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Wear Behavior of Commercial Pure Copper with Al and Zn under Dry, Wet and Corrosive Environment

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Abstract

This paper reports the study of the sliding wear behaviour of the Cu–alloys at ambient condition under dry, wet and 3.5% NaCl corrosive environment. Wear tests are conducted using a pin-on-disk tribometer. The applied load of 20N is used at sliding velocity of 0.385 ms^{-1} and sliding distance varies ranging from 115.5m-2772m. The results show that addition of Zn does not play a great role on wear properties but Al strengthens Cu and improve the wear properties especially in wet and corrosive environment because it imparts oxidation resistance by forming a tenacious alumina-rich surface film. It is indicated that frictional coefficient of pure Cu is higher because of its lower hardness. It is much greater for all the alloys in dry sliding environment than under wet and corrosive environment due to sealing effect. The worn surfaces are characterized by optical and scanning electron microscopy. The deep grooves parallel to the sliding direction are shown on the worn surface in dry sliding condition whereas in wet and corrosive environment, wear tracks displayed are smoother.

1. Introduction

Copper and copper alloys constitute one of the most important groups of commercial metals. They are familiar materials that are extensively used in industrial applications due to their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication, and good strength and fatigue resistance [1-4]. Unalloyed copper is quite soft compared to common structural metals. An alloy with aluminium added to copper is known as aluminum bronze; the resulting alloy is stronger and harder than either of the pure metals. When zinc is added to copper form alloys known as brass. It should be noted that neither ‘bronze’ nor ‘brass’ is a concrete, technical term. Tin, manganese, nickel, and silicon can also be added to make stronger copper [5, 6]. Another copper strengthening method is precipitation hardening. The process involves quenching a supersaturated solid solution from an elevated temperature, then reheating to a lower temperature to allow the excess solute to precipitate out and form a second phase [7]. The second phase can be a metal or an inter-metallic compound precipitated from a solid solution by an ageing treatment [8-10].

Copper based materials also used as bearing materials because they have high thermal and electrical conductivity, self-lubrication property, good corrosion and wear resistance [11, 12]. However, the major failure of copper is its surface wear, which induces the surface’s deformation, lowering the strength and hardness of copper materials compared to other materials. Therefore, there has been a great demand for improving the performance of its surface [13, 14]. There are several studies and investigations dealing with wear resistance improvements of these materials. Wear resistance is one of the most important properties of these alloys. The wear response of the alloys significantly depends on their alloying

elements. It is well known that tribological properties are not just essential properties of materials, but are strongly dependent on working conditions [15, 16]. The working condition includes not only operating parameters but also environmental factors like dry, wet, lubricant, corrosion etc [17, 18].
The objective of the present investigation was to examine the influence of alloying elements like Al and Zn in copper on its friction and wear behaviour under dry, wet and corrosive environment. Ten weight percent of each alloying element was incorporated in copper. Simple binary alloys were selected for study to isolate the influence of a single alloying element on friction and transfer behaviour.

2. Material and Methods

The materials used in the current study were commercially pure Cu, Cu-10Al and Cu-10Zn alloy. In the development of the alloys, the commercially pure copper, aluminium and zinc were taken. Melting was carried out in a clay-graphite crucible in a natural gas fired pit furnace under suitable flux cover. The final temperature of the melts was always maintained at 1300±15°C. A preheated steel mould (200°C) size of 20× 100 × 150 in millimeter was prepared which was coated inside with a film of water-clay. The melts were then allowed to be homogenized under stirring at 1200°C and poured in that preheated mould. All the alloys were analyzed by spectrochemical method and the chemical compositions of the alloys are given in Table 1. The cast samples were first machined to skin out the oxide layer from the surface. Cold rolling of the cast alloys were carried out with a laboratory scale rolling mill of 10HP capacity at 40% of reduction. The alloys were pieces into 15 x 20 x 150 mm and the deformation given was about 1 mm per pass. After cold rolling the thickness became 9 mm from the 15 mm thickness. The samples of 9 x 20 x 20 mm^3 size obtained from the cold rolled samples and the alloys processed through different routes were aged at different temperatures for one hour. The samples were sanded mechanically with emery papers of rough one and the one of 1500 grits. Microhardness of the aged samples was measured with a Micro Vickers Hardness Tester. The knoop indenter was applied with 1Kg load for 10 seconds. At least seven indentations from different locations from each sample were taken.

Table1: Chemical composition of the experimental alloys (wt %)

Alloy	*Al*	*Zn*	*Pb*	*Sn*	*Fe*	*Ni*	*Si*	*Mn*	*Cr*	*Sb*	*Cu*
Cu	0.001	0.000	0.010	0.004	0.033	0.001	0.000	0.000	0.001	0.000	Bal
Cu-10Al	9.601	0.023	0.013	0.009	0.078	0.007	0.004	0.009	0.007	0.079	Bal
Cu-10Zn	0.013	10.300	0.012	0.007	0.057	0.005	0.004	0.009	0.007	0.005	Bal

The sample of 12 mm length and 5 mm diameter were machined from the cold rolled alloys for wear study by following ASTM Standard G99-05. The samples were also aged at 200°C for one hour to attend the peak hardness. The end surface (5 mm diameter) of the pin samples were polished using emery papers of 1500 grits. Later, the end surface was cleaned in running water. Finally, the samples were dried in acetone. The 309s stainless steel discs were used as the counter-body material. The hardness of the discs was HRB 85. One of the surfaces of the disc was grinded by surface grinding machine and cleaned with cotton. Surface roughness of the disc was 40µm. The frictional and wear behaviors of the experimental alloys were investigated in a pin-on disc type wear apparatus by following ASTM Standard G99-05. During the dry wear tests, the end surface of the pin samples were pressed against horizontal rotating stainless steel disc. Applied load of 20 N was used throughout the test, which yielded nominal contact pressures of 1.02 MPa. The tests were conducted at the sliding speed of 0.385 ms^{-1} with varying sliding distances ranging from 115.5m-2772m. The tests were carried out in ambient air (relative humidity 60%) under dry sliding condition (without lubrication). Wet immersion test was used where the stainless steel disc and the wear samples were immersed in distilled water and for corrosive immersion test 3.5% NaCl solution was used. All other parameters were similar to dry wear test. At least three tests were done for each type of material. Wear rates were calculated from average values of weight-loss measurements. Wear rate was estimated by measuring the weight loss (ΔW) after each test.

