Comparisons of dry sliding tribological behaviors between coarse-grained and nanocrystalline copper

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1. Introduction

Extensive investigations have been focused on tribological behaviors of ultrafine-grained (UFG) and nanocrystalline (NC) metals in recent years [1–4], since it is expected that wear resistance would be greatly enhanced with reduction of grain size according to Hall–Petch relation and Archard equation [5]. However, in comparison with coarse-grained (CG) metals, UFG and NC metals exhibited no remarkable reduction in friction coefficient (FC) and no improvement in wear resistance. For example, FC value for UFG Ti was almost the same as that of CG Ti, and NC Ni with a mean grain size of 13 nm showed merely a 44% higher abrasive wear resistance than the conventional one [1,3]. The steady-state FC of NC Cu prepared by surface mechanical attrition treatment (SMAT) decreased a little under the loading of less than 20 N, and was the same as that of CG Cu when the load was above 20 N [6]. The maximum ratio of wear volumes for CG and SMAT NC Cu was lower than 5. Concerned with the reasons for improvement of wear resistance, much attention was paid to the pronounced effects of transferred layer, surface oxidation and mechanical mixed layer (MML) for NC metals. Such interpretation was primarily based on the expectation that there was higher tendency for NC to oxidize along with continuous coverage of MML, provided that high density of grain boundaries would act as preferential nucleation sites for oxides and faster oxygen diffusion channels [1,7,8]

Nevertheless, investigations on tribological behaviors of NC are still not enough so far to understand the variations of FC and wear resistance. In our previous work, a NC surface layer was obtained in pure Cu by surface mechanical grinding treatment (SMGT) [9]. In this work, the dry sliding tribological behaviors of the NC layer and the CG Cu were studied by using ball-on-plate tribometer. The variation of FC and enhanced wear resistance for NC Cu were discussed.

2. Experimental

A commercial purity copper (99.97 wt.%) rod (10 mm in diameter and 50 mm in length) was subjected to the SMGT, of which the detailed process was described previously [9]. With a preset penetration depth, a WC–Co tool tip slides along the axis of a rotating sample at about ~ 100 °C. Plastic deformation at high strain rate of 105 [10] and cryogenic temperature of ~100 °C can induce formation of nanostructures in the surface layer of the treated Cu sample. Before treatment, the rod was annealed at 873 K for 3 h in vacuum to obtain a CG structure with an average grain size about 20–30 μm. The SMGT was performed at about 173 K for 6 passes with an indent depth of 40 μm and a rotation speed of 600 rpm. The cross-sectional microstructure characterization of processed sample was carried out on a JEM-2010 transmission electron microscope (TEM) operated at 200 kV. Microhardness was measured on an MVK-H3 hardness tester equipped with a Vickers indenter using an applied load of 5 g and a duration of 10 s. An Optimol SRV-III tester in the ball-on-plate contact configuration was used to evaluate dry sliding wear behaviors at room

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temperature (25 °C) in air with a relative humidity of 20%. Sliding wear tests were conducted under normal loads ranging from 5 N to 25 N, with an oscillating stroke of 1 mm, a frequency of 5 Hz and sliding duration time of 60 min. A WC–Co ball was used as the counterpart (10 mm in diameter, with a hardness of $H_C = 17.5$ GPa). The tribological behaviors of the annealed CG Cu were measured under the same conditions for comparison. In order to compare the worn surfaces at different sliding stages for the NC and CG Cu, wear tests were also performed with a load of 25 N after 20 and 40 min, respectively, with other testing parameters unchanged. To ensure the reliability of the data, three repeated wear tests were performed on the tested samples under the same testing parameters. During each test, the variation of the FC with sliding time was automatically recorded. Each steady state FC was calculated from the arithmetic mean of every FC value in the flat part of the recorded curve. The cross-sectional profiles were obtained by using surface profilometer. The morphologies and compositions of wear scars were investigated by optical microscope (Leica MPS 30) and FEI Quanta 600 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS).

