that oxygen content on the rubbing surface increases. The results indicate that the content Fe_3O_4 particles deposition on the ball surface increases with the increasing particle concentration in the magnetic fluid.

4 Conclusion

Fe_3O_4 based magnetic fluids with different concentrations were prepared by the co-precipitation technique. The size of the spherical Fe_3O_4 nanoparticles is about 13 nm. The load-carrying capacity and wear resistance of magnetic fluids with proper concentration nanoparticles can be improved compared with the carrier liquid. There is an optimal content of Fe_3O_4 nanoparticles in the carrier liquid, which gives the highest maximum nonseized load and anti-wear ability.

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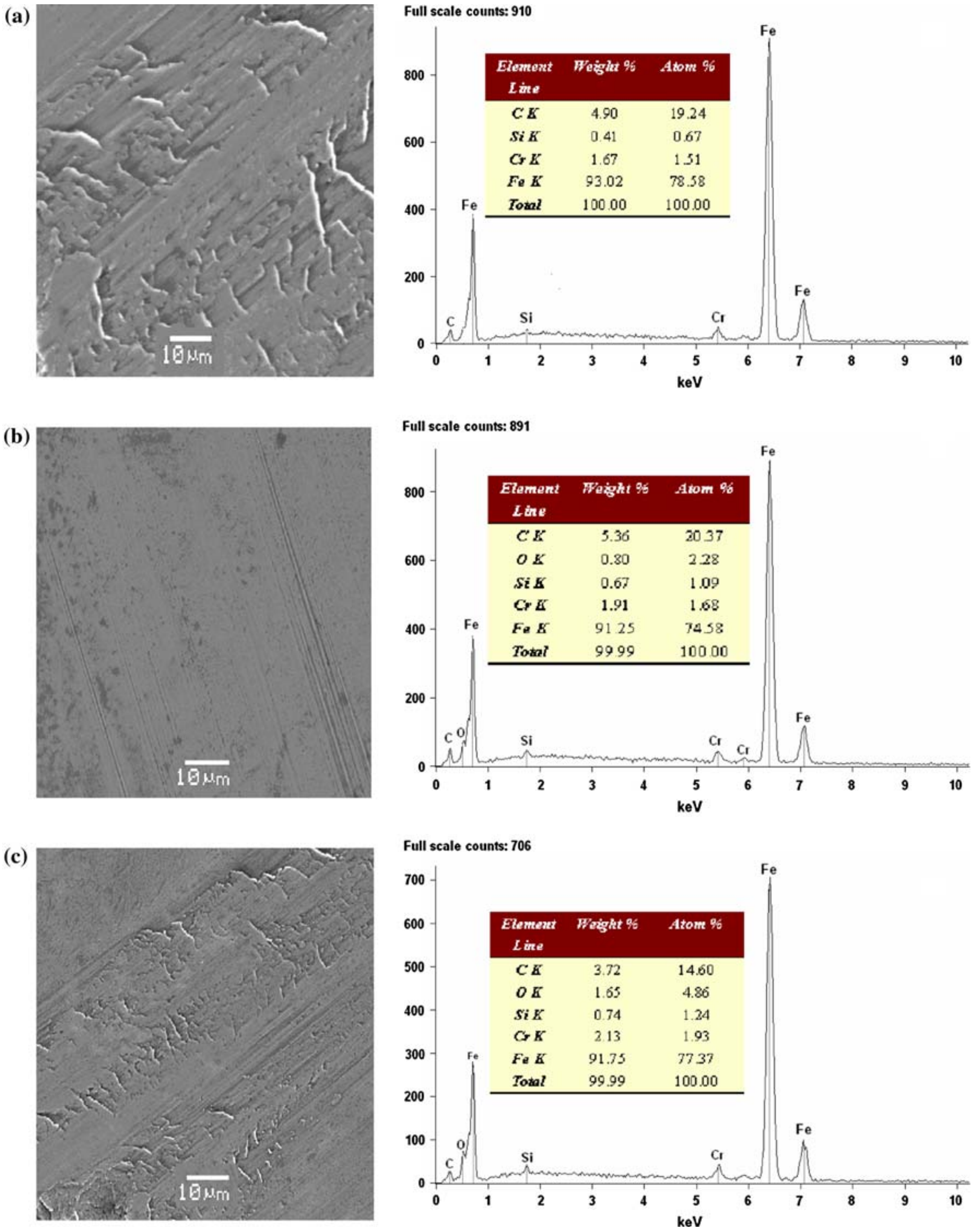

(a)

Element Line	Weight %	Atom %
C K	4.90	19.24
Si K	0.41	0.67
Cr K	1.67	1.51
Fe K	93.02	78.58
Total	100.00	100.00

(b)

Element Line	Weight %	Atom %
C K	5.36	20.37
O K	0.80	2.28
Si K	0.67	1.09
Cr K	1.91	1.68
Fe K	91.25	74.58
Total	99.99	100.00

(c)

Element Line	Weight %	Atom %
C K	3.72	14.60
O K	1.65	4.86
Si K	0.74	1.24
Cr K	2.13	1.93
Fe K	91.75	77.37
Total	99.99	100.00

Fig. 7 The images and elemental components on the worn surface of steel ball: (**a**) lubricated with carrier liquid; (**b**) lubricated with 4% magnetic fluid; and (**c**) lubricated with 7% magnetic fluid (four-ball, 1,450 rpm, 588 N, 30 min)

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