Care has been given after each test to avoid entrapment of wear debris. The wear rate was calculated using the following expression [19]-

$$W.R = \frac{\Delta W}{S.D \times L} \quad (1)$$

Here,
W.R = Wear Rate
ΔW = Weight Loss
S.D = Sliding Distance
L = Load
The optical metallography of the samples was carried out in the usual way. In case of using metallographic copper etchant a conventionally recommended one of Ammonium Hydroxide+ Hydrogen peroxide (3%) was used where the compounds were taken in 1:1 ratio. The washed and dried samples were observed carefully in optical microscope at different magnifications and some selected photomicrographs were taken. The SEM investigation of the worn surfaces was conducted by using a JEOL scanning electron microscope.

3. Results and discussion

3.1. Isochronal Ageing

The results of isochronal ageing of 40% cold rolled Cu, Cu-10Al and Cu-10Zn alloys at different temperature for 60 minutes are shown in Fig. 1. Cu and Cu-10Zn alloy show a continuous softening at increasing ageing temperatures. Initial stage of softening occurs due to stress relieving of the alloys. The results of the present experiments clearly indicate that the age hardening effect shown by the Cu-10Al alloy at 200°C due to the addition of Aluminium. Aluminium when added in small concentrations is known to cause precipitation hardening and to form a supersaturated solid solution upon solidification. In the ageing process of the alloys, the hard and brittle Al_4Cu_9, and Al_2Cu_3 intermetallic precipitates can effectively strengthen the alloys and lead to the ageing peak. There was a steep drop in hardness beyond 200°C. This occurred due to precipitation coarsening and recrystallization effect for all the alloys [20, 21].

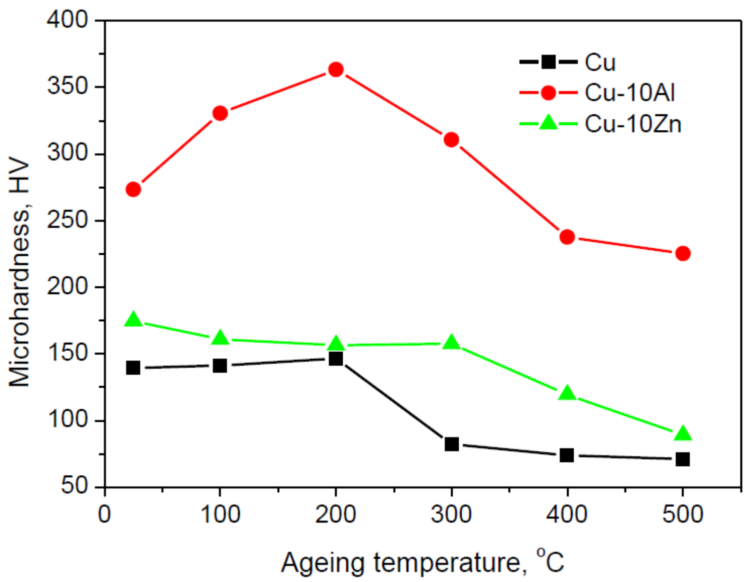

Figure 1: Isochronal ageing curve of the 40% cold rolled alloys, aged for 1 hour

3.2. Wear behaviour

Fig. 2 elucidate the variation of weight loss with the variation of sliding distance for Cu, Cu-10Al and Cu-10Zn alloys at applied pressure of 1.02MPa (Normal Load = 20N) in dry sliding condition. It can be seen from the figure that, as the sliding distance increases the weight loss increases typically for all the alloys. The increase of weight loss for all the alloys because as sliding distance increases, the contact between rotating disk surface and sliding surface of specimen becomes more familiar with elapse of time; for the reason that the temperature between the rotating disk surface and sliding surface of specimen increases and leads to softening of materials and plastic state of materials occurs. Similar observations have been made by other investees [22, 23].

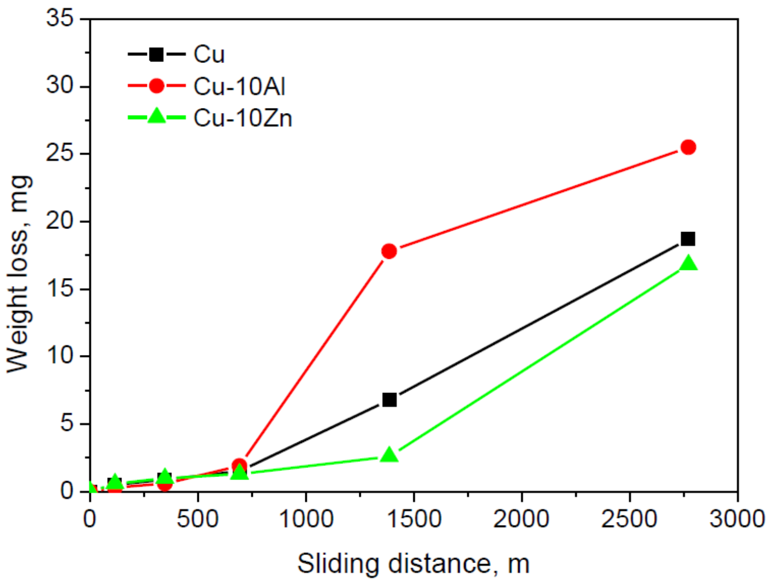

Figure 2: Variation of weight loss with the sliding distance in dry sliding condition

