Dry sliding tribological behavior of nanocrystalline and conventional polycrystalline copper

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Dry sliding tribological behavior of an electro-deposited nanocrystalline Cu (nc Cu) and a conventional coarse-grained Cu (cg Cu) has been investigated using a ball-on-disc tribometer with cemented tungsten carbide ball as the counterface. Experimental results showed that the wear resistance of copper with the nanocrystalline microstructure was enhanced relative to the coarse-grained form. The steady-state friction coefficient of the nc Cu was obviously lower than that of the cg Cu when the load is below 20 N. The wear volume of the nc Cu was always lower than that of the cg Cu for the applied load range from 5 to 40 N. With increase of the load, the difference in wear resistance between the nc and the cg Cu decreased. The enhancement of the wear properties of the nc Cu was associated with the high hardness and the low work-hardening rate of the nanocrystalline structure, and easily being oxidized of wear debris, which was attributed to grain refinement.

KEY WORDS: copper, unlubricated wear, electrodeposition, nanocrystalline

1. Introduction

Nanocrystalline materials have exhibited many unusual mechanical, physical, chemical and electrochemical properties compared with conventional polycrystalline as a result of the considerable reduction of grain size and their significant volume fraction of grain boundaries [1]. The very high strength and hardness of nanocrystalline metals suggest various potential structure applications, and have provided an impetus for the development and mechanical characterization of many nanostructured metals, alloys, and composites [2].

Although there are numerous studies on the mechanical behavior of nanocrystalline metals through standard hardness, compression or tension testing, the mechanisms of friction and wear have received little attention in the nanocrystalline range, perhaps owing to the difficulty in producing bulk samples suitable for wear tests [3]. Most investigations on wear behavior have focused on a nanocrystalline surface layer or coatings of metals and alloys, they suggest that nanostructured materials exhibit improved wear resistance compared with their coarse-structured counterparts [4–6]. Systematic studies of wear in pure nanocrystalline metals are less common because of the difficulty in synthesizing bulk nanocrystalline samples suitable for friction and wear tests.

The electro-deposited nanocrystalline Cu (nc Cu) sample used in the present paper was made as an “ideal” nc specimen, i.e., single-phase, with a high degree of purity and free of contamination, porosity, and micro-strain [7]. The objective of this work is to compare the wear characteristics of an electro-deposited nc Cu with a conventional Cu with coarse grains (cg Cu), and to understand the nature of the difference of the friction and wear behavior with different microstructure.

2. Experimental procedure

The nanocrystalline Cu (nc Cu) was prepared by an electro-deposition technique with an electrolyte of CuSO$_4$ [8]. The nc Cu was deposited on a substrate of Ti to a thickness of about 1.5 mm. The purity of the Cu cathode was about 99.99 wt.%. The current density in the electrodeposition process was about 13 mA/cm$^2$. The pH of the electrolyte was 0.9 and the bath temperature was kept at 20±1 °C. An annealed nc Cu with grain sizes in the range of 50–100 μm (denoted as cg Cu) was employed to compare with the nc Cu.

The purity of the nc Cu was better than 99.995 wt.%. The impurity of the nc Cu was determined by using a LECO AA-404 Graphite Furnace Atomic Absorption Spectrum analysis. The result is as follows (wt.%): Bi < 0.0001, Sb 0.0001, As 0.0001, Pb 0.0001, Fe 0.004, Sn 0.0001, Ni 0.0002, Zn 0.0002, Co 0.0001, Ag < 0.0001. The purity of the cg Cu was about 99.99 wt.%. The total oxygen content in the as-deposited nc Cu sample was determined by using a LECO TC–436 Oxygen/Nitrogen Determinator analysis, being
about 24±1 ppm, and that of the cg Cu was about 63±1 ppm. The nc Cu density was measured by means of Archimedes principle, being about 8.91±0.03 g/cm³, which was equivalent to 99.4±0.3% of the theoretical density for pure Cu (8.96 g/cm³).

Quantitative XRD measurements of the nc Cu samples were carried out in a Rigaku D/MAX 2400 X-ray diffractometer with Cu Kα radiation. According to the diffraction line-broadening analysis of seven single Bragg reflection peaks (111), (200), (220), (311), (222), (400) and (331) using the Scherrer and Wilson method, an average grain size of about 30 nm was obtained.

HREM experiments were performed on a JEM 2010 high-resolution transmission electron microscope at an operating voltage of 200 kV. The thin foils were prepared by using an electrochemical polish (the solution is a phosphoric acid-alcohol mixture) at about −20 °C. HREM observations indicated that the as-deposited nc Cu sample consists of ultra-fine crystallites (or crystalline domains) with sizes ranging from a few nanometers to about 80 nm. Statistical results showed that the average grain size of the nc Cu was about 20 nm, which was close to the XRD results [7].

The micro-hardness of the samples was measured by using a Vickers microhardness tester with a load of 10 g and a duration of 10 s. An average of 10 measurements was performed on the surface of the samples.

