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FRETTING BEHAVIOR OF NANO-Al_2O_3 REINFORCED COPPER-MATRIX COMPOSITES PREPARED BY COPRECIPITATION

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Abstract

A new series of copper–Al_2O_3 composite materials (CACMs), which show improved electrical conductivity and tribological properties, were developed. The CACMs were prepared by powder metallurgy (P/M) route with nano-Cu/Al_2O_3 powder, which was deoxidized from CuO/Al_2O_3 powder synthesized by method of coprecipitation using NH_4HCO_3 as precipitation and $CuSO_4$+$NH_4Al(SO_4)_2$ as maternal solution. The fretting test against 440C stainless steel was carried out at room temperature by using the ball-on-flat configuration with 300μm amplitude at various normal loads in the range of 0.1~1 N. The influences of load and addition of Al_2O_3 (wt.%) on the friction coefficient and wear-loss were investigated. Results show that with increased addition of Al_2O_3 the wear-loss decreases firstly showing a minimum at 2% Al_2O_3 and then increases with further of addition of Al_2O_3. Electrical conductivity of 82% International Annealed Copper Standard (IACS) corresponds to the minimum of the wear-loss. The friction coefficient of the CACMs is larger than that of the copper, but the wear-loss of CAMs is always lower than that of copper at any load. The lowest wear-loss, i.e. the best wear resistance, possesses the composite reinforced with 2% Al_2O_3.. The wear mechanism of copper is adhesive wear, whereas it becomes adhesive wear associated with oxidation wear for additions of Al_2O_3 up to 1%, or abrasive wear associated with the delaminating fatigue in CAMs with higher content of Al_2O_3.

Key words: copper–Al_2O_3 composite; fretting; nano-powder; coprecipitation method; wear mechanisms

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Introduction

Copper matrix composites are widely applied in electrical sliding contacts such as those in homopolar machine, railway overhead current collection system, lead frame in large scale integrated-circuit, welding electrodes, transfer switches, and electrical contact material [1-3]. The incorporation of ceramic particulate reinforcement can significantly improve the high-temperature mechanical property and wear resistance, without severe deterioration of thermal and electrical conductivity of the matrix. On account of cheaper price, oxidation resistance and superior high temperature mechanical properties, Al_2O_3 particle has been mostly selected as the reinforcement phase [4-7].

The most widely applied methods for the production of Cu–Al_2O_3 composite materials (CACMs) are based on casting techniques such as the squeeze casting of porous ceramic preforms with liquid metal alloys [8-9] and powder metallurgy (P/M) methods [6, 10-13]. Conventional melting and casting techniques are not useful because they are unable to give good uniformity of dispersoids. The production of CACMs by the P/M method has become very popular. The raw material for P/M, the composite powder, is usually prepared by high energy ball milling technique [10-12], internal oxidation method [13-14], and chemical process [15-16]. However, the traditional methods for the synthesis of these composites have some limitations, mainly related with manufacturing costs, grain size, and the homogeneity of the final product, which negatively influences the mechanical and electrical properties. In recent years studies on the synthesis of nano-scale CACMs have been attracting scientific interest [17-19], since nano-structured-type materials are expected to have special physical and mechanical properties. For example, Lee's studies confirmed [16-17] that the superfine Cu–Al_2O_3 composite powders with 20 nm in diameter and produced by thermochemical process possess a more homogeneous microstructure, higher electrical conductivity and hardness in the hot-extruded bulk than powders processed by the conventional internal oxidation process. Unfortunately, this process also seems to be complicated and costly. In our earlier work the nano-CuO/Al_2O_3 composite powder has been synthesized by means of coprecipitation, in which the content of well-distributed fine Al_2O_3 particles can be precisely controlled [20]. In the present work CACMs have been fabricated from chemically prepared nano-CuO/Al_2O_3 powder via hydrogen reduction followed by shaping and sintering.

Previous study [21] shows that the electrical contacting fretting, which normal load is about 0.1N, may cause a rapid increase of contact resistance resulting in decrease of contact reliability and distortion of electrical signal. Many studies have been undertaken on the preparation, corrosion [22] and the sliding wear behavior [23-24] of the CACMs. However, studies on the fretting wear in such a weak load have been less reported. Based upon the abovementioned premises, the aim of this paper is the fretting behavior characterization of nano-CACMs obtained using the proposed methodology.

