ICMIEE20-202

Tribological Behavior of *Sn*-Doped *Cu* under Varied Sliding Environments

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ABSTRACT

Copper (*Cu*) materials are widely used and with the rapid technological advancement the use of *Cu* is getting continuous rising demands. As such, old *Cu* is popular to reuse in many components, but sometimes tin (*Sn*) is doped in to *Cu*, which may alter its mechanical properties including friction and wear. In this context, the present paper is reporting the sliding wear behavior of *Sn*-doped *Cu* under dry, fresh water (FW) and sea water (SW) environments. Here, friction and wear tests are conducted using a pin-on-disk type of tribometer. The normal load of 20N is applied for varied period up to 90 minutes to cover up the sliding distance of 2772 m at a speed of 0.513 ms^{-1}. The present investigation shows that inclusion of little amount of *Sn* in *Cu* has significant role to play on micro-hardness and wear behavior. As such, micro-hardness, wear rate and coefficient of friction have been found to be improved. 'The harder the wear resistant' has been matched with the present results. The results also illustrate the effect of environmental conditions during sliding operations causing the wear rate and frictional coefficient to be varied to a significant level. The wear properties especially in FW and SW environments are related to the formation of patina oxidation film and its onward breaking up. Moreover, wear rates have also been observed to be affected by the lubricating effect of FW and SW. The surfaces observed before and after sliding wear have demonstrated the combined outcome of adhesive as well as abrasive wear. The intense grooves are observed parallel to the sliding direction on the dry sliding worn surface whereas wear tracks are found relatively smooth for sliding in FW and SW environments.

Keywords: Copper (*Cu*); Tin (*Sn*)-inclusion; Sliding wear; Water lubrication

1. Introduction

Copper (*Cu*) is extensively used in many industrial, maritime and automotive applications due to several factors including excellent electrical and thermal conductivities, outstanding corrosion resistance, wear resistance, fatigue resistance and ease of fabrication along with good mechanical strength [1,2]. Mariners do prefer the use copper at sea water environments for propeller, rudder, sleeves, shaft sliding bearings, bush bearings, heat-exchanger tube stacks and so on for such worthy properties [3]. With the rapid scientific and technological advancement as well as economic development, the use of Cu has got more rising requirements continuously [4]. To meet such extensive demand of copper based materials, it is important to get copper from old products/scraped items considering the depletion level of its ores in the nature [5]. Scraped Cu can be utilized in two ways – (i) recycling of copper through extraction process, or (ii) reusing the same at their leftover state for suitable engineering applications. Recycling is very difficult and costly, but preferred for regaining the properties as close to original state [6]. Conversely, reusing is very cheap but properties are yet to be anticipated. Because, old *Cu* items might have come across tin (*Sn*) during the operational life or maintenance period. Inclusion of Sn may be very minor in *Cu*, but its effects on the associated properties including friction and wear are not negligible [7,8].

In this context, long term old/used *Cu* materials require the characterization of attainable properties for producing high value engineering products along with additional attention for surface behavior, because major failure of a component occurs from surface wear. Number of studies dealing with wear resistance of *Cu* materials are found in the literature and few of the works amongst them have delt to investigate the wear properties of *Cu*-*Sn* alloys [9-13]. But the effects of Sn inclusion in *Cu* on wear behavior against sliding in varied environments especially over stainless steel counter surface have not been detected in the literatures. Whereas, shipbuilders and mariners are presently demanding *Cu* based bearings for stainless steel shafts along with reliable wear information for life cycle assessment of the component. All these factors necessitate the characterization of *Sn*-doped *Cu* on friction and wear behavior at dry, fresh water (FW) wet and sea water (SW) wet sliding conditions.

2. Materials and Methods

Scraped *Cu* collected from wires and machine parts which had an extensive age of about 50 years and suspected to be affected by little amount of tin or so was the focused material to carry out the study. The

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collected pieces of old *Cu* (about 25 kg) were melted together using a clay-graphite crucible in a natural gas fired furnace covered under suitable flux while the final temperature of the melt was maintained at 1300±15°C. In the casting process, preheated (200°C) steel moulds of size 150mm×100mm×20mm were prepared and their insides were coated with a water-clay film. Stirring was continued to make the melts to be homogenized at 1200°C and then the melt was poured in the preheated mould to have the cast materials.