3. Results

3.1. Microstructure and hardness of the NC layer

Fig. 1 shows the cross-sectional microstructures of SMGT Cu. The grain boundaries in the topmost surface layer of about 70 μm thick could not identified, underneath which grain boundaries are bent towards one direction from the optical microscope observation, as shown in Fig. 1a. The detailed TEM observations showed that the roughly equiaxed grains were formed in the topmost layer (Fig. 1b). The average grain size is 27 nm within topmost layer of about 10 μm thick (Fig. 1c). In the subsurface layer, ultrafine grains were formed (Fig. 1d). Underneath ultrafine grains, the microstructure is characterized by dislocation cells (Fig. 1e). Fig. 1f shows the variations of longitudinal and transverse sizes...
of refined grains/dislocation cells with distance from the treated surface. Obviously, a uniform NC layer (with average grain sizes below 100 nm) of about 50 μm thick is formed in the SMGT sample. The layer thickness of nanocrystalline and ultra-fined grains is about 200 μm. In Rigney’s work [11], a nanostructured layer was formed near the surface of Cu as a result of sliding deformation during wear. This layer can induce mechanically mixed materials and submicron sized grains were formed due to dynamical recrystallization during wear. It should be pointed that the NC layer induced by SMGT is different from that induced by wear. The contamination from transferred materials was removed in the nanostructured layer of SMGT Cu. No W element was detected on the surface of the SMGT Cu and neither W nor C was detected at the depth of 24 nm, as shown in Fig. 2. The measured values from X-ray photoelectron spectra are listed in Table 1. Dynamic recrystallization would not take place due to cryogenic deformation of −100°C during SMGT so that the formed nanocrystalline grains survived. In other words, a surface layer having a nanocrystalline grain size and without contamination was obtained in the SMGT Cu, which can be regarded as a nanostructured material processed by plastic deformation to investigate its properties and behaviors. The hardness value of top surface layer is about 1.8 GPa, which is reasonable in comparison with the hardness of 1.6 GPa for the bulk nanostructured pure Cu processed by dynamic plastic deformation (DPD) considering higher purity and larger grain size of DPD Cu. This indicated that the enhanced hardness of SMGT Cu is attributed to grain refinement rather than oxidation and other solute effect. The measured hardness of SMGT Cu decreases from 1.8 GPa in the topmost NC surface layer to about 0.75 GPa in the CG matrix, as seen in Fig. 3. The trend of variation in the hardness of SMGT Cu is consistent with the reported results in [12,13].

3.2 Friction and wear behaviors of the NC and CG Cu

For CG Cu, variations of FC with sliding time can be divided into two stages. In the first stage, FC increases initially to a peak value and then decrease, which is mainly attributed to plastic deformation of the subsurface layer of the CG Cu and oxidation of wear surface under the mating ball [14]. In the second stage, FC tends to a steady-state value. The average steady-state FC is about 0.33 under the load of 5 N, and it increases to about 0.63 at higher loads. On the contrary, no obvious peak FC value appears in the NC samples.

Table 1
Element contents at the topmost layer and the depth of 24 nm from the treated surface in the SMGT Cu sample.

<table>
<thead>
<tr>
<th></th>
<th>Surface</th>
<th>24 nm deep</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>At.%</td>
<td>Wt.%</td>
</tr>
<tr>
<td>Cu</td>
<td>31.82</td>
<td>68.64</td>
</tr>
<tr>
<td>O</td>
<td>28.07</td>
<td>15.14</td>
</tr>
<tr>
<td>C</td>
<td>40.11</td>
<td>16.22</td>
</tr>
<tr>
<td>W</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 2. X-ray photoelectron spectra at the topmost and the depth of 24 nm from the treated surface in the SMGT Cu sample.

Fig. 3. Variation of measured microhardness with depth from the topmost surface of the SMGT Cu.
As seen in Fig. 4a and b, FCs of the NC Cu keep nearly unchanged with sliding time under a load below 25 N. When the load applied is 25 N (Fig. 4c), FC gradually increases until attaining the steady-state value of the CG Cu sample. The average steady-state FC values are about 0.36 under the loads less than 25 N while the value is up to 0.60 under the load of 25 N. It is interesting to note that the steady-state FC values of CG Cu are consistent with those of NC Cu at the loads of 5 N and 25 N, respectively, as shown in Fig. 4d.