Additionally, Figs. 3-5 depict the variation of wear rate with the variation of sliding distance for the alloys in dry, wet and 3.5% NaCl corrosive environment respectively. It is clear from the figure that in Cu-10Al alloy has poor wear performance compared to Cu and Cu-10Zn alloys under dry sliding condition (Fig. 3). Cu-10Zn displays better wear resistance compared to copper. Despite the fact that Cu-10Al alloy is harder than Cu-10Zn alloy, it is seen that Cu-10Zn brass still gives better wear resistance. This can be due to the modification occurring on the counterface surfaces or the debris generated in the interface. It is suggested that the removed material from Cu-10Al alloy is very hard and may attack both rubbed surface when they are on their way out of the interface zone. This results in three-body abrasion, which results in high material removal as reported by many researchers [24]. In the case of Cu and Cu-10Zn alloy, there could be coating process occurring during the sliding, which assist to cover the stainless steel counterface during the sliding resulting in very low material removal [25]. Another thought could be that the hardness of Cu and Cu-10Zn alloy debris might not be as hard as Cu-10Al alloy debris, which in turn resulted in low material removal from the sample surface.

When the environment is changed from dry to wet, wear rate of the Cu, Cu-10Al alloy and Cu-10Zn alloy exhibits a contradictory tendency to either increase or decrease slightly (Fig. 4). The effects of the environment have yet to be clarified. Whilst some researchers claim that a wet environment promotes wear due to hydrogen attack, others affirm that wear reduces the tendency for abrasive particle embedment and has lubrication effects, leading to lower weight loss than in dry environment [26, 27]. The various mechanisms, as stated above may act simultaneously during abrasive wear in wet environment, and that the extent of the different effects depends on the test conditions. Aluminum strengthens copper and imparts oxidation resistance by forming a tenacious alumina-rich surface film. Cu-10Al alloy singly or in combination for higher strength and or corrosion resistance in specific media.

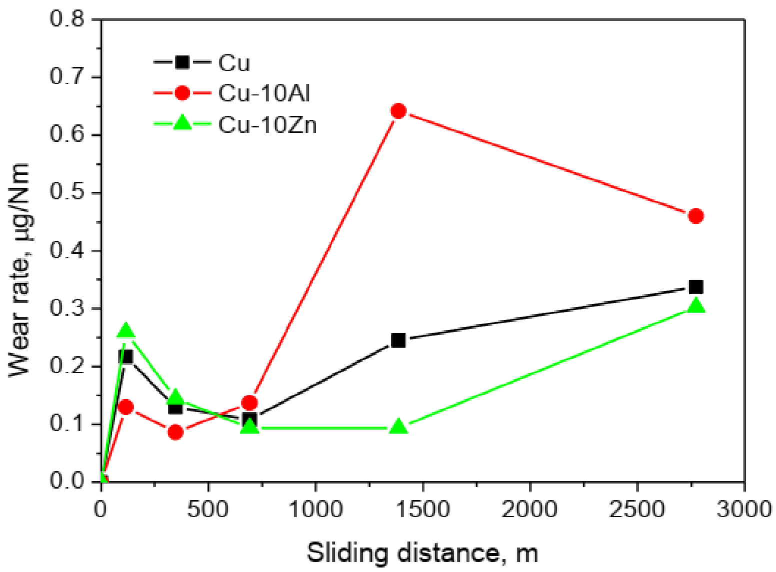

Figure 3: Variation of wear rate with the sliding distance in dry sliding condition.

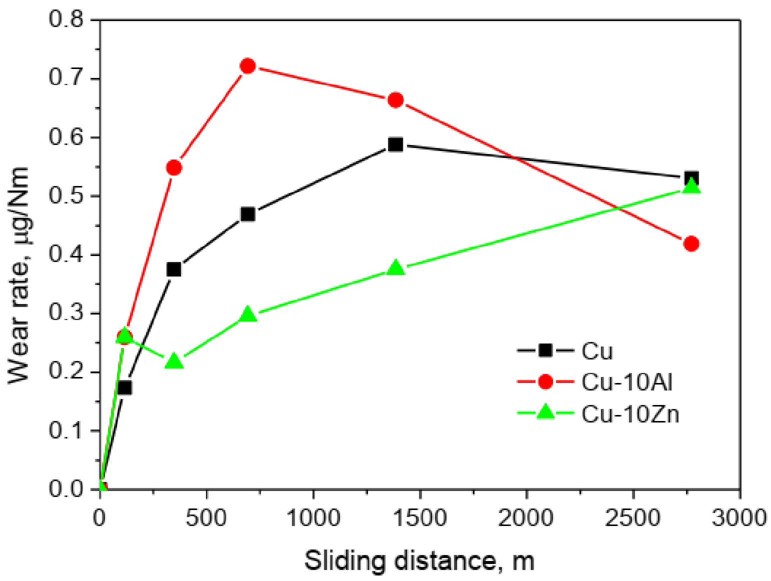

Figure 4: Variation of wear rate with the sliding distance in wet sliding condition.

