Investigation of the mending effect and mechanism of copper nano-particles on a tribologically stressed surface

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The mending effect and mechanism of metal nano-particles in an area undergoing wear are quite important for both the fundamental theory of nano-tribology and the development of lubricant additives. This paper presents research on the mending effect of copper nano-particles added to lubricant oil. Pin-on-disk experiments and Scanning Electron Microscopy (SEM) observations show that copper nano-particles do display an excellent mending effect. The observation by Scanning Tunnelling Microscopy (STM) reveals that the mending effect results from the deposition of copper nano-particles onto the wear scar. It has also been disclosed by heating simulation that, due to nano-scale effects, which bring about decrease in the diffusion temperature of copper nano-particles, the heat generated by friction leads to the diffusion of copper nano-particles and their subsequent deposition, which finally results in the so-called mending effect.

KEY WORDS: copper nano-particles, friction, wear, lubricant additive, mending effect

1. Introduction

Putting additives into oil to reduce friction and wear or to mend a worn surface has been widely applied in lubrication engineering for quite a long time. Although there have been several generations of additives that have been developed, research and development into more effective additives has never been stopped, since additives in current use are not perfect, particularly with respect to their behavior concerning the reparation of worn regions "wear mending." Researchers in the lubrication research field have been searching for new wear-mending materials as lubricant additives.

In the past few years, nano-materials have emerged as a new choice in additive development. Many novel studies have been carried out with nano-materials, many encouraging achievements have been obtained and the tribological properties of lubricant oil have been clearly enhanced [1–7]. The mechanism of anti-wear and friction reduction of this kind of additive has been believed to involve the nano-particles acting as a spacer between the two friction surfaces. It has been proposed that the nano-particles may roll like micro-spheres in the grinding area, which leads to the reduction of the friction coefficient [1]. But, nowadays, it is more widely believe that nano-particles deposit on the friction surface and compensate for the loss of mass, which has been called it "mending effect" [8–9]. However, specifically designed investigation of the mechanism of the mending effect of nano-particles have rarely been performed.

The surface mending effect holds a fundamental position in the theory of nano-tribology with nano-materials, therefore, the mechanism involved needs to be examined and understood in some detail.

2. Experiments

The experiment has been designed in two parts, as follows.

The first step involves collecting the experimental data for the calculation of friction coefficient from two pin-on-disk tests, and subsequently observing the area with scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM).

The second step involves heating nano-particles to simulate the thermal processes occurring in grinding and then observing the heated nano-particles with TEM.

2.1. Preparation of the lubricant oil with copper nano-particles

Copper is one of the softer metals, so copper nano-particles has been chosen as the experimental nano-particle material. The copper nano-particles used herein were fabricated in our own laboratory by the electric arc plasma evaporation-deposition method. The TEM morphologies of copper nano-particles are presented in figure 1(a). Their typical shape profiles

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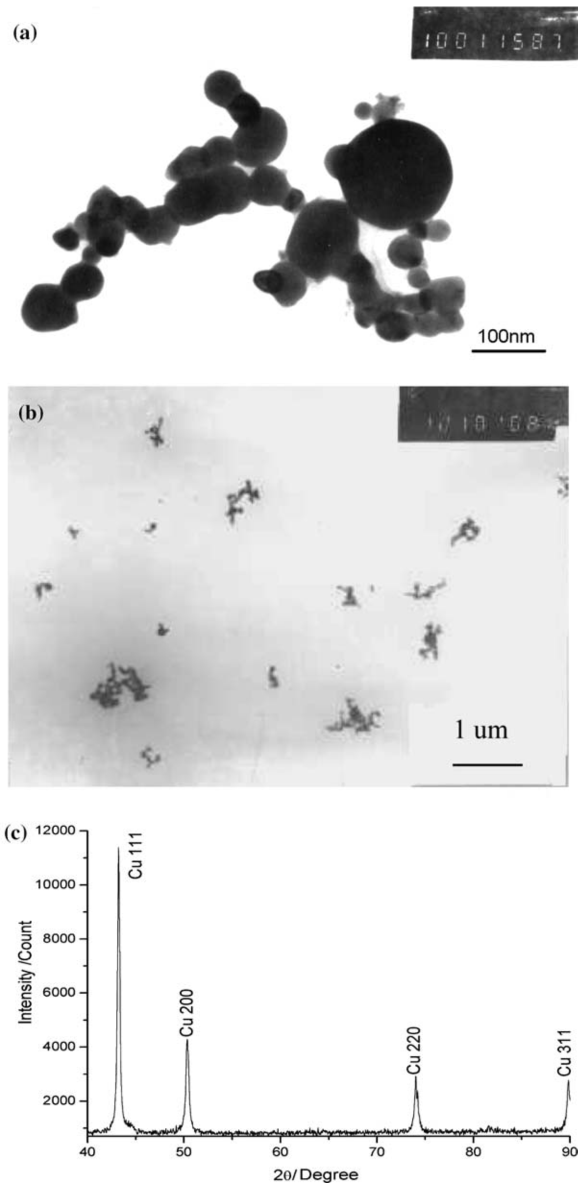