The wear volume is a measure of wear resistance of a material. As shown in Fig. 5, the values of wear volume for the CG Cu are rather large, being about $3.6-31.5 \times 10^{-3}$ mm$^3$ in the range of measured loads. The NC sample exhibits much lower values than those of the CG counterpart, although the enhancement in wear resistance decreases with an increasing load. The wear volume value of CG Cu is more than 20 times higher than that of NC one under the load of 5 N, and more than one magnitude even under the highest load of 25 N. The enhanced wear resistance of NC Cu is also indicated by the wear depth, as shown in Fig. 6a. The wear depth of the NC sample is much shallower than that of CG one under all loadings. With increasing loads, the wear depth of CG Cu obviously increases from about 7 µm to 27 µm while the level of increasing depth is much smaller in NC Cu. It is found that the wear depth of NC Cu under the largest load (25 N) is still smaller than that of CG Cu under the smallest load (5 N). It should be pointed that the maximum wear depth in NC Cu (7 µm) is much smaller than the thickness of the NC layer (~50 µm). Besides the great differences of the depth and width of the wear scars, their contours are distinctly different. Obvious pile-ups appear on the sideways of the wear scar on CG Cu and the interior of the scar is much rougher compared with NC one, as shown in Fig. 6b. The pile-up is related to plastic deformation around the wear scar and accumulated wear debris, while the large interior roughness corresponds to its wear mechanism, which will be proved by the following SEM observations.

3.3. Worn surfaces of counterparts and Cu samples

Under the load of 25 N, localized asperity contacts of ball and Cu sample produce numerous scratches running parallel to the sliding direction on ball. The width size of scratch of the ball mating with CG Cu is more than two times larger than that of NC Cu (Fig. 7), implying that the ball penetrates much deeper into CG sample. Neither W nor Co was detected on the Cu and no Cu on the WC. Obviously, it is not superior for NC Cu to facilitate the formation of transferred layer on the counterpart in this work, which is different from the results of UFG Ti under dry sliding [1] and NC Cu under oil lubricating conditions [15].

For the wear morphologies, most of plowing grooves on NC Cu keep nearly intact under the load of 5 N after 60 min sliding while they have been destroyed obviously on CG. Both O and W elements were detected on the CG sample, but only O was detected in NC Cu. The O content on CG Cu is much higher than that of NC Cu. In order

**Fig. 4.** Variations of friction coefficient of the NC and the CG Cu with time under an applied load of (a) 5 N, (b) 15 N, and (c) 25 N, respectively; (d) Variations of the steady-state friction coefficient with the applied load.

**Fig. 5.** Variation of the wear volume with load with a wear duration of 60 min.
to reveal the distinct variations of morphology and composition during sliding process, wear morphologies and EDS spectra for NC sample after 20, 40 min, 60 min, and CG after 20 min under the load of 25 N are studied (Fig. 8). After 20 min, wear surface on NC Cu is fairly smooth with shallow grooves running parallel to the wear scar (Fig. 8a1 and b1). Neither O nor W element is detected across the wear scar (Fig. 8c1). As the sliding time is prolonged to 40 min, the wear morphology keeps almost the same, but a little O and W can be detected. When the sliding time comes to 60 min, the smooth surface is broken down and peeling-off occurs sporadically. It is noted that this process corresponds to the gradual increase of FC value in Fig. 4c. Contrary to the distinct transformation on NC Cu, there appears consistent characteristic of wear morphology on CG. As for CG Cu after sliding 20 min, the wear surface is rough and various areas have been delaminated away (Fig. 8a4 and b4). From the EDS line scan, obvious content of O is found (Fig. 8c4). Besides, a little W appears across the wear scar, which indicates the formation of MML. Characteristics after sliding for 40 min and 60 min remain the same as that of 20 min except the degree of oxidation and area of delamination. The measured contents of O and W elements for the NC and CG Cu samples are listed in Table 2.

4. Discussion

Although there may be some differences in the oxidation kinetics of NC and CG metals because of their different densities of grain boundaries, it does not contribute markedly to preferential formation of oxides on NC during reciprocating sliding tests in our experiments. In fact, the later oxidation of metallic debris shares the most important proportion in the origin of oxides besides oxidation of the apparent area of contact [16]. Based on the comparison of morphology and composition between NC and CG under the same load and sliding time in Fig. 8, larger wear scar size and asperity wear mode are responsible for more debris that retain within the scar in CG sample, which leads to the earlier occurrence of oxidation and formation of MML. Alternatively, this process would involve incorporation of oxygen and subsequent removal of the MML.