Experimental

Preparation of the composite bulk

The synthesis of the Cu–Al_2O_3 composite powder was carried out according to the following procedure: (a) the composite precursor was prepared by method of coprecipitation, i.e. using NH_4HCO_3 as precipitation and $CuSO_4$+ $NH_4Al(SO_4)_2$ as maternal solution, dipping NH_4HCO_3 into the mixed solution of $CuSO_4$ and $NH_4Al(SO_4)_2$; (b) the precursor was dehydrated and dried at 80°C for 24 h after rinsing by distilled water and ethanol, and then the composite powder of CuO-Al_2O_3 was obtained after calcining the precursor at 500°C; (c) the composite powder of nano Cu-Al_2O_3 was finally fabricated from the chemically prepared nano CuO–Al_2O_3 mixture by hydrogen reduction at 500°C, the majority of particles were about 60nm in diameter. In order to obtain nanostructure with certain characteristics, adequate processing techniques and a strict control of the experimental conditions are required (for a good review on this topic see ref. [20]).

The CACMs bulk was prepared by the method of hot-pressing sintering technique in the vacuum sintering furnace. The composite powder was heating compressed into a briquette of Φ30mm×6mm under the load of 27.5MPa followed by sintering at 920°C for 2 h. In order to obtain the best mechanical and electronic properties, a series of samples were designed with various proportions (in wt.%) of Al_2O_3 powder selected as 0 (pure copper), 1, 2, 3, 4 and 5 for the contrastive experiment.

The technological process of CACMs bulk preparation is shown in Fig. 1.

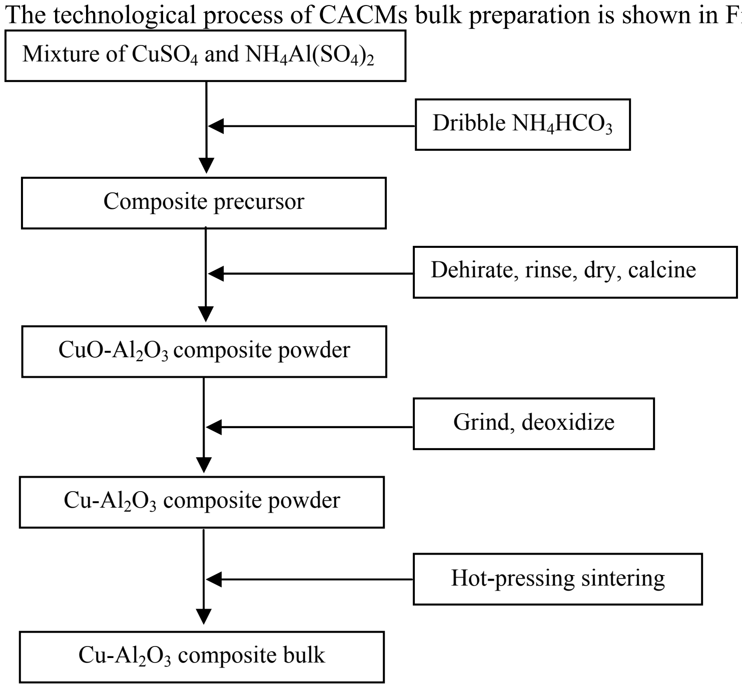


Fig.1 Schematic diagram of preparing CACMs bulk

Friction test

Ball-on-flat fretting tests were performed on UMT-2MT tribometer (CETR, USA). Fig.2 shows a schematic configuration of the fretting test. The commercially available 440C stainless steel ball of 4mm in diameter with 61 HRC hardness was used as the mating ball. It was clamped at the top grip and kept motionless. The CACM sample was screwed in the lower table and moved reciprocal. Being endured high frequency and low load, according to the background of electronic field, the frequency was appointed as 20 Hz, and the amplitude was designed as 300 µm. The experiments were conducted at room temperature for 0.5 h at four different loads (N) which were selected as 0.1, 0.2, 0.5 and 1 N.

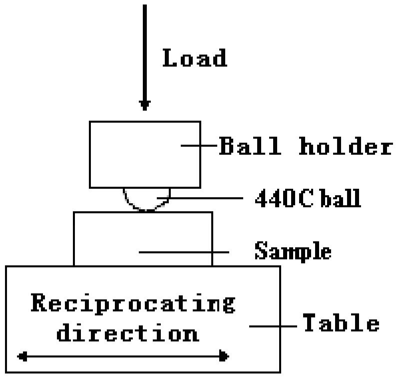


Fig.2 Schematic of reciprocating test configuration

Prior to each wear test, all the specimens were abraded from 800 to 1500 grit SiC paper step by step. The steel ball and specimen were all ultrasonically cleaned in acetone for 10 min and then dried in air for each test.

