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ORIGINAL PAPER

Effect of Nano-Cu Lubrication Additive on the Contact Fatigue Behavior of Steel

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Abstract Effects of four different concentrations of nano-Cu lubrication additives on contact fatigue properties of GCr15 steel friction pairs were evaluated on a ball-rod contact fatigue tester. The anti-fatigue mechanisms of these additives were analyzed by means of scanning electron microscopy and X-ray photo electron spectroscopy. The test results and analyses show that all of these additives can raise the contact fatigue life of steel ball elements to a certain extent. The action of 10% additive is the better. It is confirmed that the main failure of the steel ball element is fatigue desquamation. The anti-fatigue mechanism of lubrication additives mainly accounts for forming a chemical reaction film on the steel rod and ball surface and decreasing in friction between the ball and rod, enhancing the ability of anti-wear.

Keywords Contact fatigue · Nano-Cu · Lubrication additive · Ball-rod contact fatigue tester

1 Introduction

In the past few years, metal nanoparticles have been of considerable interest by virtue of their unique physical and chemical properties. Soft metal nanoparticles and their alloys have be used as additives and have been proved to possess excellent antiwear and extreme pressure properties, and their tribological behavior and mechanism have been studied and discussed [1]. Due to the remarkable tribological properties of Cu nanoparticles, together with good self-repair functions to the worn surface, and an excellent environmental-friendly property, they have been desired for an excellent candidate for traditional lubricant additives.

Many influencing factors have been considered, and the tribological behaviors of Cu nanoparticles as an additive have been investigated, such as the concentration of nanoparticles in oil, sliding speed, applied load, contact form of friction pairs and lubricating oils. Zhou et al. [2, 3] pointed out that the size and additive concentration of copper nanoparticles have a remarkable effect on their lubricating properties. The antiwear ability, friction-reduction properties and load-carrying capacity were attributed to a synergistic effect between the reaction film formed by the surface modification agent and the deposited film of Cu during the friction process. Choi et al. [4] found that there was no considerable effect of nanoparticle size on the friction coefficient as between 25 and 60 nm copper nanoparticles, the nano-oil mixed with the two copper nanoparticles have a lower friction coefficient and less wear on the friction surface. The effect of temperature on tribological properties of Cu nanoparticles was also investigated on a four-ball tester. The results indicate that the higher the oil temperature applied, the better the tribological properties of Cu nanoparticles were [5]. It is observed that copper nanopowder additive to SAE 30 motor oil reduces friction most effectively at higher loads and higher sliding speeds [6]. The tribological properties of DDP-capped Cu nanoparticles in different base oils studied by Yang et al. [7] indicate that copper nanoparticles exhibit excellent antiwear and friction-reducing properties in all kinds of oils. Unfortunately, until now, few investigations

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have mentioned the contact fatigue life effect of solid–liquid nano-metal additive.

In this paper, we studied the contact fatigue and crack effect of the copper additive in the base lubricant oil after forming the solid–liquid lubricant. Furthermore, the mechanism was investigated as well, which may provide a new way to improve the contact fatigue properties of rolling bear and to open out self-repairing lubricant.