Figure 1. TEM morphologies and XRD pattern of copper nano-particles. (a) TEM morphology of copper nano-particles. The particles' diameter ranges from 10 to 140 nm with mean value about 40–50 nm. (b) Copper nano-particles dispersed in the base oil. The assembled structures vary from 0.1 to 1 μm in size, mostly about 0.4–0.5 μm. (c) X-ray diffraction (XRD) pattern exhibits the typical peaks of crystalline copper.

are spherical or similar. Their diameter distribution varies from 30 to 120 nm, and the mean diameter is around 50 nm. After being post-treated, an oxide shell can be generated [10]. This oxide shell can protect the copper core so well that the copper nano-particles are stable not only at ambient but also at elevated temperatures. Moreover, they will not react with other components in the lubricant due to the existence of this protective oxide shell.

The base lubricant oil used in this general purpose experiment is 500SN, a commercial lubricant. The content of copper particles is 0.1 wt%. The mixture of oil and copper particles was dispersed ultrasonically vibrator for 30 min at around 50 °C. In order to maintain the copper particles steadily suspended in oil after dispersing, 0.1 wt% dispersant (polyisobutylenebutadimide) has been added into the mixture. Figure 1(b) shows that copper particles can be suspended in the base oil in the shape of irregular clusters with a branching skeleton. The size of a typical cluster is about 0.5×0.5 μm, which was small enough to prevent the copper particles from sinking in the oil.

2.2. Process of pin-on-disk experiment

The experiments were carried on a pin-on-disk testing machine (model MG-200). The disks were made of 20CrMnTi steel. After being surface-carburized, their hardness reached 62 HRC. The pins were made of H62 bronze, the geometric parameters of these cylinders were $\Phi 8 \times 20$ mm. Two pairs of pins and disks were prepared because this experiment consisted of two trials. The first pair was marked as No. 1 for the trial with blank base oil assigned as test No. 1. Another pair marked as No. 2 was for the trial with copper nanoparticles added to the oil assigned as test No. 2. The parameters applied in both trials are shown in table 1. The torque induced by frictional force was measured and recorded by a dynamic strain gauge and X–Y recorder for the calculation of the friction coefficient.

The procedure of each trial can be described as follows:

First, trial No. 1 was done with the parameters shown in table 1. The 0.5 mL of base oil was added to the disc surface at 3 min intervals. The experiment was continued until the total running time reached 36 min. During the trial, the blank base oil has been added 12 times, corresponding to a total volume of 6 mL.

The same experimental procedure and parameters have been applied in trial No. 2 except for two differences:

First, the oil being added was the mixture of base oil and copper nano-particles.

Secondly, when the experiment time reached 30 min, which corresponded to the 10th oil addition, all the nanoparticle oil was wiped off the disk and the surface cleaned with acetone while the disk was still rotating. Then, the base oil was applied again at the same adding rate and volume. The total experimental time and oil volume were the same as those in trial No. 1.

Table 1.
Parameters of the pin-on-disk trials.

