The Behavior of Dry Sliding Wear for Aluminium Bronze Alloy Reinforced by Al₂O₃ and TiO₂ Nanoparticles

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Abstract. In this investigation deals with a dry sliding wear of Aluminium bronze alloy reinforced by nanoparticles of α-Al₂O₃ and Rutile-TiO₂. Stir casting method was used by induction furnace to increase wettability between nanoparticles and melting matrix. The copper base alloys reinforced with different percentages of (1.5 and 3 weight percent) of nanoparticles α-Al₂O₃ and Rutile-TiO₂ separately and together. These samples were tested to investigate wear behaviour, using Ball-on-Disc technique, and examined with some variables of wear parameters, such as applied load, and rotational speed with a fixed time of 20 minutes. The Scanning Electron Microscope was used to study the effect of Al₂O₃ and TiO₂ nanoparticles on the topography of worn surfaces of samples. The hardness values were increased to 227.6 Hv after addition equal amounts of 3%wt Al₂O₃ and TiO₂ nanoparticles. The friction coefficient increases to 0.71 when a load of 20 N and it decreases when a rotational speed increases. The wear rate of alloy decreases to (1.38×10⁻⁷ g/cm) when added equal amounts of 1.5%wt Al₂O₃ and TiO₂ nanoparticles under the best condition at 20 N, 300 rpm and 20 minutes. While the wear rate becomes (1.17×10⁻⁷ g/cm) when adding equal amounts 3wt% of the Al₂O₃ and TiO₂. The microstructure of the worm surface showed the reduction in delamination occurs due to enhancing in the wear resistance of alloys and improve the hardness of alloys by nanoparticles reinforcement.

Keywords: Aluminum bronze, Stir casting, Nanoparticles, Wear rate, Microhardness, Reinforcement.

1. Introduction
Many metal matrix composites such as copper composite have been gained attention due to their good mechanical, thermal and tribological properties [1, 2, 3]. Among various dispersions, alumina Al₂O₃ and TiO₂ particles are commonly used to reinforce copper alloys. These oxides dispersion strengthened copper alloys have been reported to show higher elevated temperature strength, increased hardness and improved creep resistance compared to pure copper[4]. Processes of production dispersion-strengthened copper matrix composites involve ingot casting and powder metallurgy. Friction and wear properties of Cu and Cu alloys are determined mainly by plastic deformation and break down in surface layers [5]. The problem of wear and friction is one of the major problems experienced by all machines that have frequency or slip movement because of their effect on the efficiency of these machines. Wear resistance studies of copper reinforced with nanoparticles addition by stir casting are still limited. Aleksandar et al. (2014) [6] studied three alloys, copper-based composites reinforced with micro-sized Al₂O₃ particles, nano-sized Al₂O₃ particles Cu-4.7 Al₂O₃ were produced by powder metallurgy, and compared with Cu-0.4Cr-0.08Zr alloy produced by casting.
technique. The wear tests were carried out by Ball-on-Disc tribometer. The results show that the addition of micro-size of Al$_2$O$_3$ particles did not reduce the wear rate due to a three bodies wear form. While the nano-sized Al$_2$O$_3$ particles reinforced composite increase hardness considerably and then improve wear resistance. Akhtar et al. (2009) [7] studied the microstructure, mechanical properties, processing, and wear behaviour of copper matrix composites produced by stir casting methods and reinforced by titanium carbide. The results show that titanium carbide particles were uniformly distributed in the matrix. Titanium carbide with average grain size ratios was introduced as variables to calculate wear resistance of composite materials. Safari et al. (2017) [8] investigated the behaviour of sliding wear of copper alloys, reinforced by nanoparticles. The γ-Cu5Zn8 nanoparticles with different contents (1wt%, 3wt%, 5wt%, and 7wt %) of Nano-sized added to the pure copper powder. Mechanical milling has carried out for 20 h in a high-energy planetary ball mill with 1.5% stearic acid under argon atmosphere mechanical milling method has produced. Wear tests by Pin-On-Disk machine with conditions of sliding speed of 0.5 m/s and a load of 10 N has conducted for 1000 m a total sliding distance. The copper-based alloys reinforced by particles that fabricated by powder metallurgy methods were studies by Dhokey et al. (2009) [9] and Mohammad et al. (2016) [10]. The aim of this study is to investigate the wear resistance of Aluminum bronze alloy (Cu-7.7wt%Al) reinforced by Al$_2$O$_3$ and TiO$_2$ nanoparticles by the dry sliding condition on Ball-on-Disc tribometer that produced by stir casting methods.