Sliding wear tests were performed on an oscillating friction and wear tester (SRV III, Optimol, Germany) in a ball-on-disc contact configuration under dry conditions at room temperature (25–30 °C) in air with a relative humidity of 45–50%. Discs were cut from the nc and the cg Cu specimens to a dimension of 7×7×2 mm. The balls of 10 mm in diameter were made of WC–Co with a hardness of Hv 1750. The friction and wear tests were carried out at an oscillating amplitude of 2 mm, normal loads of 5–40 N, a frequency of 5 Hz, and a sliding distance of 36 m. Prior to each test, the pins were polished to a roughness less than 0.1 μm, ultrasonically cleaned in acetone for 5 min and dried. Three specimens were tested for each condition.

The friction coefficient values reported in this paper, which were continuously recorded, are considered normal values that represent the predominant behavior during the majority of each test.

Following the wear tests, the profiles of wear scars were measured using a Profilometer so as to determine the wear volume as $V = AL$ (where $A$ refers to the worn area determined by its profile and $L$ to the oscillating amplitude).

The morphologies of the worn surface at different wear conditions were investigated by using optical microscopy (OM) and scanning electron microscopy (SEM). The specimens were ultrasonically cleaned in acetone for about 10 min before SEM observations. Energy dispersive spectroscopy (EDS) was used to analyze the composition of the worn surface.

### 3. Results and discussion

#### 3.1. Hardness, friction and wear behavior

The microhardness measurements on the nc Cu sample showed that a hardness value of 1.05 GPa was obtained, which was two times as high as that of the cg Cu sample (0.5 GPa).

Figure 1 shows the friction coefficient as a function of the sliding distance under a load of 5 N (a) and 10 N (b) for the nc and the cg Cu samples. The basic shape curve remained similar under different loads for both samples. Each curve was characterized by two friction regimes. Initially, the friction coefficients in both samples increased gradually until they reached the steady-state values respectively. The nc Cu sample showed a transition to steady-state friction under a load of 5 N in a longer time compared with the cg Cu sample. However, the nc Cu sample took less time to reach steady-state under a load of 10 N than the cg Cu sample. The steady-state friction coefficient for the nc Cu sample under a load of 5 N or 10 N was obviously lower than that for the cg Cu sample.
Figure 2 shows a variation of the steady-state friction coefficient with the applied load for the nc and cg Cu samples. The steady-state friction coefficient with the applied load for the cg Cu stabilized at about 0.74. It can be seen that the steady-state friction coefficient of the nc Cu sample was obviously lower than that of the cg Cu sample when the load was below 20 N. The nc Cu exhibited a low steady-state friction coefficient of about 0.54 and 0.69 under 5 N and 10 N respectively. When the applied load exceeded 20 N, the steady-state friction coefficient of the nc Cu (about 0.71 under the load of 20 N and 0.72 under the load of 40 N) was close to that of the cg Cu (0.74).

The variation of wear volume with applied load for the nc and the cg Cu samples is shown in figure 3. Wear volumes of both samples increased with increase of the applied load, but the increasing slope for the nc Cu was not as steep as that of the cg Cu. An obvious difference was found between the nc and cg Cu samples. For the nc Cu sample, wear volume was always lower than that of the cg Cu sample for an applied load range from 5 N to 40 N, which showed that the nc Cu sample exhibited better wear resistance than that of the cg Cu.

Figure 4 indicates the ratio of wear volume of the nc Cu and the cg Cu samples as a function of the applied load. When the load increased, the ratio of $W_{nc}/W_{cg}$ increased, that is to say, relative wear resistance of the nc Cu decreased with an increase of the applied load. For example, under a load of 5 N, the wear volume for the nc Cu sample was 23% as much as that of the cg Cu sample, which showed that wear resistance of the nc Cu was obviously enhanced compared with that of the cg Cu. While under a load of 40 N, the wear volume for the nc Cu sample was 74% as much as that of the cg Cu sample, which showed that the enhancement of wear resistance of the nc Cu was limited for increasing applied load.

The enhancement of wear resistance with hardness increase due to grain size reduction, is often expressed using Archard’s equation [9], i.e.

$$ W = k \frac{L \cdot S}{H} $$

which gives the relationship between wear volume $W$, applied load $L$, sliding distance $S$ and hardness $H$ of the softer materials in contact. The experimental results given above indicated that the improvement of wear resistance of the nc Cu was associated with the increase of hardness, which was attributed to grain refinement. It has also been reported that the nanocrystalline metal and alloy may have lower friction coefficient than coarse-grained metal and alloy when the grain size was small enough [10], which may be attributed to high hardness and other reasons.

3.2. Worn surface morphologies and wear mechanisms

The difference in the wear behavior between the nc and the cg Cu samples can be understand by observation of the worn surface morphologies. Figure 5 shows OM
and SEM micrographs of the worn surfaces of the nc Cu and the cg Cu samples under loads of 5 N and 20 N.

During dry sliding wear, high contact pressure at the interface resulted in plastic deformation. Generally sliding wear consisted of the surface deformation and removal of worn materials from the surface. In the case of a WC/Co ball sliding on a softer copper plate, hard asperities could penetrate and cut deeply into the softer surface, causing continuous ploughing and severe plastic deformation and resulting in a certain amount of material removal.