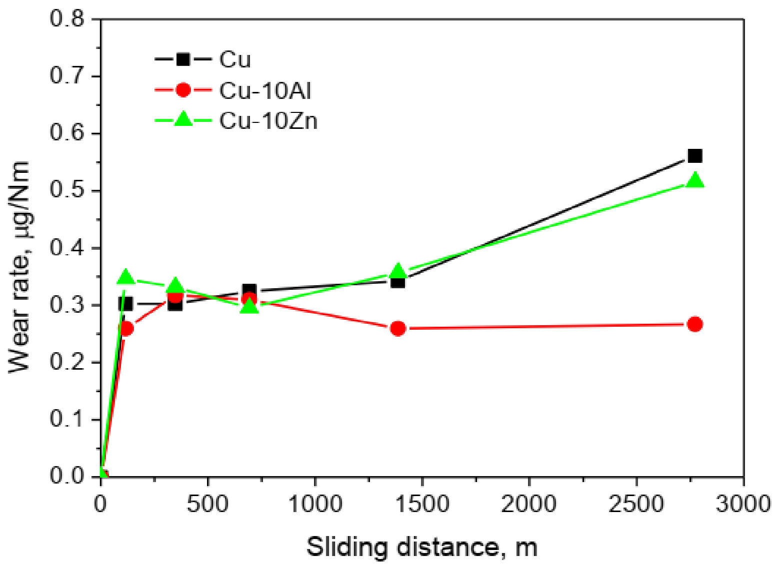

Figure 5: Variation of wear rate with the sliding distance in corrosive sliding condition.

This form of wear occurs when sliding takes place in corrosive environment. In the absence of sliding, the products of corrosion form a film on the surface, which tends to slow down or even arrest the corrosion [28]. However, the formation of non-porous chromium oxide on the Cu-10Al alloy and stainless steel surface can reduce the corrosive wear (Fig. 5). The coefficient of friction obtained from the experiment is plotted against sliding distance in Figs. 6-8 under dry, wet and corrosive environment respectively. It can be seen that the coefficient of friction reaches a steady state after showing a sharp increase during the initial sliding distance. The increase of coefficient of friction is due to rough contact surfaces between pin sample and the stainless steel disc. Once upon a time they reach an ideal contact, and then the result shows almost constant value [19].

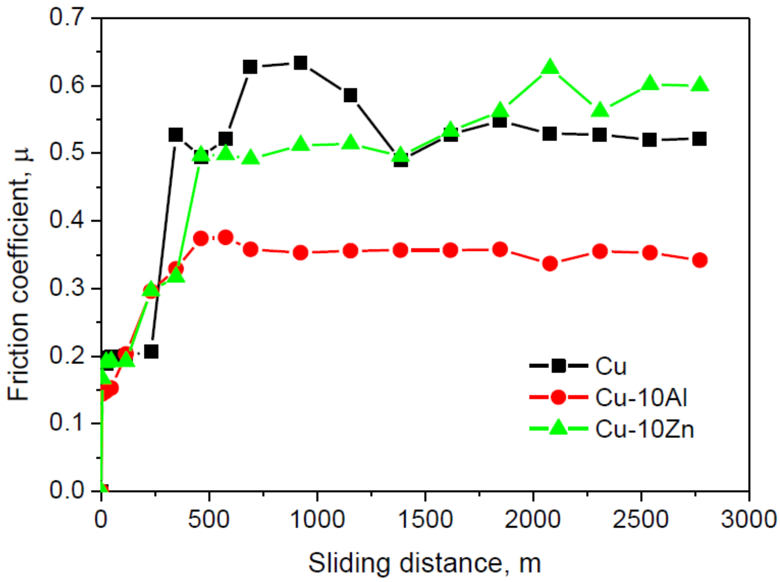

Figure 6: Variation of friction coefficient with the sliding distance in dry sliding condition.

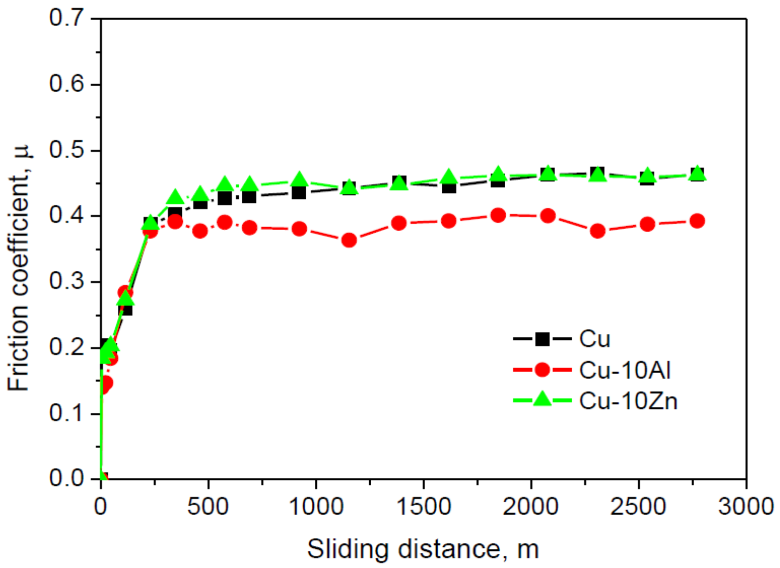

Figure 7: Variation of friction coefficient with the sliding distance in wet sliding condition.

In most cases, higher hardness is strongly related with the reduction of coefficient of friction. From the results obtained, commercially pure Cu had a higher degree of COF followed by Cu-10Zn and Cu-10Al alloys. The same results were also reported earlier where the reinforced copper composites revealed a low value of COF [29-31]. From the figs it is also shown that the frictional coefficient for dry environment is much greater than under wet and salty wet environment for all the alloys. There are numerous reasons behind this observable fact. The cause of this friction reduction is not due to any hydrodynamic effects that come into play, but rather the “Sealing Effect”, which reduces the roughness of the surfaces in contact.