Along with material under investigation, commercially available pure *Cu*, i.e., bulk copper ingot was taken to have comparison in friction and wear behavior. Collected pure copper was also melted and casted following exactly the same procedure that was done for old *Cu* material so that both the materials can be of similar footing. Moreover, both the materials were heat treated equally through homogenization for eight hours at a temperature of 500°C and solution treatment for two hours at a temperature of 700°C. The cast sample materials were then machined to remove the oxide layer from the surface. Finally, the chemical compositions of the two sample materials were tested using XRF machine of model Olympus DPO-2000-CC having silicon drift detector for element identification, and the results found are presented in table 1.

Table 1 Chemical composition of sample materials used in the study (mass fraction %)

Material	Cu	Sn	Pb	P	Si
Cu	99.9836	0.0008	0.001 0	0.0083	0.0073
Cu-Sn	98.4368	1.2986	0.0678	0.0862	0.1106

The sample materials were then cut into cylindrical pieces of size 12 mm length and 5 mm diameter for wear study using pin-on disk (POD) tribometer following ASTM Standard G99-05. Experimental setup, few samples and one sample on the disk are shown in figure 1. From each material 56 samples were prepared to carry out the investigations. Then they were mechanically ground with 300, 600, 900, 1200 and 1500 grits of SiC emery paper successively. On completion of dry grinding, faces of all the samples were wet polished using alumina paste and dried up through air blow at room temperature. On preparation, micro-hardness readings of the sample materials were taken using Micro Vickers Hardness Tester (HV-100) with 1 kgf load applied for 10 seconds. The average micro-hardness of pure *Cu* and *Cu-Sn* alloy were found to be 60.71 HV and 68.42 HV, respectively.

The 309s stainless steel circular disks having the chemical composition of 60% Fe, 23% Cr, 14% Ni, 2% Mn, 0.84% Si, 0.08% C, 0.05% P and 0.03% S were used as the counter surface material whose hardness was 168 HV. The surfaces of the disk were ground by a grinding machine and cleansed with dry yarns. Roughness of the disc surface was on average 40μin (~1μm). The disk was fixed horizontally with an arrangement to rotate at the preset speed of the drive motor. A load cell along with digital indicator was used to measure the frictional force. The pin end surface was placed on horizontal rotating 309s stainless steel disk under pressure against the applied load of 20 N yielding contact pressures of 1.02 MPa. The track diameter of the rotating disk was 49 mm. Therefore, the sliding speed was 0.513 ms^{-1} during conducting the wear tests and the sliding distance was varied up to 2772 m at that speed. The wear track and the samples were cleaned with acetone and the pin was weighed for each test run using the weighing machine (model: Sartorius Entris 224-1S having pan diameter of 90 mm with the maximum weighing capacity of 220 g) of 0.01mg precision. The initial weights of pure *Cu* and *Sn*-doped *Cu* samples were 3.6112 g ans 3.5664 g respectively. Ultrasonic thickness gauge (model: CG100 ABDL having measurement resolution of 0.01mm) was also used to examine the thickness to calculate the volume loss of the pin. The frictional forces and applied load for each individual test run were measured by using the experimental setup arrangements. The pin-on-disk sliding experiments were carried out at three environmental conditions such as dry, FW wet and SW wet conditions. The dry sliding condition was in ambient air with relative humidity of 60% without any arrangement of lubrication. For FW as well as SW wet conditions, water droplet was applied continuously on the stainless steel disk and the samples for each test run. Here, FW means the distilled water and SW means the water collected from the Bay of Bengal having pH value of 7.2, dissolved minerals 28000 mgL^{-1}, sulphate 1320 mgL^{-1}, chloride 21000 mgL^{-1} and electrical conductivity 4.8 Sm^{-1}.

Fig. 1 Experimental setup: (a) Pin-on-disk apparatus, (b) Samples and (c) One sample on the disk.