Concerning equivalent steady-state FC values of NC and CG at the applied loads of 5 N and 25 N (Fig. 4d), it is drawn that during the steady-state sliding stage, the tribological behavior mainly depends on the surface condition rather than initial microstructure [2]. The variation of steady-state FC values for either NC or CG Cu is closely related to delamination of wear surface. It is found that prior to delamination on the wear surface (inset Fig. 8A), FCs for NC and CG are lower and their FCs are equal within reasonable error. When larger delamination areas are found on the wear surface (insets Fig. 8B and C), their FCs are raised to higher value. FC values can be slightly increased with delamination area fraction within the measured of loads.

When the wear scar is shallow for either NC or CG Cu, the amount of wear debris is little and a majority of them can be removed off. During this stage, no oxidation occurs and the FC values for NC and CG are low and comparable, such as for NC Cu under the loads of 5, 10 and 15 N, and for CG Cu under the load of 5 N. The average FC...
value is about 0.35, representing the wear behaviors of wear contacting pairs between WC–Co and NC or CG Cu. As the depth of wear scar becomes large, MML was formed. Then, delamination occurs because of poor strain compatibility between MML and metallic matrix [17,18], during which the FC increases to higher value, such as for NC Cu under the load of 25 N, and for CG Cu under the loads of 10, 15, and 25 N. The average FC value is about 0.63. In fact, when MML forms on the wear surface of whether NC or CG Cu samples, the wear pair of WC–Co and Cu has changed into that of WC–Co and MML. The consequent wear mechanism changes from plowing into delamination, resulting in the change of FC. The oxidation and MML prefer to form on the surface of CG Cu due to its lower hardness compared with NC Cu. Hence, even under the same loading (10 and 15 N), the composition and contacting state of NC surface are completely different from that of CG, which results in their distinct FC values. It is found that despite the protective role of MML [6,7], the patchy morphology determines that it may be only a marginal effect on the reduction of FC. As delamination destroys the integrity of the wear scar, the FC value of NC Cu increases. On the other hand, with the accumulated work-hardening of CG matrix [19], the hardness gap between NC and CG Cu dwindles, which may also contribute to equivalent FC.

The higher hardness and consequent plowing wear behaviors are responsible to the enhanced wear resistance of NC Cu in comparison with CG Cu. The wear volume of NC Cu induced by plowing

Table 2
Comparisons of the EDS measurement results of O and W element contents for the NC and CG Cu samples marked in red rectangularity Fig. 7b1–b4.

<table>
<thead>
<tr>
<th></th>
<th>O (wt.%)</th>
<th>W (wt.%)</th>
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<tbody>
<tr>
<td>c1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c3</td>
<td>3.79</td>
<td></td>
</tr>
<tr>
<td>c4</td>
<td>9.89</td>
<td>5.26</td>
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Fig. 8. Overview of the wear scars for the NC samples (a1–a3) under a load of 25 N after 20, 40, and 60 min, respectively; for the corresponding CG sample (a4) under a load of 25 N after 20 min; (b1–b4) are detailed observations of the wear scars (a1–a4); (c1–c4) are the EDS measurement results of O and W element contents in the area marked in red rectangularity in (b1–b4).
is much smaller than that of CG Cu by delamination. Furthermore, even if delamination also happens in NC Cu, the thickness of its delaminated layer is much smaller in comparison with CG Cu since mechanical mixing in NC Cu is not as severe as in CG and the thickness of its work-hardened layer induced by sliding is smaller [20]. For CG Cu, the plastic deformation of subsurface facilitates the delamination process [21] and helps increase the surface roughness so that the wearing process is deteriorated, which eventually increases the wear volume during sliding.

5. Summary

The dry sliding tribological behaviors of NC and CG Cu were studied by using ball-on-plate tribometer with a counterface of cemented tungsten carbide ball.

(1) The obtained FCs of both NC and CG Cu samples are closely related to their oxidation and delamination of wear surface. Prior to oxidation and delamination, the steady-state FCs of NC and CG Cu are equal within a reasonable error, being about 0.35. As the oxidation and delamination of wear surface occur, the FC for either CG or NC Cu increases gradually until the steady-state FC (~0.63) is attainable. Meanwhile, the wear pair of WC–Co and Cu has changed into that of WC–Co and MML.

(2) The wear resistance of NC Cu was enhanced by at least one order of magnitude under the measured loads (from 5 N to 25 N) in comparison with CG Cu. This is mainly attributed to the higher hardness of NC Cu.

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