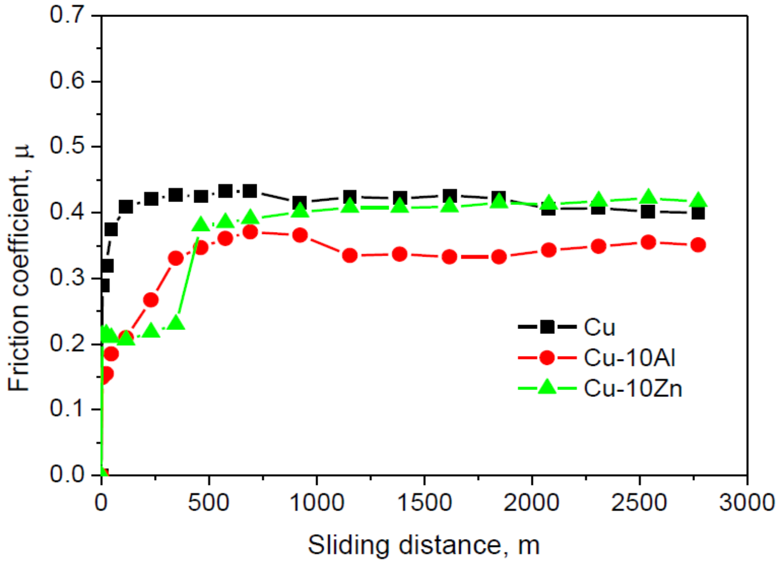

Figure 8: Variation of friction coefficient with the sliding distance in corrosive sliding condition.

On a wet contact surface, the water may partially or totally interrupt the contact between the experimental samples and stainless steel counter body surface, which, in turn, leads to a decrease in the coefficient of friction [32]. Salt water act as a lubricant which decrease some extend friction coefficient of the experimental alloys by separating the surfaces by the lubricant layer. The frictional behaviour for all the materials seems to be steady especially with Cu and Cu-10Zn alloy. Cu-10Al alloy exhibits a bit of fluctuation in the value, which represents a modification on the surface during the sliding. Such behaviour has been reported previously when the materials transfer from surface to another and detachments occur leading to fluctuations in the frication coefficient [33].

The effect of variation of applied load on friction behavior of the alloys in different sliding condition is shown in Fig. 9-11. It is observed that increasing the applied load reduces the friction coefficient for all the alloys.

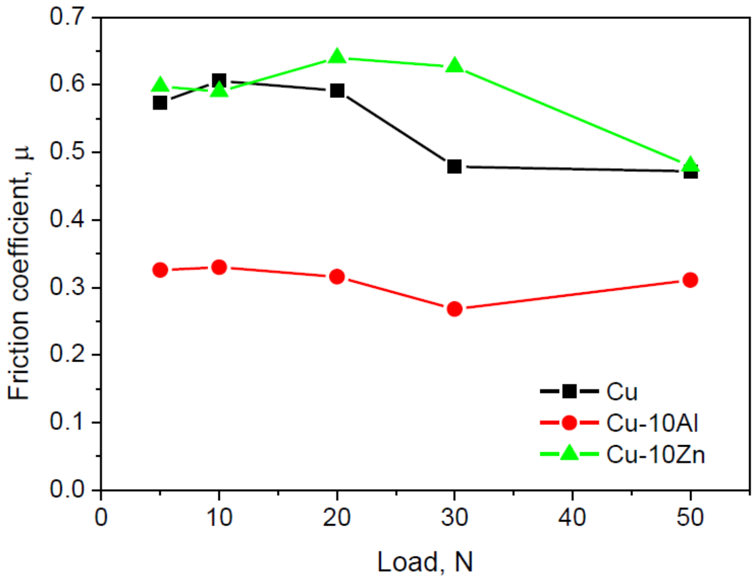

Figure 9: Variation of friction coefficient with applied load distance in dry sliding condition

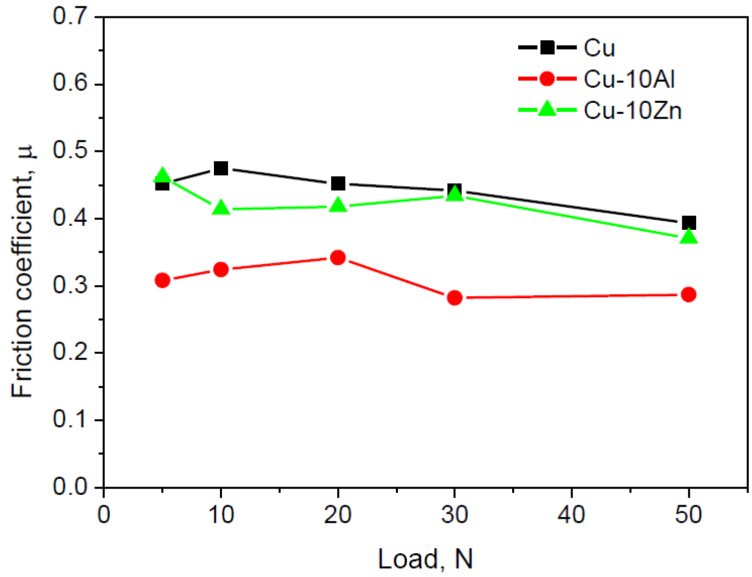

Figure 10: Variation of friction coefficient with applied load distance in wet sliding condition