2 Experimental

2.1 Contact Fatigue Test

A ball-rod contact fatigue tester made by Harbin Polytechnical University (Harbin, China) was used to carry out the contact fatigue test. The details about the tester are provided elsewhere [8]. Briefly, a steel rod (AISI-1045 steel, ∅11 mm × 200 mm, root mean square (RMS) roughness $Ra = 0.14$ μm, HRC 58–62) is driven by a motor to run against a set of steel balls (AISI-1045 steel, ∅11 mm, HRC 58–62, $Ra = 0.12$ μm; three balls arranged laterally around the steel rod at an in-between angle of 120°) at a pre-set speed. A counterweight is used to apply force. The force is magnified by a lever and transferred by a load cover, followed by magnifying with tapering to generate a high contact force between the steel balls and steel rod. An auto-heating unit is installed with the tester to monitor the temperature of lubricating oils, and the tester is designed to automatically stop at a certain level of contact fatigue. The contact fatigue life is recorded by an auto-timing unit. It's very important to choose suitable load that is the beginning contact stress during the high-speed contact fatigue test. If the load is too high, the rotation between the steel ball and the rod will become difficult, leading to the tester not to worker. On the contrary, if the load is too low, the steel ball will not become fatigued in a long time, which will lead to the test period too long. Based on a series of screening test, a load of 110 N is selected in the present research, at which a contact pressure of 6.85 GPa is realized. At the same time, no. 20 mechanical oil was used as the lubricating basestock, and DDP (surface-capped by dialkydithiophosphate) was used as the oil soluble nano-copper additive. Figure 1 shows its TEM image, which indicates that the additive consists of non-aggregated nanoparticles with a diameter of 5–7 nm, and the additive prepared at our laboratory was ultrasonically dispersed in the base oil at a volume fraction of 2.5, 5.0, 7.5 and 10.0%, respectively. Aiming at revealing its effect on the contact fatigue behavior of the steel–steel pair, six repeat tests were conducted for the base stock and the four oil samples doped with nano-Cu additive. The numerical analysis of the six repeat tests were reported in this article.

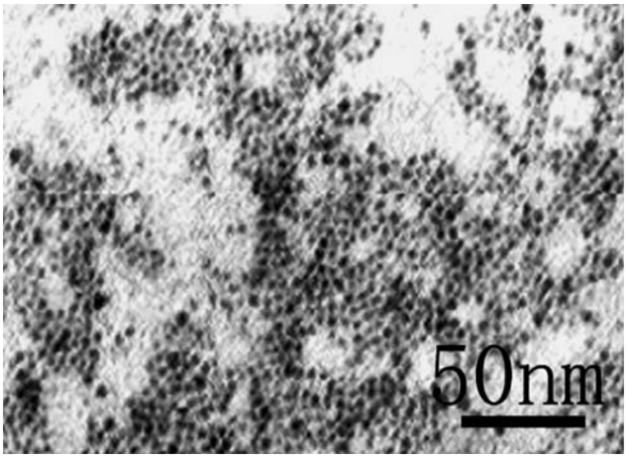


Fig. 1 TEM image of oil-soluble nano-copper additive

2.2 Analysis of Fatigued Surfaces of the Steel Pair

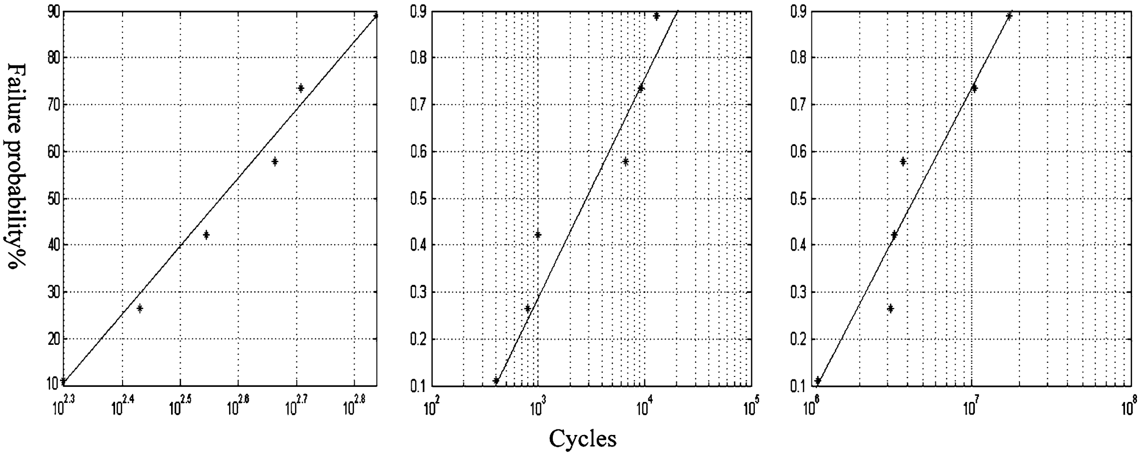
A JSM5600 scanning electron microscope (SEM, with an accelerating voltage of 30 kV) was used to observe the morphologies of the fatigued surfaces of the steel pair. The chemical states of some typical elements on the fatigued surfaces of the steel pair were analyzed by means of X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultra, Shimadzu Group Company, equipped with a standard and monochromatic Mg K_α source). The binding energy (BE) scale was calibrated against the BE of C1s at 284.80 eV.