Load / N	Rotary speed/ rpm	Oil volume increment/ mL	Track diameter/ mm	Total time/ min
196	100	0.5	40	36

After the two trials were finished, both pin No. 1 and No. 2 were observed with SEM (XL30) and STM (CSPM9100).

2.3. Heating simulation process

In order to understand the mending mechanism, a heating experiment has been done on copper nano-particles simulating the thermal experience that nano-particles undergo while being squeezed into the grooves and valleys of the wear zone. The heating simulation experiment has been done in a conventional electric resistance furnace, with the copper nano-particles heated from 100 to 900 °C as shown in figure 2.

In this experiment, whenever the temperature rose by 100 °C, some of the copper nano-particles were taken out of the furnace and kept as a sample for the corresponding temperature. All the samples were observed by TEM to trace the change of copper nano-particles.

3. Surface mending effect

The mending effect of copper nano-particles in the wear zone can be understood by analyzing the data of the pin-on-disk experiment, SEM observation, and STM measurement.

3.1. Result of pin-on-disk experiment

In figure 3, there are two curves of friction coefficient versus time. The curve designated with solid squares is the friction coefficient derived from Test No. 1 and the other one marked with solid dot is the friction coefficient derived from Test No. 2

Test No. 1, with blank oil and the square plot trace, had the friction coefficient fluctuating around 0.046 with the mean fluctuating amplitude the about 0.0015, with the friction coefficient remaining steady especially in the last stage of the experiment.

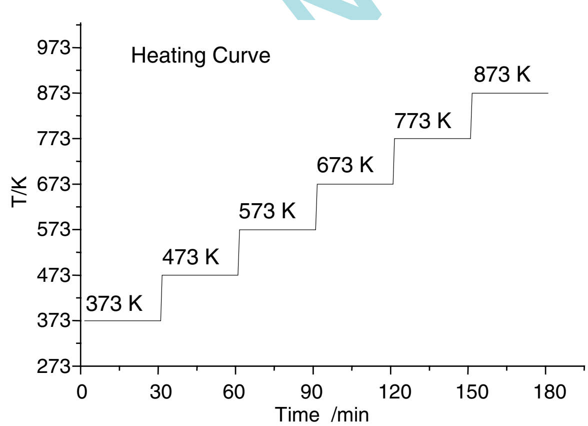

Figure 2. The heating curve applied in the thermal simulation experiments.

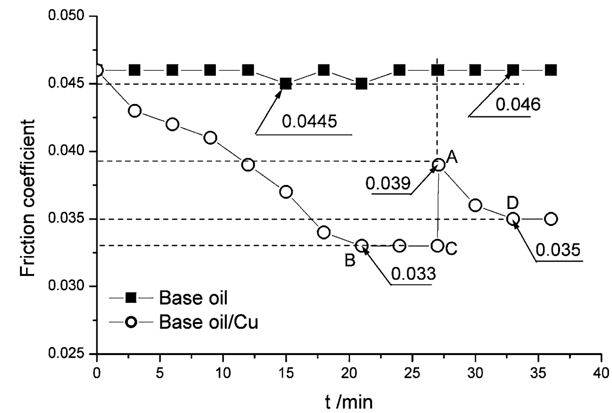

Figure 3. Variation of friction coefficient in testing.

As shown by dotted curve in figure 3, in test No. 2, the lubricant oil with copper nano-particles, the friction coefficient continuously drops from 0.046 in the beginning to 0.033 after 21 min. After point "B," it remain steady. Compared with the blank oil, the copper nano-particles oil has a 33% lower coefficient of friction.

At point "C" in figure 3, the copper nano-particle-containing oil was wiped from the friction surface and the friction surface was re-lubricated by blank base oil. Immediately after the oil change, the dotted curve shows that the friction coefficient rises to 0.039 at point "A" and then quickly falls back and keeps steady at 0.035.

Although the friction coefficient rises 0.002 from 0.033 right before point "C" to 0.035 at point "D" on the dotted curve, the friction coefficient is still reduced 24.4%, when compared to 0.46 from the square curve. After point "A," the oil is blank base oil rather than copper nano-particles containing oil, but the friction coefficient continues to decrease. This tendency implies that something occurred on the friction surface which decreases the friction coefficient even without copper nano-particles being actively added.