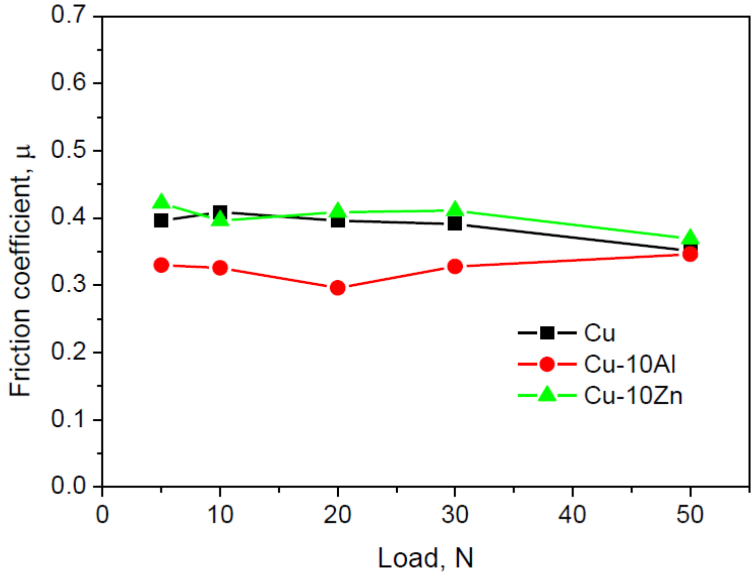

Figure 11: Variation of friction coefficient with applied load distance in corrosive sliding condition

Surface irregularities play a major role for friction coefficient. Surface roughness increases and a great amount of wear debris are supposed to be responsible for the decrease in friction with the increase in normal load [34]. In wet and corrosive sliding environment the surfaces become smooth owing the mixed lubrication is developed. Lubricant formed film which may be stable due to the smooth geometry between surfaces. In non-conformal contact, full film lubrication condition exists between the mating surfaces which are responsible to developed elastohydrodynamic lubrication. The result is little reduction in friction coefficient [35].

3.3. Optical Microscopy

The worn surfaces for all the alloys in different experimental conditions are presented in Fig. 10. Polished Cu, Cu-10Al and Cu-10Zn alloys before wear test consist of moderately smooth surface in comparison to others and exhibit no symptom of plastic deformation or drawing. They show some scratches of the sand paper, which may be formed during surface preparation. Many large wear particles, oxide debris and particles, and the deep grooves parallel to the sliding direction are presented in figure when the alloys are tested under dry sliding condition. Moreover, the plastic deformation and many large cracks can be detected.