2. Experimental Procedures

2.1. Material

Aluminum bronze alloy and nanoparticles of α-Al$_2$O$_3$ and TiO$_2$ as raw materials have used in this study. These materials were analysed by X-Ray fluorescent in Baghdad Central Laboratory, Ministry of Construction and Housing. This analysis was done to identify chemical compositions as indicated in Table 1.

| Materials analysis   | Alloy   | Cu    | Al    | Si    | Mn     | P     | Ag     |
|----------------------|---------|-------|-------|-------|--------|-------|--------|
| CuAl                 | 92.217  | 7.7   | 0.012 | 0.017 | 0.001  |       | 0.104  |
| Cu powder            | 99.721  | --    | 0.082 | --    | 0.012  | 0.104 | 0.082  |

| Powder analysis      | Nano powder | α-Al$_2$O$_3$ | TiO$_2$ | Cr$_2$O$_3$ | CuO | Tm$_2$O$_3$ |
|----------------------|-------------|--------------|--------|-------------|-----|-------------|
| α-Al$_2$O$_3$         | 99.777      | --           | 0.007  | 0.001       |     |             |
| RutileTiO$_2$         | --          | 99.929       | --     | 0.008       | 0.062 |             |

2.2. Tool and Equipment

The cast iron mold with two holes diameter 10mm and 16 mm was using by stir casting methods that consisted of induction furnace, graphite crucible, mixer with speed about 600 RPM. The microhardness test using a Digital Micro Vickers Hardness Tester TH714 of (300) g load are applied. Ball on disk Micro Test Wear-Madrid used in the experiments. XRD Shimadzu 6000 X-ray diffraction target CuKα1 radiation with 20 angle covered from 15 to 120 degree was used. Scanning electron microscopy (SEM) with EDS used to investigate the microstructures of materials.

2.3. Casting and Molding

The process is started with the preparation of the charge containing required quantities of different elements such as CuAl, Al$_2$O$_3$, and TiO$_2$. Stir casting method with argon atmosphere was adopted for producing the samples in this experimental study. Preheat of casting molds for about (100–150) °C before pouring is very important to minimize the casting defects such as shrinkage cavities [11]. Then weighed amount of nanoparticles (1.5, and 3) wt% of Al$_2$O$_3$, and TiO$_2$ added to the CuAl alloy melt. After five minutes, the alloy dissolved, the nanoparticles added and the melt stirred vigorously. The melt surface covered with fluxes, usually based on borax, due to the ability to dissolve and collect
objectionable oxide and makes it possible to obtain a structure free from solid non-metallic [12]. These alloys have poured in a steel mold to produce rods casts. The chemical analysis of these casts has tableted as shown in Table 2. The obtained analysis has agreed with aluminium bronze alloy standard C95600 [13].

| Samples No. | Additive before casting Wt% | Additive after casting Wt% |
|-------------|-----------------------------|---------------------------|
| 1           | Cu8 Al                      | Cu7.7 Al                  |
| 2           | Cu8Al+1.5Al2O3              | Cu7.7Al+1.5Al2O3          |
| 3           | Cu8Al+ 3 Al2O3              | Cu7.7Al+ 3 Al2O3          |
| 4           | Cu8Al+ 1.5TiO2              | Cu7.7Al+ 1.5TiO2          |
| 5           | Cu8Al+ 3 TiO2               | Cu7.7Al+ 3 TiO2           |
| 6           | Cu8Al + 1.5 Al2O3+ 1.5 TiO2 | Cu7.7Al + 1.5 Al2O3+ 1.5 TiO2 |
| 7           | Cu8Al +3 Al2O3+ 3 TiO2      | Cu7.7Al +3 Al2O3+ 3 TiO2  |

2.4 Sample Preparation

The ingots diameter of 16 mm and a length of 120 mm cast as rods as shown in Figure 1. These materials are cut to prepare specimens with dimensions of 5 mm length and 16 mm diameter for wear test [13].

![Figure 1. Shows the rod casts sample.](image)

2.5 Wear Test

The dry sliding wear has studied using Ball on disk Micro Test Wear-Madrid Spain with steel ball made of 100 Cr6 martensitic bearing steel with the constant radius of (5mm) in accordance with ASTM G99. The time of test was 20 minutes and sliding distance of (100 m) as shown in Figures 2.