Examination and measurement

The microhardness of the CACMs was measured for 5 times at 0.98 N for 10 s by a digital microhardness meter (HXD-1000TMC, China), and the microhardness value listed here was the average. The electrical conductivity was measured by an eddy-current device (7501type, China).

The friction coefficient was obtained directly from the software of above-mentioned tribometer. The morphology and composition of the wear scars, material transfer, and wear debris were observed and analyzed by using scanning electron microscopy (SEM, Hitachi 3000N, Japan) equipped with energy dispersive spectroscopy (EDS, EMAX-250). The wear tracks for surface characteristics, such as surface topography, profile curves, and wear volume-loss were further determined by using a Micro XAM non-contact optical profilometer (ADE, USA).

The wear resistance of the material was evaluated by using the relative wear resistance (ε), which is calculated as:

$$\varepsilon = W_s / W_c \tag{1}$$

where W_s is the wear volume-loss of copper, W_c is the wear volume-loss of the composite under the corresponding condition.

Results and discussion

Effect of addition of Al_2O_3 on the mechanical and electrics properties

The electrical conductivity, in form of International Annealed Copper Standard (IACS), and hardness of CACMs with different addition of Al_2O_3 was given in Table 1. It is obvious that the hardness was markedly increased with the addition of Al_2O_3, while the electrical conductivity shows a decreasing tendency.

It is reported that the electrical conductivity must be higher than 80 IACS for an electronic material [3]. The electrical conductivity of the CACM with 2% Al_2O_3 is 85 IACS and then descends as the addition of Al_2O_3 increases. Therefore, the CACMs with less than 2% Al_2O_3 prepared here are suitable for electronic material.

Table 1 Mechanical and electrical properties of the CACMs with different addition of Al_2O_3

Addition of Al_2O_3 (wt.%)	0	1	2	3	4	5
Electrical conductivity (%IACS)	100	93	85	78	75	68
Microhardness (HV)	71.05	83.5	96.28	100.13	105.7	111.98

Effect of Al_2O_3 addition on the friction coefficient and wear-loss

Fig. 3 shows the friction coefficient curves of the CACMs with different Al_2O_3 addition after fretting at the load of 0.1N within 0.5 h. All coefficients arrive at the stable state after a short running-in-period. The mean stable friction coefficients, averaging the coefficients in stable period, reveal that the friction coefficient of copper has the lowest value of 0.419 and as the addition of Al_2O_3 increases it increases and reaches the maximum value of 0.538 at 4%, then decreases to 0.483 at 5%. It can be interpreted that the addition of Al_2O_3 results in much asperities exposed to the surface during the fretting process and the friction force increases accordingly, i.e. the higher addition of Al_2O_3 , the higher the friction coefficient is. However, in the case of 5% Al_2O_3 the spherical Al_2O_3 particles probably flake off and act as bearing ball due to the weak bond caused by the bad wet-ability between ceramic and metal [25] causing the friction coefficient to drop again.

Fig.4 shows dependence of wear volume-loss and relative wear-ability of the CACMs on the addition of Al_2O_3. One can see that the wear-loss decreases with the addition of Al_2O_3 up to 2% and then increases as the addition of Al_2O_3 continuously increases. It indicates that the lowest wear-loss, i.e. the best wear resistance possesses the composite reinforced with 2% Al_2O_3. These results correspond to the relative wear-ability, which shows a tendency of increasing firstly and then decreasing, evidenced by the solid line in Fig.4. The relative wear-ability reaches maximum of 3.13 at the peak of 2% Al_2O_3.