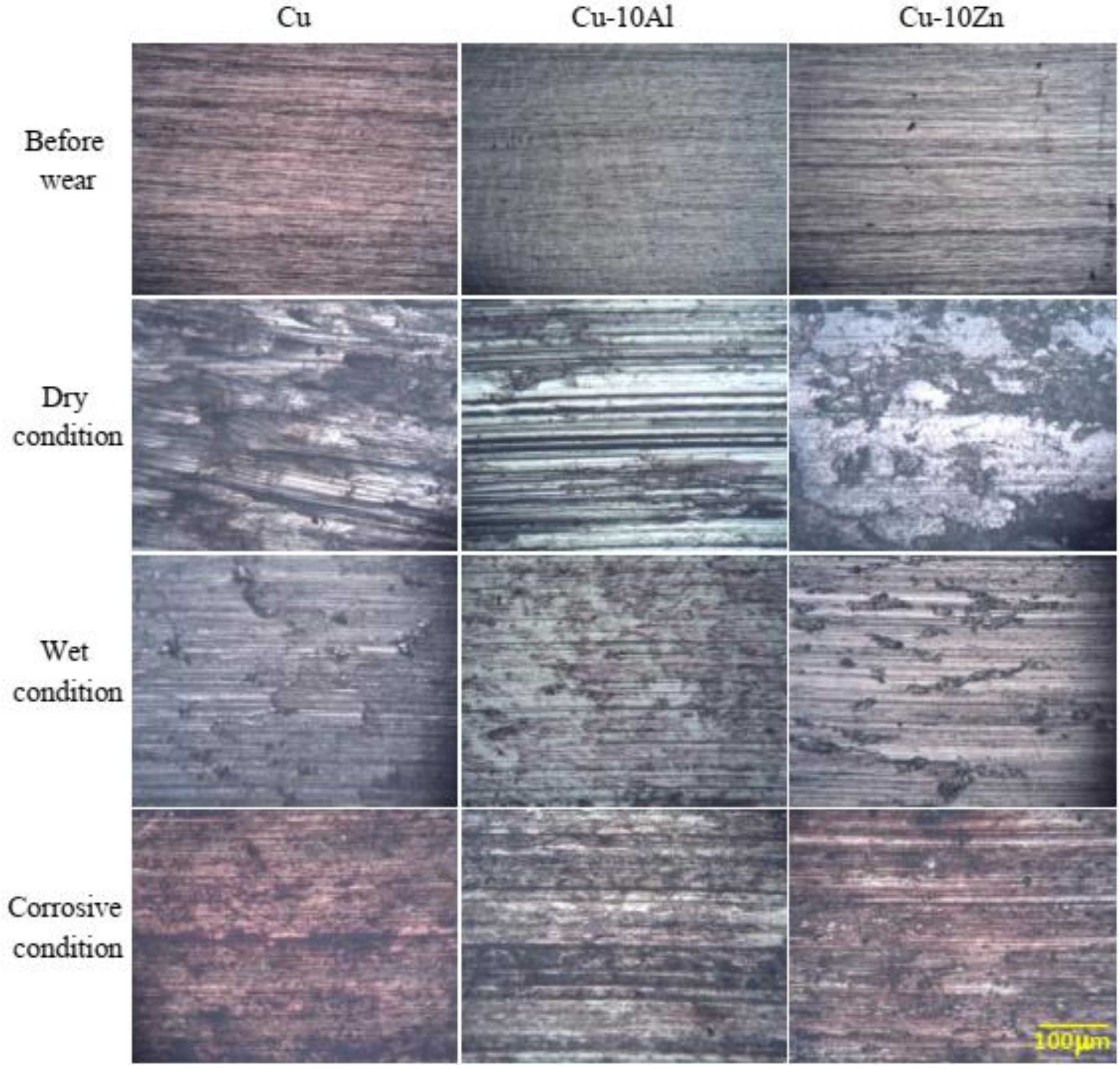

Figure 12: Optical micrograph of worn surfaces of Cu, Cu-10Al and Cu-10Zn alloys before wear, after wear for 2772m at applied pressure of 1.02MPa (Load = 20N) and sliding velocity of 0.385 ms^{-1} in dry, wet and corrosive sliding condition

The delamination of a large amount of material scan is observed. Cu and Cu-10Zn alloy worn surfaces show the surface morphology of low cracks with superficial grooves. Moreover, the worn surface of Cu-10Al alloy is covered with grooves and delamination, accounting for the protective role of the oxidation film. Nevertheless, the wear scratches and grooves are deeper, and there is much wear debris distributed on the worn surface. The wear scars and fragments demonstrate the wear mechanisms of abrasive wear as well as delamination and oxidation wear. Whereas in the wet environment, the wear tracks displayed on the worn surface are smoother. The cracks can hardly be detected. Moreover, the debris and grooves are observed only in limited regions. Besides, there are some dark areas seen due to the lubricating and cooling effects. The heat concentration, local stress, and friction of shear decreased in the liquid environment, thus inhibiting the generation of cracks and debris. Furthermore, most of debris and particles were washed away by the water during the sliding process, which alleviated the abrasive wears. As a result, the frictional properties in the liquid environment are much better than that in the ambient air condition. However, the wear mechanism was changed in the 3.5% NaCl corrosive environment. In fact, the corrosion-wear occurred in the corrosive fluid, forming the oxidation film. Subsequently, the oxides were broken down and the wear debris was generated during the wear testing. Moreover, the friction heat was generated on the interface, leading to the formation of additional oxides. The crack and

plastic deformation are not observed, and the size of debris and particles is smaller than that of the dry sliding condition [36].
The optical microstructures of 40% cold rolled Cu, Cu-10Al and Cu-10Zn alloys after ageing at 200°C are shown in Fig. 13. There are elongated and broken grains in rolling direction. During cold working the microstructure is permanently deformed with the grains being elongated in the direction of the applied forming stress. The size distribution of the grains of Cu is not homogeneous and some finer grains are evident between the coarse grains (Fig. 13.a). Also, several twins are present within the grains [37]. It is also seen from the Fig. 13.b that the microstructure of Cu-10Al alloy consists of three phases namely α phase, β' phase and κ phase. More specifically α phase which is a fcc copper-rich solid solution, eutectoid phases of "β phase" or retain β', and four intermetallic κ phases designated as κi, κii, κiii and κiv [38]. In the normal casting fabrication, Cu-Zn alloys exhibit a single α-phase fcc state below 35 wt.% Zn. The resulting microstructures of Cu-10Zn alloy reveal the single-phase α brass where zinc is melted into copper and forms of a homogenous α crystal structure (Fig. 13.c) [39, 40]. The α crystal structure occurs as zinc dissolves into copper forming a solid solution of uniform composition.

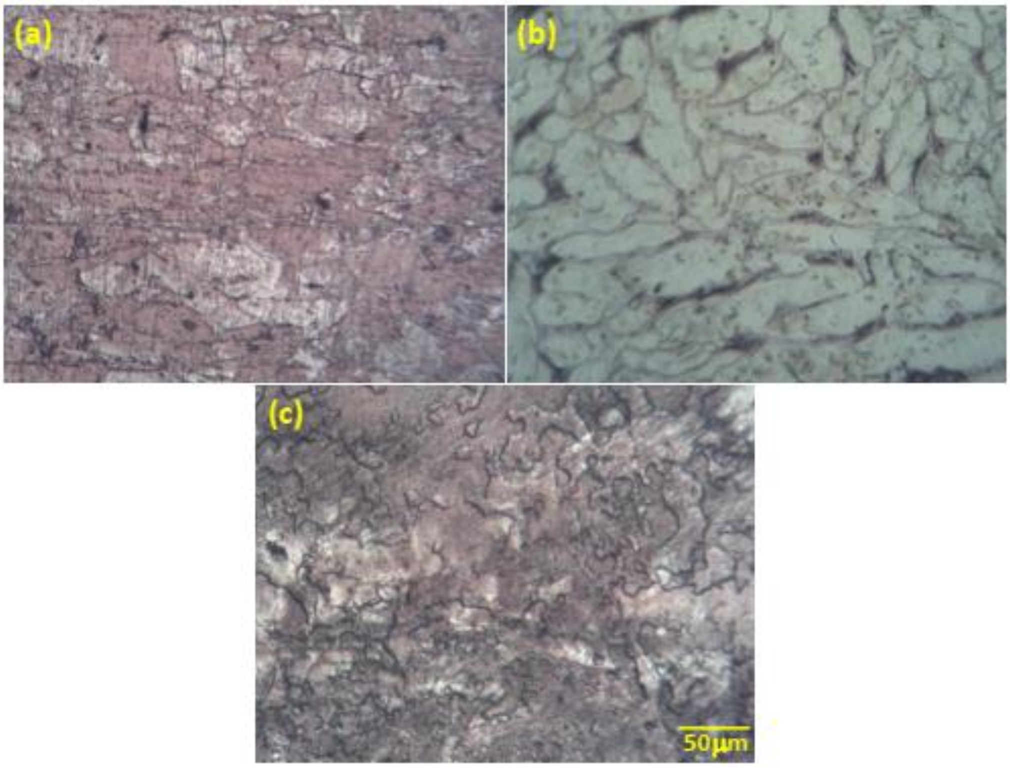

Figure 13: Optical micrograph of 40% cold-rolled alloys (a) Cu (b) Cu-10Al and (c) Cu-10Zn alloys aged at 200°C for one hour