![Figure 2. Shows the wear device of micro test Ball on disk](image)

These tests has done at different loads and speeds of (5, 10, 15 and 20) N, and (300, 400, 500, 600) RPM; respectively, using test facilities available at University of Babylon, Material Engineering College. The coefficient of friction (COF) and wear resistant have measured. The wear rate calculated by the following equation [7]:-
\[ \text{Wear Rate (WR)} = \frac{\Delta W}{\pi D t} \]

\( \Delta W \): Weight loss for the test (g)
\( D \): Diameter of the sliding circle (0.5 cm)
\( t \): Wear test time (20 min)
\( N \): Rotational speed of disc (rpm)

3. Results and Discussions

3.1. X-Ray of specimens alloy

XRD analysis of copper aluminum alloy reinforcement by nanoparticles has performed in the specimens showing strong peaks of the Cu-rich \( \alpha \) phase. The 2\( \theta \) angle covered is from 15 to 100 degrees. The smallest peaks of the CuAl\(_2\) phase that formed in the matrix as the intermetallic compound in the cast alloy as shown in Figure 3.

![Figure 3. Shown the XRD of copper aluminum alloy reinforcement by nanoparticles.](image)

3.2. Hardness test

Table 3 shows that microhardness value increases with the presence of Al\(_2\)O\(_3\) and TiO\(_2\) nanoparticles. This value increases from 166.1 HV for the matrix to 227.6 HV for composites with equal amounts for both nanoparticles of 3 wt%. This is due to the interactions of grain boundary strengthening and strain hardening that result from the obstacles of dislocation movement. In addition, these nanoparticles act as nucleation sites during solidification as proposed by Iman et al [14].

| Samples No. | Additive | Microhardness HV |
|-------------|----------|------------------|
| 1           | Cu8 Al   | 166.2            |
| 2           | Cu8Al+1.5Al\(_2\)O\(_3\) | 174.6            |
| 3           | Cu8Al+ 3 Al\(_2\)O\(_3\) | 177.8            |
| 4           | Cu8Al+ 1.5TiO\(_2\) | 191.3            |
| 5           | Cu8Al+ 3 TiO\(_2\) | 194.2            |
| 6           | Cu8Al+ 1.5 Al\(_2\)O\(_2\)+1.5 TiO\(_2\) | 223.4            |
| 7           | Cu8Al+3 Al\(_2\)O\(_2\)+3 TiO\(_2\) | 227.6            |

3.3. Friction Coefficient

The friction coefficient of Cu-7.7Al wt % alloy is proportional to the rotational speed and load. At an early stage of friction, the coefficient of friction increases and the steady state within 20 minutes has established due to the surface roughness that generated between surfaces during sliding. The reason for the reduction in the coefficient of friction at the early stage is due to the presence of an oxide layer on a Cu-7.7Al wt % alloy surface [15]. The contact surfaces have separated by the oxide layer formed. The friction coefficients become in the range of 0.31 to 0.4 after initial rubbing, increased load from 5 to 15 N, and rotational speed was 300 rpm. Then, it increased to 0.71 when applied load increased to 20 N, as shown in Figure 4.
The influence of load on the friction coefficient at 300 rpm of Cu-7.7Al alloy.

The increased in friction coefficient is due to the oxide layer will break down to make a true contact between the surfaces. When the rotational speed increases from 300 to 600 rpm and the load is 20 N, the friction coefficient decreased from 0.72 to 0.32. The increase in the rotational speed leads to an increase in the oxidation rate due to the rising temperature. This leads to producing the voids or micropits on the surface contact, which can be filled by the counterpart and some materials debris due to breaking down of the surface layer, which in turn acts as a solid lubricant [15]. As a result, the friction coefficient decreases with an increase in the rotational speed as illustrated in Figure 5.

The influence of rotational speed on the friction coefficients at 20 N load of Cu-7.7Al alloy.

3.4. Wear rate

The influence of different additions of Al₂O₃ and TiO₂ nanoparticles on the wear rate under the dry sliding condition has investigated. Here, the load, rotational speed and time were kept constant at 20 N, 300 rpm and 20 min, respectively. From Figure 6, it noted that the wear rate for Cu-Al shows a high value of wear rate of 6.79×10⁻⁷ g/cm compared with other alloys because of the microscopic nature of that alloy being soft and containing single phase (α). The wear rate of alloy decreases to (1.38×10⁻⁷ g/cm) when adding 1.5wt% of Al₂O₃ and TiO₂ particles [16]. Figure 7 shows the wear rate for Cu-Al at the same conditions decreased to (1.17×10⁻⁷ g/cm) when adding 3wt% of the Al₂O₃ and TiO₂. This implies that the wear resistance of the alloy is greatly enhanced when adding the nanoparticles compared to the matrix. This considered due to the nanoparticles that may cause an increase in the hardness. Therefore, reducing the plastic deformation between the contact surfaces and acting as a load-bearing element [17]. It can be observed that an increase in the percent of nanoparticles leads to a reduction in the wear rate or increase in the wear resistance of alloys.
Figure 6. The influence of 1.5 wt% nanoparticles on wear rate of Cu-Al alloy in 20 N load, 300 rpm and 20 minutes time.