3 Results and Discussion

Table 1 shows the fatigue test results for different oil samples. Figure 2 gives the fatigue life curve based on the Weibuer probability statistic method. It is seen that the introduction of the nano-Cu additive contributes to greatly increasing the fatigue life of the base oil, and the fatigue life increases with increasing concentration of the nano-Cu additive. In particular, the base oil containing 10.0% nano-Cu had the longest fatigue life in the present research, indicating that a relatively high additive concentration

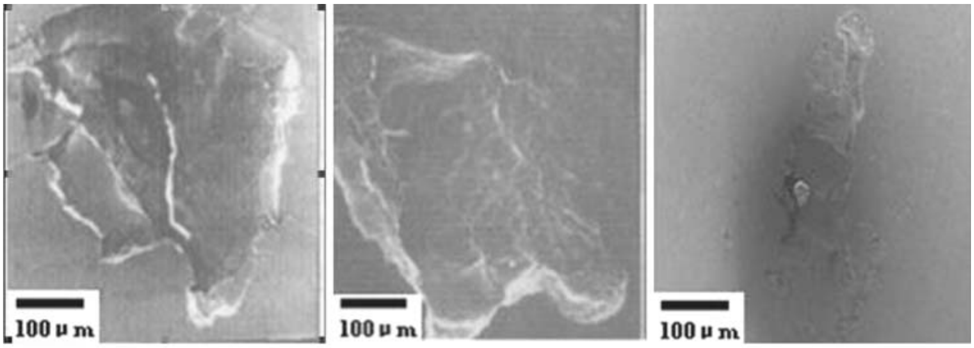
Table 1 Fatigue test results for different oil samples

Oil sample	Weibuer slope (k)	Characteristic life (Np, $\times 10^5$ times)	Fatigue life (L_{10}, $\times 10^5$ times)
No. 20 mechanical oil	2.324	30.535	11.597
No. 20 oil-2.5% nano-Cu	4.013	65.031	19.122
No. 20 oil-5.0% nano-Cu	2.977	72.235	22.605
No. 20 oil-7.5% nano-Cu	3.104	111.23	62.414
No. 20 oil-10.0% nano-Cu	3.988	171.12	75.634



(a) base oil **(b)** 5% nano-Cu **(c)** 10% nano-Cu

Fig. 2 Fatigue life curve of several oil samples



(a) base oil **(b)** 5% nano-Cu **(c)** 10% nano-Cu

Fig. 3 SEM images of the fatigued surface of steel balls lubricated with different oil samples

could be beneficial to improve the anti-fatigue behavior of the base oil.