3.4. SEM observation

Figure 14 shows the SEM images of the worn surfaces of pure Cu, Cu-10Al and Cu-10Zn alloys under dry sliding condition. In the case of pure copper (fig. 14.a), it is observed that the deepest and severity of grooves and scars could be noticed along the sliding direction. It is due to the sliding of hard counter surface over the softer surface of copper matrix which caused the microcutting [31]. The wear results showed that under dry sliding condition Cu-10Al has the higher material removal from the surface (fig. 14.b). However, the micrographs showed that the surfaces were subjected to pure adhesive. It seems that there is high plastic deformation occurring in the interface, which led to the higher material removal and smoothening of the surface at the same time. This can further be clarified with the micrographs of the debris. For Cu-10Zn alloy, the worn surface clearly shows plastic deformation despite there being a rough area, which can be seen in Figure 14.c. It seems that the high applied load assists in adhesion of the debris on the worn surface, i.e. stabilised the surface which results in good wear performance in dry sliding condition of Cu-10Zn alloy [41].

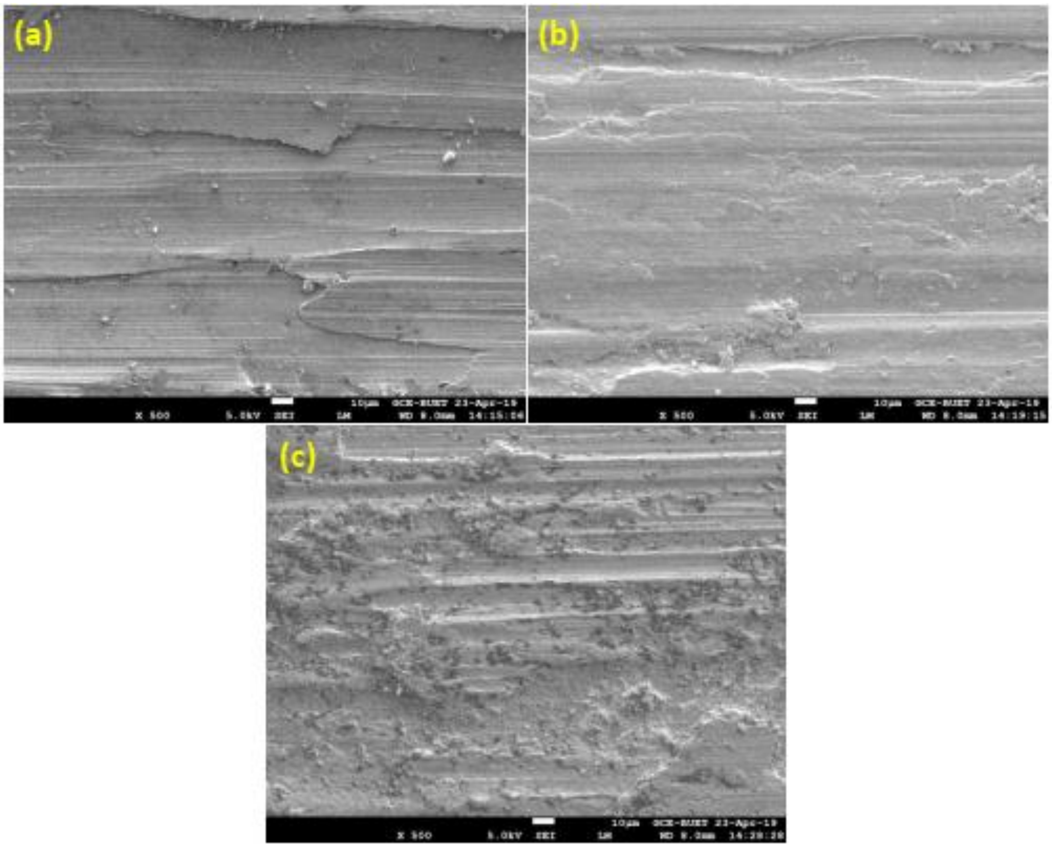

Figure 14: SEM images of the worn surfaces of the a) Cu, b) Cu-10Al and c) Cu-10Zn alloy after wear for 2772m at applied pressure of 1.02MPa (Load = 20N) and sliding velocity of 0.385 ms^{-1} in dry sliding condition

Conclusion

Pure Cu, Cu-10Al and Cu-10Zn copper-based alloys obtained by casting flowed by 40% rolling and ageing at 200°C for one hour. Wear properties were studied in dry, wet and 3.5% NaCl corrosive environment. According to the tribological results it is obvious that the addition of Al considerably increases hardness of Cu and improves the wear resistance especially in wet and corrosive environment to a significant extent, and also reduces the coefficient of friction. In case of Zn addition by 10% the alloy does not play a huge function on wear properties. The worn surfaces of the experimental alloys in dry sliding condition are shown deep grooves parallel to the sliding direction but in wet and corrosive environment the surfaces exhibit smoother.

Acknowledgements

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