As for the increase of friction coefficient at point "A," from the test procedure described above, it should be caused by the oil being remove and the surface being clean with acetone. During the removing and cleaning, the disk kept rotating and the pin was not lifted. Thus at the time around point "A," there was nearly no oil on the disk surface, so the friction coefficient goes up due to the absence of an oil film. After point "A," the disk surface was gradually re-lubricated again, as a result, the friction coefficient drops rapidly.

3.2. Explanation from the SEM observation

The SEM observation provides an explanation for the mending phenomenon mentioned above.

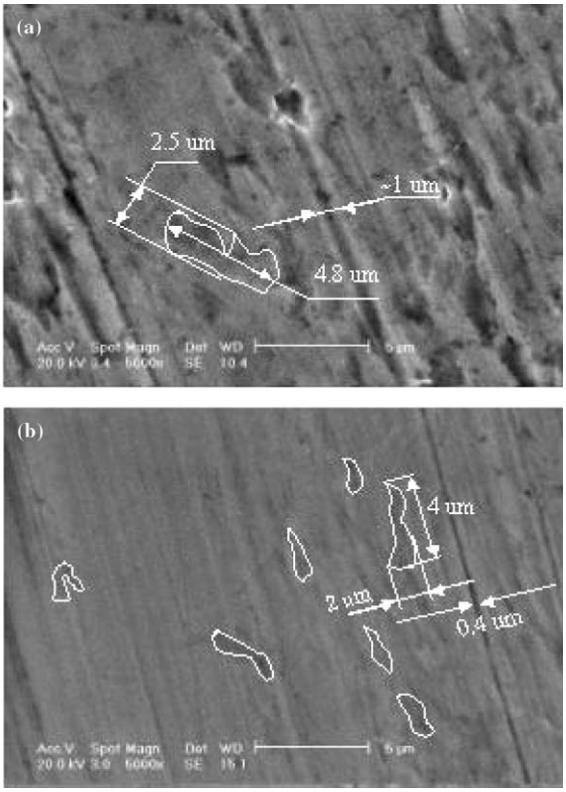

Figure 4. SEM images of the pin's wear zone. (a) Lubricated with blank base oil. (b) Lubricated with copper nano-particle added oil

In figure 4(a), it can easily be found that after running for 36 min while lubricated with blank oil, the observed area of Pin #1 is full of grooves and scars, which are deep with edges like blades. Figure 4(b), the SEM image obtained from the wear zone of Pin #2, which was lubricated with copper nano-particles containing that is oil, has an appearance significantly different, which can be described as flat and smooth, compared with the image of figure 4(a). The grooves and scars in figure 4(b) are obviously less severe than those in figure 4(a). The width of the biggest groove in figure 4(a) is about $\sim 1\ \mu m$, the typical size of a big scar is around $2.5 \times 4.8\ \mu m$. In figure 4(b), the width of the biggest groove is only $0.4\ \mu m$. Although the biggest scar is also around $2 \times 4\ \mu m$, it is obviously much more shallow than that in figure 4(a). The size of typical scars as indicated with white rings is about $1{\sim}2 \times 2{\sim}2.5\ \mu m$, smaller than those in figure 4(a). All these results mean that a mending effect has occurred in the wear zone.

The visual impression is in accordance with the testing results of friction coefficients in the pin-on-disk experiments. So, it could directly be derived that the decrease in friction coefficient during both parts of Test No. 2 were due to the smoothing of the wear zone. Except for the copper nano-particles, the other components of the oil and parameters used in Trial No. 1 and Trial No. 2 were exactly the same. Therefore, it could only be inferred that the copper nano-particles being added into the lubricant oil have smoothed the friction surface. This phenomenon is the so-called mending effect.

3.3. Further information from STM

The following measurements with STM have further illustrated the smoothing mechanism observed above. The STM tip was platinum-iridium alloy. During the STM measurement, the measuring parameters have been set as follows: Z-voltage-range is ± 5 V; I-bias is 1.5 nA; V-bias is 50 mV; f_{scan} is 20 Hz; Number of sampling points is 256. Before measuring, the pins were cleaned with acetone in an ultrasonic bath for 10 min.