Figure 3 shows the SEM images of the fatigued surface of steel balls lubricated with different oil samples. It is seen that the steel ball was dominated by fatigued peeling off under the lubrication of base oil and base oil containing 5.0% nano-Cu, while micro-cracking was the dominant wear mode under the lubrication of the base oil containing 10.0% nano-Cu. At the same time, a much smaller wear scar was obtained under the lubrication of the base oil containing 10.0 nano-Cu additive as compared with the base oil or base oil containing 5.0% nano-Cu, corresponding well to the greatly extended fatigue life in the former case. Therefore, it can be inferred that the introduction of the nano-Cu additive at a higher volume fraction (10.0% in the present research) would be helpful to increase the wear resistance and fatigue resistance of the steel–steel pair under oil-lubricated conditions. The fatigue eroding of steel is originated from the source of crack related with structure. Owing to the non-uniform microstructure of steel, stress concentration is formed under the effect of cycling contact stress, leading to the formation of small cracks at the defect zones. Furthermore, during the process of rotating contact, the shearing force increases with increased friction, forming a source of crack on the surface in contact. Once the crack source is originated, whether from the bulk interior or on the surface, it will grow and be extended into the bulk under cyclic contact stress, finally causing rupture at a certain level of extension. Hereafter, new cracks will be generated along with the rupture and lead to secondary and tertiary cracks, causing fatigue eroding ultimately due to continuous spreading of the cracks [9, 10]. Noticing that the steel–steel pair showed better wear resistance and fatigue resistance, it could be rationally anticipated that the introduction of nano-Cu additive in the base oil would affect formation of micro-cracks, which should be closely related to the deposition of the nano-Cu additive particulates at the defect zones of the surfaces in motion. Also, Cu nanoparticles in the base oil can greatly enhance the fatigue life, especially in the concentration between 5 and 10%. On the concentration between 5 and 10%, Cu nanoparticles can deposit and melt on the fatigued surface to form a layer of compact protection film. However, on the concentration between 2.5