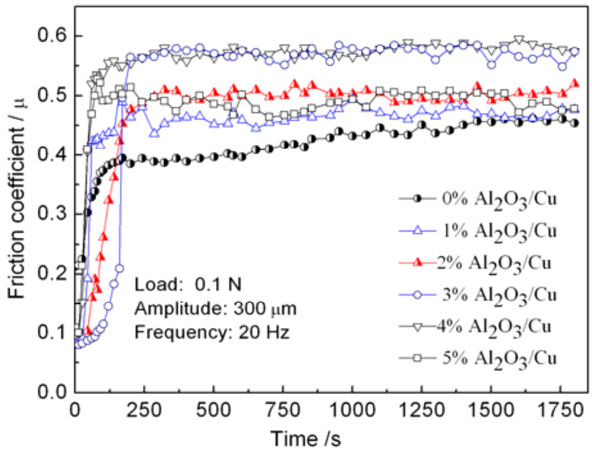


Fig.3 Friction coefficient curves of the CACMs with different addition of Al_2O_3 at fixed load of 0.1N within 0.5 h

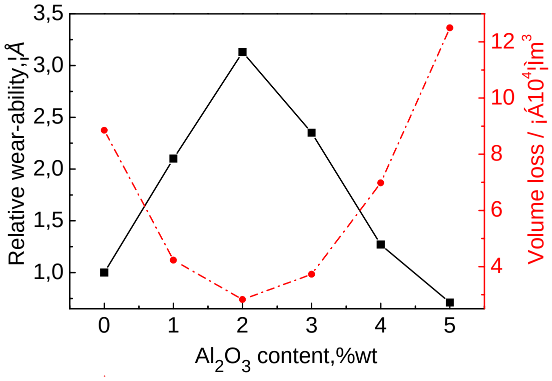


Fig.4 Dependence of wear-loss and relative wear-ability of the CACMs on the addition of Al_2O_3 at the load of 0.1N. The solid line and dotted line correspond to the relative wear-ability and wear-loss respectively.

Contrary to the friction coefficient which increases with the addition of Al_2O_3, the wear-ability of the CACMs is improved. It can be well explained with the *Orowan theory* [26], i.e. the hardness and strength of the composite would be improved with increased addition of the second phase. It is well known that the fine nano-Al_2O_3 particle dispersed in the matrix can considerably increase the moving resistance of the dislocation and sub-grain boundary. The dislocation is difficult to slip, and the strength is enhanced accordingly. Note that the strengthening effect is not significant with the small amount of Al_2O_3 in the CACMs since the dislocation line can easily pass by the second phase. In other words, as the addition of Al_2O_3 particles increases, the remarkable pinning effect of dislocation would occur resulting in higher hardness and improved wear-ability. However, the wear-ability was not proportional to the addition of Al_2O_3, i.e. it decreases instead of increasing when addition of Al_2O_3 increases from 2 to 5%. As reported previously, the wet-ability between metal and ceramic deteriorates and the nano-particles are easier to reunite as the addition of Al_2O_3 increases [25], the binding force and the strength of the composite decreases consequently, especially for the wear resistance. In present work the wear resistance decreases to 0.71 at 5% Al_2O_3, being even worse than that of copper.

The wear scars of the CACMs are regular pits, as presented in the 3D-morphology are in Fig.5. The profiles of different composite across their centers are presented in Fig. 6. It is worth noticing that as the content of Al_2O_3 increases, the approximately U-shape profiles become wider and deeper, among which the composite with 2% Al_2O_3 possess the minimum cross section, implying a best wear-ability. It agrees well with the experimental results.