Figure 5(a) shows the surface obtained by STM for wear point of the Pin #1. No unusual features are observed in the images, obtained from the friction surface of a pin after an ordinary pin-on-disk experiment. The image shows there are numerous humps and grooves scattered about the tested area. In figure 5(b), the STM image, which was obtained from the wear point area surface of Pin #2, reveals on papillae of semi-spherical shape within the area being imaged.

Figure 5(c) shows further details of the papillae. According to the scale in the bottom of figure 5(c), it can be measured that the long axis and short axis of these semi-elliptical papillae are around 40–50 nm and 20–30 nm respectively. Notice that the mean diameter of copper particles in figure 1(a) is also around 50 nm. That means these papillae match the copper nano-particles quite well in geometric dimensions. Pin #1 displays no such papillae. As Pin #2 was lubricated with the nano-copper particle containing oil and Pin #1 was lubricated only with the blank base oil, it is therefore firmly believed that the papillae can only result from the deposition of copper nano-particles.

The deposition of copper nano-particles filled the grooves in the wear zone, making the surface smoother than that without copper nano-particles, thus leading to the "mending" effect. As a result, the pressure at the contact point of the friction surface between the pin and the disk is reduced, which results in the decrease in adhesion and plough in reducing the friction coefficient.

The mending effect of copper nano-particles can explain the friction reduction quite well in the pin-on-disk experiment. However, the deposition mechanism requires further study.

4. Investigation of the surface mending mechanism

Heating copper nanoparticles to different temperatures in air in an electric resistance furnace cause the outline profile of these copper nano-particles to gradually change, as exhibited in the TEM morphologies in

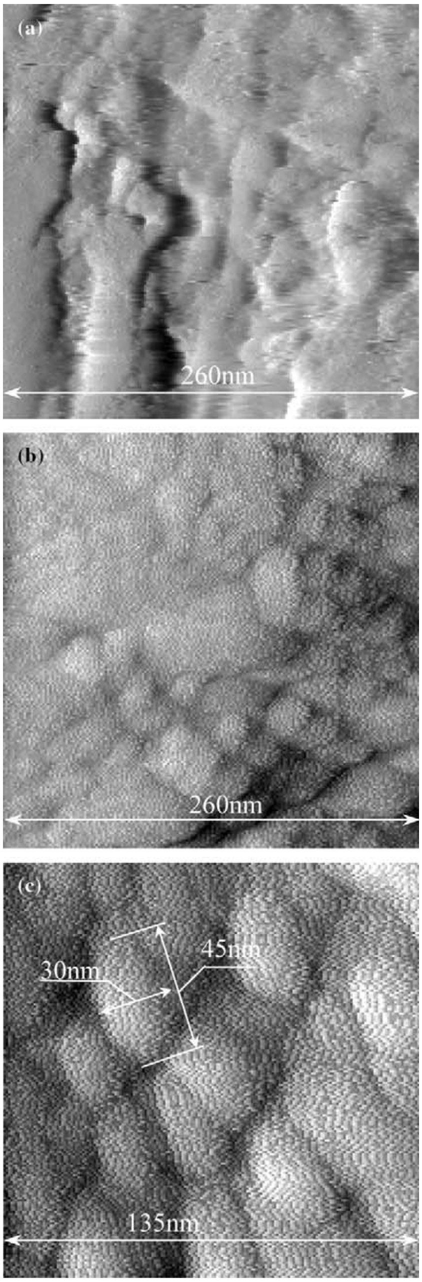

Figure 5. Appearances of the wear point area given by STM. (a) Lubricated with blank base oil. (b) Lubricated with copper nano-particles added oil. (c) Lubricated with copper nano-particles added oil.