For both the cg and the nc Cu samples, at the low load of 5 N, the worn surfaces (figure 5(a) and (b)) exhibited similar morphologies with many grooves. The dominant wear loss was caused by ploughing. As expected, the cg Cu exhibited a very poor wear resistance as evidenced by the deeper and wider wear tracks on the surface. Sliding for 36 m produced a wear track of 440 \( \mu \)m in width and 2.8 \( \mu \)m in depth on the cg Cu sample surface. However, for the nc Cu sample, the wear track was 280 \( \mu \)m in width and 1.35 \( \mu \)m in depth under the same sliding conditions. The difference in the worn surface morphologies between the two Cu samples was that the plastic deformation on the cg Cu sample surface was more intensive than that on the nc Cu sample surface.

At the high load of 20 N, the difference in the worn surface morphologies (figure 5(c) and (d)) between the two Cu samples was obvious. The cg Cu sample underwent much heavier deformation than the nc Cu, which indicated that the nc Cu sample also exhibited better load-bearing ability than the cg Cu sample. For copper, which is a ductile metal that work-hardens, as the applied load increases, the reciprocated sliding action causes repetitive work-hardening [11]. However, the repetitive work-hardening on the cg Cu surface was much more severe than that on the nc Cu surface. As shown in the enlarged micrographs (figure 6) of the wear tracks under a load of 20 N, some cracks propagated on the worn surface of cg Cu, which may result in spalling of the materials in figure 6(c) and (d). Evidently, the dominant wear mechanism of the cg Cu sample began to change to plastic removal and delamination. But for the nc Cu sample, there were more grooves on the surface than on the cg Cu surface, and the damage was characterized by plastic removal as well as ploughing. Meanwhile, the debris particles look like black, their composition is mainly CuO according to EDS analysis. The oxide debris covered the surface of wear track and provided a surface protection. For a nanocrystalline metal, it is easy to be oxidized because of the presence of more grain boundaries which act as nucleation sites for the oxides and diffusion paths of oxygen during the sliding process. So much more debris on the wear track of the nc Cu may provide more effective protection than that of the cg Cu. However, with an increase of the load, the wear mechanism of the nc Cu also began to change to delamination with a load of 40 N, which corresponded to an abrupt decrease of the difference in wear volume between the nc and the cg Cu as a result of the decrease of the load-bearing capacity of the nc Cu under the higher load.

Compared with the cg Cu, the load-bearing capacity of the nc Cu was improved. It is well known that high
hardness is one reason for the good wear resistance of materials. For ductile copper, plastic deformation may easily result in work-hardening. The formation of a hardened subsurface layer may be helpful for its wear resistance. Otherwise, excessive work-hardening may cause spalling of the materials by delamination, as seen in the wear track of the cg Cu sample (figure 6(d)). Compared with the cg Cu sample, the nc Cu sample had only a slight work-hardening rate, which has been proved by cold rolling tests in our previous studies [7,12]. It was also in agreement with the dependence of the deformation zone depth \( \delta \), which can be expressed by the formula [13], i.e.

\[
\delta = \sqrt{\frac{L}{2\sigma}}
\]

where \( L \) is the load, and \( \sigma \) is yield strength. The thickness of the hardened layer in the nc Cu sample was smaller than that in the cg one because of the significant increase of the yield strength \( \sigma \) of the nc Cu (119 MPa) over that of the cg Cu (30–70 MPa) [14]. Therefore, apart from the increased hardness of the nc Cu sample, the slight work-hardening rate can also be used to understand the other reason for the enhanced wear resistance. Detailed studies [12] on this kind of as-deposited nc Cu sample in the present study showed that grain refinement has been shown to result in reduced dislocation activity of nanocrystalline metals. Dislocation activities were no longer a dominating mechanism in the continual deformation. Instead, grain boundary activities (grain boundary sliding or grain boundary diffusional creep) may be activated and became dominant in the deformation. So a small work-hardening rate of the nc Cu may be helpful for the better wear resistance of the nc Cu, which was also observed by other researchers [15]. Moreover, much more oxide debris may be helpful for the enhancement of wear resistance of the nc Cu by protecting the worn surface.

So grain refinement increased the hardness of the nc Cu sample, decreased its work-hardening, as well as led to easily be oxidized of wear debris, which also can play an important role in the deformation process during friction and wear.

4. Conclusions

(1) Compared with coarse-grained conventional copper, the wear resistance of electro-deposited nanocrystalline copper was obviously enhanced under dry sliding conditions.

(2) The steady-state friction coefficient of nc Cu was much lower than that of cg Cu when the load was below 20 N.

(3) The wear volume of nc Cu was always lower than that of cg Cu for the applied load range from 5 N to 40 N. The difference in wear resistance between the nc and the cg Cu decreased with an increase of the load.

(4) The enhancement of the wear properties of the nc Cu was associated with the high hardness, the small work-hardening rate of the nanocrystalline structure, and easily being oxidized of wear debris, which was attributed to grain refinement.
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