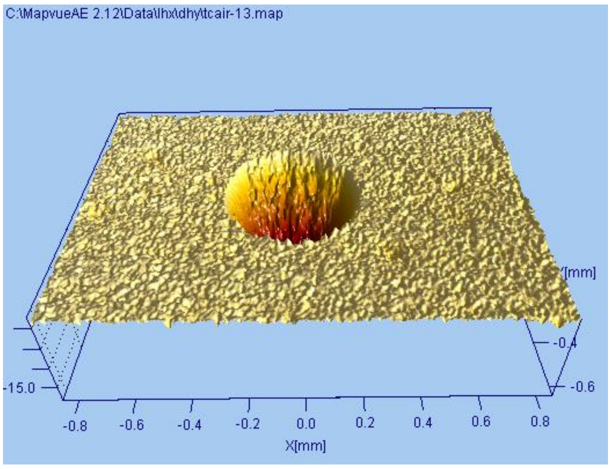


Fig.5 3D-morphography of the wear scar

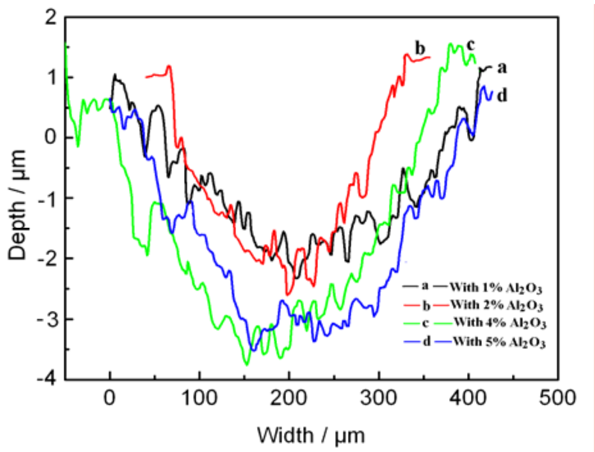


Fig.6 Profiles curves across the centre of the wear scars

Effect of load on coefficient and wear-loss

The CACMs with optimum addition of 2% Al_2O_3 was selected to evaluate the fretting properties at various loads. Reference test was also conducted with copper in this paper. The friction coefficient and wear-loss as a function of the normal load are shown in Fig.7. It is evident that the friction coefficient fluctuates slightly with the increasing load while the wear-loss increases rapidly. There is another point one should note that the friction coefficient of the composite is larger than that of copper, whereas the wear-loss of the composite is always lower at any load. There is no doubt that the wear resistance of the composite is improved with adequate addition of dispersed Al_2O_3 powder.

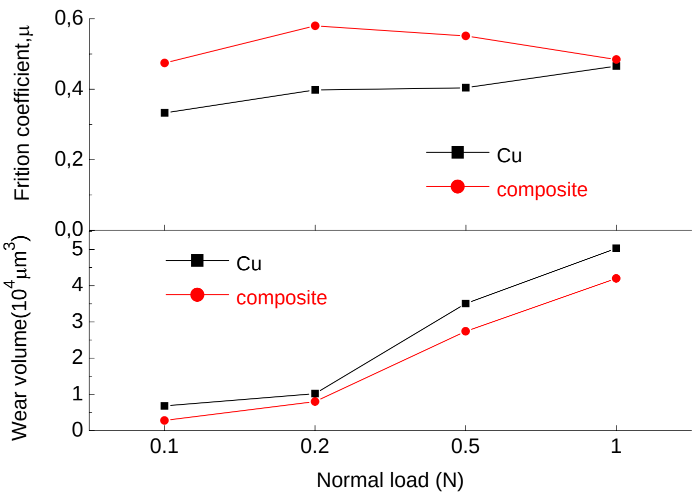
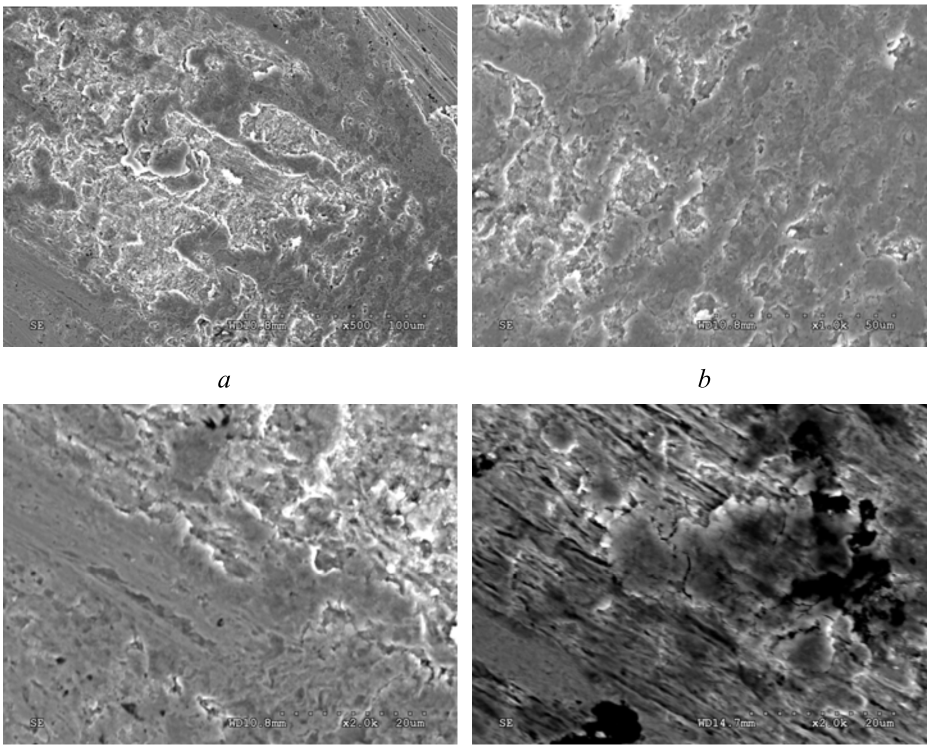