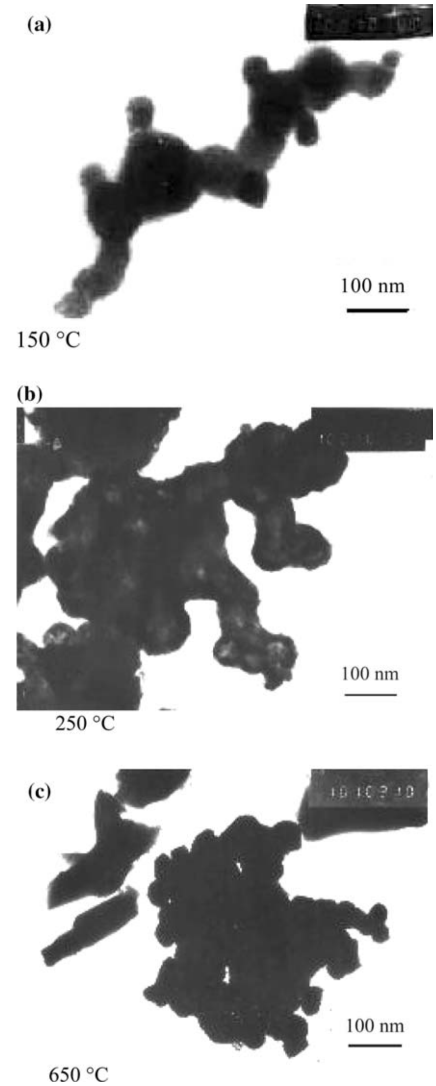

Figure 6. TEM morphologies of the copper nano-particles being heated to various temperatures. (a) 150 °C, (b) 250 °C, and (c) 650 °C.

figure 6. In comparison to the original particles at 150 °C shown in figure 1(a), particles have less well-defined outlines. When the temperature reaches 250 °C, the particles start to diffuse and shrink in volume, as shown in figure 6(b). At this temperature, the spherical outline characteristic becomes less clear than before. When the temperature reaches and exceeds 650 °C, the copper particles assemble further and diffuse to be comparatively tight clusters. But if being carefully examined and observed, the particles can still be identified even in figure 6(c) by their outline profile (see the right portion of the biggest cluster in figure 6(c)).

It can be inferred that copper particles in such clusters can maintain their spherical profile even they were considered assembled. This could therefore explain why so many papillae could be seen in figure 5(b) and figure 5(c). It is known that the melting point of bulk copper is 1083 °C. Here, depending on the specific particle size, copper nano-particles begin to diffuse within the temperature range from 250 to 650 °C. This is a typical feature of nano-metal particles when their dimension falls into the nano-scale [11].

The heating simulation experiments have shown that relatively low temperatures, lead to morphology changes in copper nano-particles. These changes can explain the mending mechanism and migration of the copper nano-particles to the wear zone.

When friction occurs, the micro-peaks on the contact areas slide against each other, and the peaks and grooves may squeeze into the other side like gears at high speed. In the meantime, the copper nano-particles may also be squeezed into the "gear" gap as well and then be compressed into the grooves on the surface. The squeezing and compressing will generate heat at the contact point between copper nano-particles and the friction surface and then lead to the localized increase of temperatures around the point of contact. The increase of temperature will definitely vary depending on experimental conditions, but it has been reported that the highest temperature could even reach 1300 K [12] at the contact point. This implies it is reasonable to expect that the temperature around the contacting point can exceed the temperature at which copper nano-particles start to diffuse and assemble as shown in figure 6, where the diffused and assembled particles may be soldered onto the contact point surface. This is why there are papillae in figure 5(c). Along with the continual deposition from the oil suspension, the copper nano-particles heaped up; gradually filling the grooves and scars of the friction surface leading to the mending effect and resulting in the decrease of friction coefficient in the pin-on disk test.

5. Conclusion

From the analysis of the experimental results and the discussion above, the following conclusions could be drawn.

1. The experimental results of pin-on-disk tests and observations by SEM have shown that there exists a mending effect on the friction surface after being lubricated with oil containing copper nano-particles.
2. It has also been shown by STM observation that the deposition of the copper nano-particles added to the oil contributes to the mending effect.
3. The heating simulation experiments have disclosed that the diffusion point of copper nano-particles has decreased significantly due to its nano-scale effect. Thus, it is likely that the heat generated during friction brings about the deposition of the copper nano-particles, which finally results in the so called mending effect.

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