Figure 7. The influence of 3 wt% nanoparticles on wear rate of Cu-Al alloy in 300 rpm, 20 N and 20 minutes time.

The wear rate and coefficient of friction for Cu-Al with nano Al2O3 and TiO2 were less than of matrix. This is due to the nanoparticles cause an increase in the oxide layers and in the hardness of these alloys.

3.5. Worn Surfaces Characterization

To study the effect of Al2O3 and TiO2 nanoparticles on the topography of worn surfaces of samples, the Scanning Electron Microscope has used. This study has applied under best conditions of 20 N load, 300 rpm rotational speed and 20-minute time with different weight percent on nanoparticles. The worn surface of Cu-Al alloy matrix is found to be more damage in worm surface, indicating a significant plastic deformation and high disruption occurred in Cu-Al alloy. In addition, the high weight loss and wear rate among the reinforced alloys are exhibited. Adhesive wear, caused by the sliding surfaces, is the main wear mechanism of Cu-Al alloy. This is lead to severe plastic deformation of surface and subsurface alloys under high load, as observed in Figure 8 (a and b). After the deformation, the work hardening for unreinforced Cu-Al alloy occurred, which led to the appearance of micro-cracks. The delamination occurs in Cu-Al alloy with 1.5 Al2O3 in Figure 8 (c) and 1.5 TiO2 in Figure 8 (d) when the small void initiates and grows and converge micro-cracks of surface and subsurface.
Figure 8. Shows the morphologies of the worn surface for CuAl alloy, a. and b. CuAl alloy, c. CuAl-1.5 Al₂O₃, d. CuAl-1.5 TiO₂, and e. and f. CuAl-1.5 Al₂O₃+1.5TiO₂ at a load of 20 N and 300 rpm.

Figure 8 (e and f) shows the adhesive wear of reinforced Cu-Al alloy with 1.5 Al₂O₃ + 1.5TiO₂. It appears that with an increase in loads leads to form welding points between contact surfaces that result in leaving voids and the softer materials fill in the micro pits in the surface.

Figure 9. Shows the morphologies of the worn surface at load of 20 N and 300 rpm, a. and b. CuAl-3 Al₂O₃, c and d. CuAl-3TiO₂, e and f. CuAl-3Al₂O₃-3TiO₂.
Moreover, it concluded that the fine grooves formed along the sliding direction, which leads to abrasive wear mechanism. The reinforced phases characterized by the delamination mechanism, where, the hard-reinforced particles cracked, fragmentized, and removed partially or totally from the matrix phase under wear conditions [18]. It is noticeable that the delamination layers number and grooves depth in the matrix are notably higher than those for reinforced alloy. Figure 9 (a to j) shows the surface morphologies of samples when adding nanoparticles 3wt% of Al2O3 and TiO2 separately and together. Abrasive grooves are caused by nanoparticles which prevent the delamination of the matrix and separate the chips from the surface as shown in Figure 9 (a to c). The surface is exhibited some clear longitudinal abrasive grooves due to the effects of harder Al2O3 and TiO2 nanoparticles as shown in Figure 9 (d and e). These hard particles prevent the occurrence of abrasion and plastic deformation as shown in Figure 9 (f to j). This is due to stress concentration on the surface contacts and the bonding between matrix and reinforcement. The reduction in delamination occurs due to enhance in the wear resistance of alloys and improve the hardness of alloys due to the reinforcement by nanoparticles [19].

4. Conclusions
The following conclusions can be drawn:
1. The microstructure of reinforced alloy is composed of a fine dendritic structure of α Cu compared to the matrix and CuAl2 as an intermetallic compound.
2. The addition of Al2O3 and TiO2 to Cu-Al alloy has been shown to increase the hardness value to 227.6 HV.
3. The Cu-Al alloy reinforced with 3wt% of Al2O3 and TiO2 have a lower wear rate compared to nano-composites reinforced with 1.5wt% of Al2O3 and TiO2, compared to the matrix under the best condition of 20 N, 300 rpm and 20 min.
4. The friction coefficient increased to 0.71 when loading 20 N and it decreases with an increased rotational speed of 600 rpm.
5. Adhesive and abrasive wear mechanisms have observed in all Cu-Al alloys reinforced by nanoparticles in the dry sliding wear.

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