Wear rates were evaluated the from average values of wear (as weight-loss) readings, applied load and sliding distance using equation (1) as follows, which is basically a modified expression based on the Archard equation [14] and the very fundamental equation (2) was used to calculate the coefficient of friction (COF).

$$\mathrm{WR} = \frac{\Delta \mathrm{W}}{\mathrm{SD} \times \mathrm{L}} \qquad (1)$$

$$\mu = \frac{FF}{L} \quad (2)$$

where,
WR = Specific wear Rate (μg N^{-1} m^{-1})
ΔW = Wear (Weight Loss) (μg)
SD = Sliding Distance (m)
L = Load (N)
FF = Frictional force (N)
μ = Coefficient of friction

The metallographic images of the samples were examined before and after wear test using computer interfaced Optical Electronic Microscope (OEM) (model: Nikon BW-S500 having 4.19 Mpixel camera) at different magnifications to find out the microstructural changes in surfaces during dry sliding experiments.

3. Results and Discussions

3.1. Wear (Weight Loss) Examination

Contacting asperities of metals deform plastically even at a very small load if continues for a certain period during relative motion, and at first, material on the contacting surface gets displaced, but little or no material is actually lost. After certain time of sliding, material starts removing from a surface and wear occurs. Wear, the surface damage generally caused by plowing, adhesion and asperity removal from one or both of two solid surfaces during sliding, is not fully a material property. It is rather a system response where material property is only a part of it [15]. The system induced wear mechanisms include the progressive extrusion of material from the asperity junctions into thin chips as debris and/or the fracture of a thin surface layer leading to flake-like debris [16]. Keeping this in mind the wear behavior of pure *Cu* and high *Cu-Sn* alloy have been observed at the speed of 0.513 ms^{-1} with the normal load of 20 N in dry, FW wet and SW wet sliding conditions and the results obtained are illustrated in Fig. 2. It indicates that the weight losses have followed the rule of nature and the values have been observed for both pure *Cu* and *Cu-Sn* alloy to be increased non-linearly with the increase of sliding distance for all three sliding environments. However, *Cu* and *Cu-Sn* alloy have not shown the same incremental rate of overall wear due to diverse surface configuration, different micro-hardness and time-variation for reaching to the plastic state of materials. The weight losses of *Cu-Sn* alloy are observed to be significantly less than that of pure *Cu* for the entire sliding period in dry, FW wet and SW wet sliding environments as revealed in Fig. 2(a), (b) and (c), respectively. Moreover, the weight loss in FW sliding is less than that of dry sliding and the lowest value is observed in SW wet sliding, which is illustrated in Fig. 3. As such, the weight losses have been reduced due to improved lubricating level in FW and SW wet environments compared to dry sliding on average by 23% and 30%, respectively. As such, after the sliding period of 90 minutes, i.e., sliding distance of 2770 m, the wear of *Cu-Sn* alloy in dry sliding, FW sliding and SW sliding have been found to be of 13 mg, 10 mg and 9 mg, respectively.