Fig.7 Friction coefficient and wear volume-loss at various loads

The hardness of the CACMs is larger than that of copper as mentioned above, therefore, the copper is easier to be worn under the operation of the tribo-ball even at a very weak load. With the load increasing the asperities would also be inevitably worn to pit. Because the coarse surface and exposed Al_2O_3 protrusions can hold back the wear process, the friction coefficient of the CACMs would be larger than that of copper. When the normal load increases to a certain extent the Al_2O_3 particles would probably flake off and be reserved in the contact zone between tribo-matches together with the debris. They can act as bearing ball, and the friction coefficient thus reduces again.

Wear mechanism

Fig.8 depicts the surface SEM images of copper and CACMs with different amount of Al_2O_3. Typical adhesive wear was observed in the wear scar of copper, as shown in Fig.8 (a). The CACMs with 1% Al_2O_3 still corresponds to adhesive wear. The EDS analysis of the wear scar confirms that elements such as Al, C, Fe, and O can be detected besides the main element Cu, among which the content of Fe is richest in the wear scar as evidenced in Fig. 9. Fe came from the counterface when the test sample slided against the steel ball. It can be deduced that the transfer of material from the mating ball to the disk occurs. Furthermore, the proportion of O element in the wear scar is obviously increased after fretting, which implies that Cu in the composite and Fe transferred from the mating ball have been oxidized since the flash temperature developed on the contact surface is often high enough to reach the oxidation temperature of the fine wear debris. Thus, it can be concluded that the wear mechanism of CACM with 1% Al_2O_3 is adhesive wear associated with oxidation wear. When addition of Al_2O_3 is increased to 2% the wear surface gets smoother and exhibits slightly abrasive wear. Obvious delamination layer and some scratch lines parallel to the direction of friction were observed on the surface of the CACM with 5% Al_2O_3, indicating that the wear mechanism of the composite is abrasive wear associated with delaminating fatigue. Meanwhile, the well-marked holes in the wear scar demonstrate the poor wet-ability between Al_2O_3 particles and Cu that worsen the bind-ability and wear-ability.



a *b* *c* *d*

Fig.8 SEM micrographs of CACMs with different addition of Al_2O_3 (wt%): (a) 0 (copper); (b) 1; (c) 2; and (d) 5 %

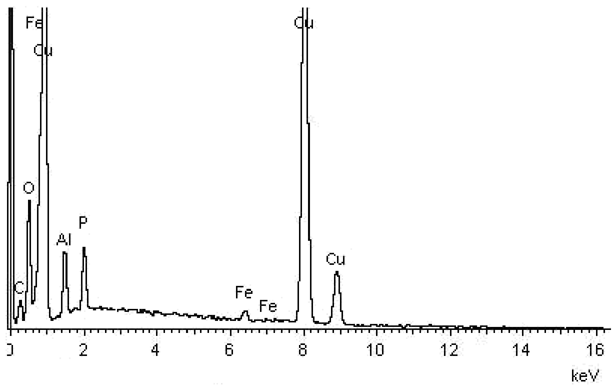


Fig.9 EDS spectrum of CACMs with 1% Al_2O_3 after friction

Conclusion

The major conclusions resulting from the work presented in this paper can be listed as follows:

1. The wear-loss of CACMs decreases firstly and then increases with the increase of addition of Al_2O_3 in the range (wt.%) from 1 to 5, exhibiting a minimum wear-loss at 2% addition of Al_2O_3 and a maximum relative wear-ability of 3.13 times as much as that of copper. It indicates that the optimum of Al_2O_3 addition is 2%.

2. The friction coefficient of the CACMs fluctuates slightly with the increasing load. It is larger than that of the copper. On the other side, the wear-loss of CAMs is always lower than that of copper at any load. The lowest wear-loss, i.e. the best wear resistance, possesses the composite reinforced with 2% Al_2O_3.

3. The wear mechanism of copper is adhesive wear, whereas it becomes adhesive wear associated with oxidation wear for lower addition of Al_2O_3 in CACMs. For higher amount of Al_2O_3 (5%) the wear mechanism of CACMs is abrasive wear associated with the delaminating fatigue.

Acknowledgments

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