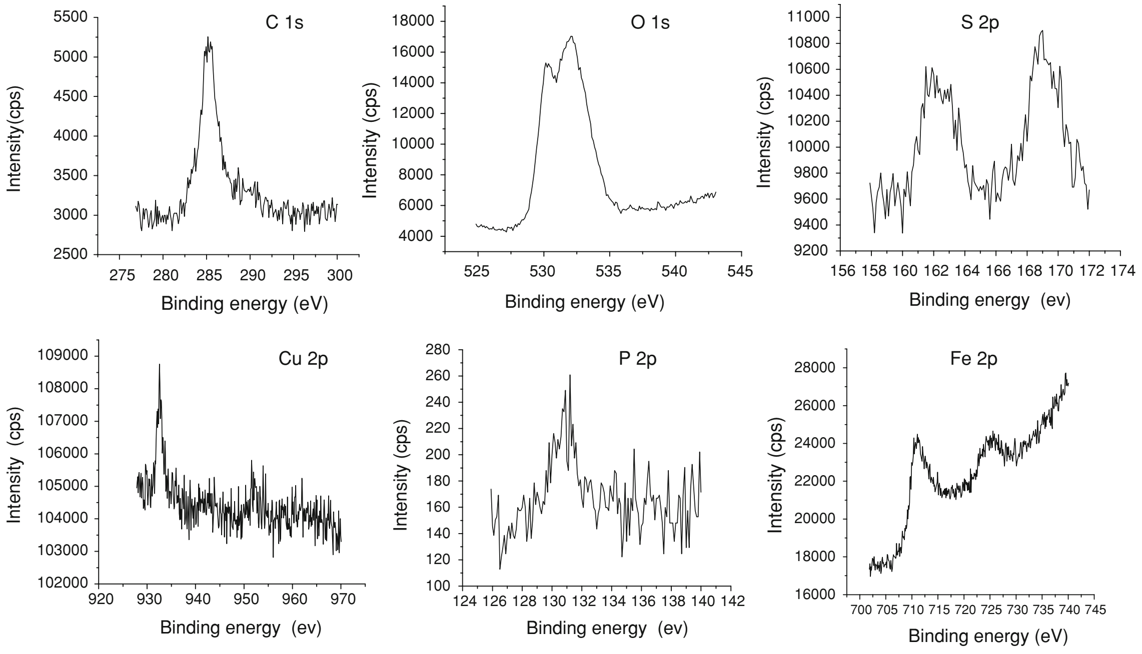


Fig. 4 The XPS spectrum of the fatigue surface of the steel ball

and 5%, the tribochemical reaction film formed by the elements of S and P is mainly responsible for the anti-fatigue property; therefore, the anti-wear and anti-fatigue properties of the reaction film are poor for S, P elements and a small amount of Cu deposited on the fatigued surface, which leads to the Cu nanocore not being able to form a good boundary film; as a result, the steel ball will scuff and wear severely. Besides, the concentration of more than 10% was selected for the test; however, the fatigue life was decreased, which was probably due to the increasing concentration of Cu nanoparticles leading to the increase of the base oil viscosity. As a result, the nano-Cu will be difficult to transfer to the steel ball to form an excellent boundary film. Therefore, the increasing of fatigue life is not linear with the nano-Cu concentration in base oil. This supposition can be confirmed by the XPS analysis of the fatigued surface of the steel ball. Taking the steel ball lubricated by base oil containing 10% nano-Cu additive as an example, Fig. 4 shows the chemical states of several typical elements. It can be seen that a Cu2p peak appears around 932.6 eV, indicating that Cu originated from the nano-Cu additive had been indeed deposited on the fatigued surface of the steel ball. Moreover, $FeSO_4$ (Fe2p: 712.1 eV, S2p: 168.8 eV, O1s: 532.4 eV) and iron oxides (Fe_2O_3 and/or Fe_3O_4, Fe2p: 710.4–710.8 eV, O1s: 530.2 eV) were also detected on the fatigued steel surface, indicating that the active element S in the surface-capping agent DDP had chemically reacted with the sliding steel surface, resulting in a tribochemical reaction film mainly composed of Cu, S, P, Fe and O via. The tribochemical reaction film in connection with the antiwear and repairing nano-Cu particulates deposited on the steel surface contributed to greatly improving the wear resistance and fatigue resistance of the steel–steel pair. Namely, on one hand, nano-Cu additive is capable of reducing friction and wear by way of the so-called ball bearing effect, causing a transfer of the sliding friction to rolling friction and hence reducing friction and shearing stress. As a result, the contacted fatigue life of the steel-steel pair is enhanced [11, 12]. On the other hand, the active elements P and S in the surface-capping agent DDP are able to tribochemically react with iron and form a tribochemical reaction film, which together with the boundary lubricating film formed on the fatigued steel surface under cyclic stress at a high speed would also contribute to increasing the extreme pressure performance

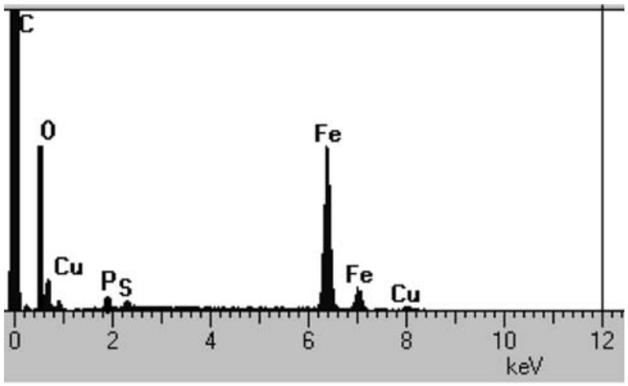


Fig. 5 The EDS analysis of the fatigue surface of the steel ball

of the base oil and extending the antiwear ability and anti-fatigue life of the steel–steel pair. In order to further prove the deposited Cu film on the steel ball, the energy-dispersive spectrum (EDS) result was obtained, as shown in Fig. 5. Obviously, the Cu, S and P elements can be found, which was consistent with the XPS analysis.

4 Conclusions

Nano-copper surface-capped by DDP as an additive in no. 20 mechanical oil is able to greatly improve the anti-fatigue ability of a steel–steel pair in a ball-to-rod contact configuration. The best anti-fatigue ability was obtained under the lubrication of base oil containing 10% nano-Cu additive. The improvement in the antiwear ability and anti-fatigue performance of the steel–steel pair could be closely related to the special worn-surface repairing effect of the nano-Cu additive and the tribochemical reaction among the active elements P and S in the surface-capping agent DDP and steel substrate leading to the formation of boundary lubricating film and tribochemical reaction film. The steel–steel pair under fatigue test conditions was dominated by fatigued peeling off and micro-cracking, which could be effectively retarded and eliminated by introducing nano-Cu in the base oil at a higher volume fraction (10.0%).

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