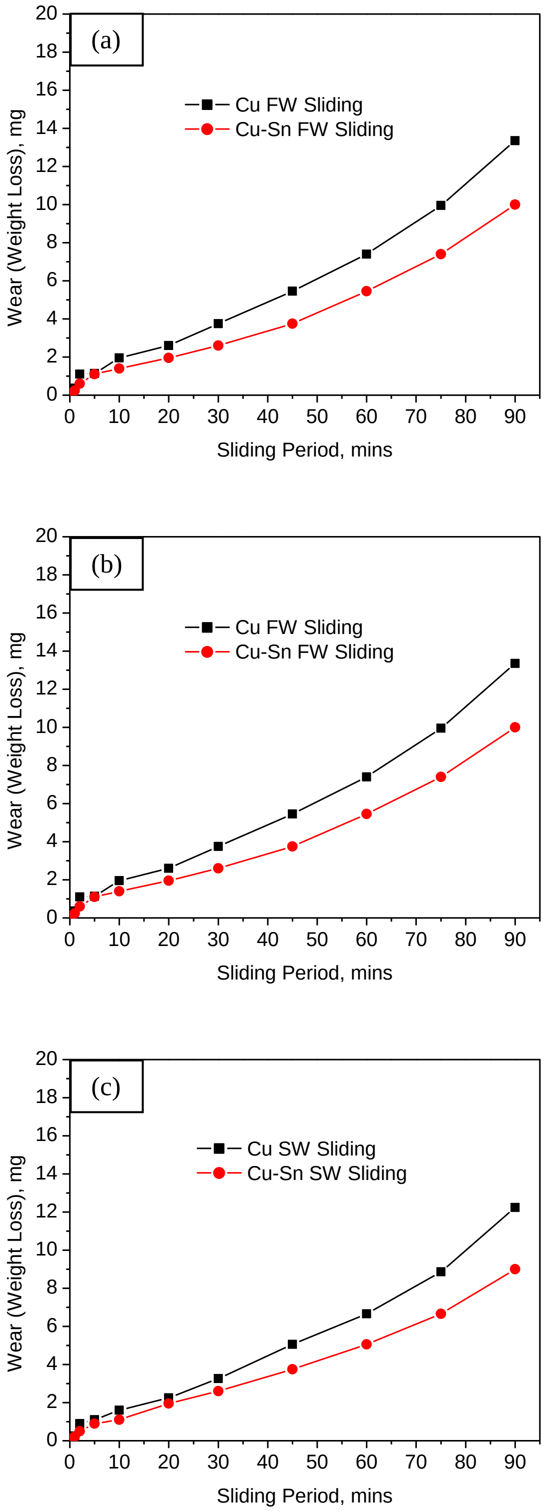

Fig. 2 Wear (weight loss) against sliding period at the speed of 0.513 ms^{-1} with the normal load of 20 N: (a) in dry sliding condition, (b) in FW sliding condition and (c) in SW sliding condition

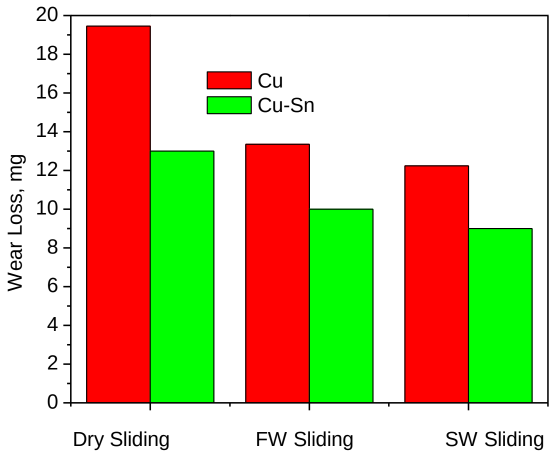

Fig. 3 Wear (weight loss) against the sliding environment for the sliding period of 90 minutes at the speed of 0.513 ms^{-1} with the normal load of 20 N

3.2. Wear Rate Analysis

Wear rate magnitude depends on the surface roughness, relative hardness of the two contacting surfaces, size/shape of wear debris, and reaction products trapped between them. Besides, wear rate varies for sliding environments at the sliding interface. Fig. 4(a), (b) and (c) elucidate that wear rate at the onset of sliding is largely controlled by the coefficient of static friction and thus the initial wear rate values are sharply higher for both the sample materials in all three environments such as dry, FW wet and SW wet conditions.

Fig. 4 also depicts that *Cu-Sn* alloy has shown superior wear performance over pure Cu, which can be correlated with the hardness. The micro-hardness values of pure *Cu* and high *Cu-Sn* alloy at room temperature have been observed to be on average from twenty readings as 60.71 HV and 68.42 HV respectively, i.e., the addition of about 1.29% *Sn* with *Cu* has increased the hardness by 12.69%. This increase of micro-hardness due to addition of *Sn* in *Cu* has played an important role on wear behavior thereby at steady state condition the wear rate of *Cu-Sn* alloy is 33%, 25% and 26% less than that of *Cu* for dry, FW and SW environments, respectively. The maximum and average wear rates of both the materials for three environmental conditions are presented in table 2.

Table 2 Maximum and average wear rates of pure *Cu* and *Cu-Sn* alloy for sliding in dry, FW and SW environments

Sample	Dry Sliding Wear Rate (μg/N.m)		FW Sliding Wear Rate (μg/N.m)		SW Sliding Wear Rate (μg/N.m)	
	Max	Ave	Max	Ave	Max	Ave
Cu	1.0069	0.5787	0.8932	0.4254	0.7308	0.3612
Cu-Sn	0.8526	0.4405	0.4872	0.2718	0.4060	0.2396

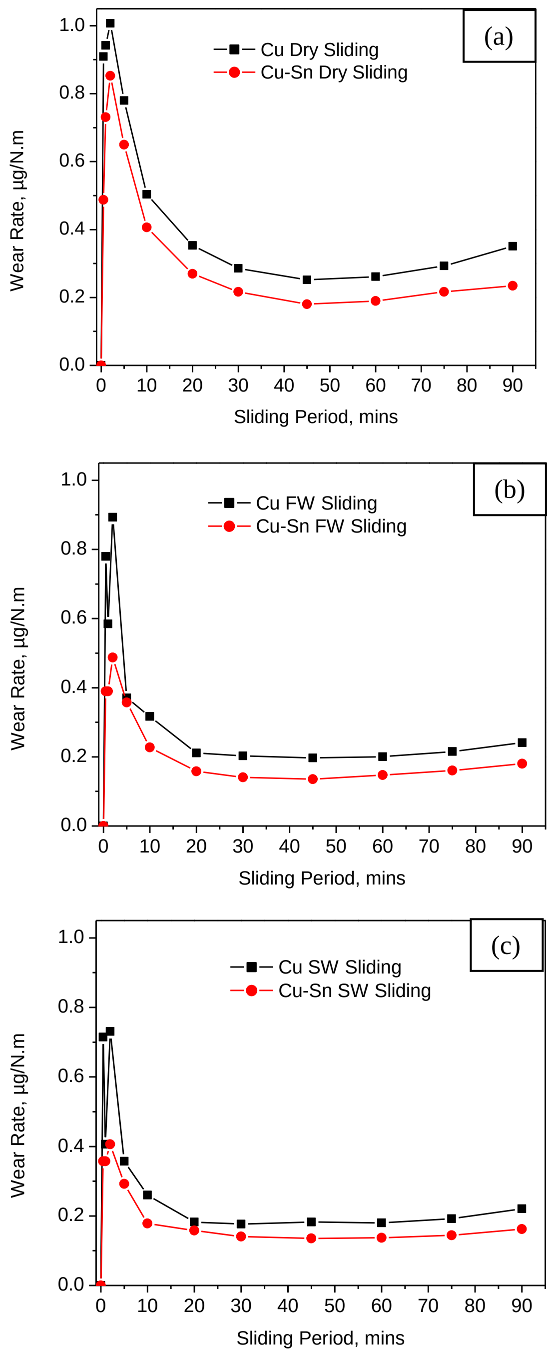

Fig. 4 Wear rates against sliding period at the speed of 0.513 ms^{-1} with the normal load of 20 N: (a) in dry condition, (b) in FW condition and (c) in SW condition

It indicates that the maximum wear rate of *Cu-Sn* alloy are 15%, 45% and 44% less than that of *Cu* and the average wear rates of *Cu-Sn* alloy are reduced by 23%, 36% and 33% compared to pure *Cu* for the three sliding conditions. Therefore, wear rate of *Cu-Sn* alloy is 44% and 39% less than that of dry sliding condition.

3.3. Coefficient of friction

Coefficient of friction (COF) readings have been obtained directly from the pin-on-disk apparatus and the results obtained have been plotted against sliding period in Fig. 5. Besides, COF values were calculated using Eq. (2) and confirmed the accuracy of machine readings. At the initial stage of sliding, COF values of *Cu* and *Cu-Sn* alloy are found to be significantly less and very close to each other for all three sliding environments. Since COF depends on plowing mechanism, height of agglomerated particles, number of particles and the tribological condition i.e., lubrication level and normal load, plastic deformation is significant at the beginning when adhesion is weak, and thus, COF is of low value. Once the sliding period is increased, COF is rising gradually but non-linearly. Fig. 5 have shown non-linear gradual increasing trend of COF up to sliding period of about 60 minutes and finally reached to some steady state level for both the sample materials. From the present results, *Cu-Sn* alloy has shown lesser COF values than that of pure *Cu* over the entire sliding period. Table 3 indicates that the maximum and average COF values for pure *Cu* and *Cu-Sn* alloy are less for FW wet sliding and further less for SW wet sliding. Therefore, COF of *Cu-Sn* alloy for FW and SW environments compared to dry sliding is reduced by 9.5% and 16% respectively.

Table 3 Maximum and average COF of *Cu* and *Cu-Sn* alloy for sliding in dry, FW and SW environments

Sample	Dry Sliding COF		FW Sliding COF		SW Sliding COF	
	Max	Ave	Max	Ave	Max	Ave
Cu	0.478	0.324	0.432	0.294	0.370	0.254
Cu-Sn alloy	0.328	0.243	0.296	0.220	0.284	0.204

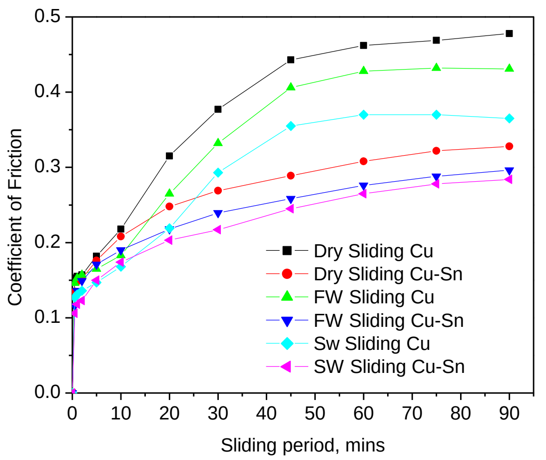

Fig. 5 COF against sliding period at the speed of 0.513 ms^{-1} with the normal load of 20 N

3.4. Microstructure Observation

As two surfaces slide against each other, the COFs get changed over time, in turn, sliding distance. This change is due to microscopic alterations in the contact surfaces with the wear behavior of the sliding system. Here, two phenomena contribute in COF values simultaneously i.e., irregularities of asperities and occurrence of lubrication. The actual effect depends on the relative resultant magnitude of the two phenomena.

The surface micrographs of materials taken before and after wear tests under different sliding conditions are presented in fig. 6. Micrographs of pure *Cu* and *Cu-Sn* alloy before wear test are shown as the first row, which indicate moderately smooth surfaces with regular asperities and without exhibition of any plastic deformation. There are some scratches of the SiC emery paper, which might have been developed during the sample preparation stage. Micrographs of the second row signpost many irregular asperities of the worn out surfaces after sliding at dry condition. Different categories of large wear particles, oxide debris and particles as well as the deep grooves parallel to the sliding direction also exist in these figures in the dry sliding condition for both the sample materials. Moreover, there are plastic deformations and a good number of cracks are noticeable here. The wear marks and the fragments reveal the mechanisms of adhesive integration with abrasive behavior along with delamination and oxidation formation.

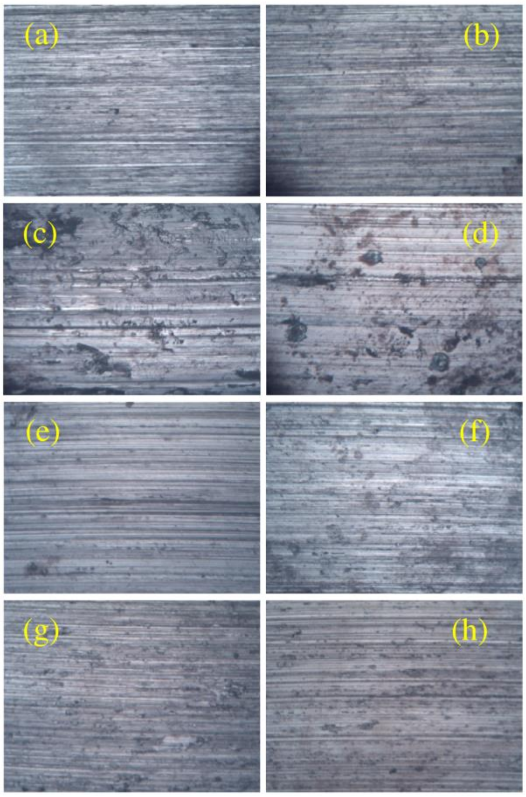

Fig. 6 Micrographs: (a) *Cu* before wear, (b) *Cu-Sn* alloy before wear, (c) *Cu* after dry sliding, (d) *Cu-Sn* after dry sliding, (e) *Cu* after FW sliding, (f) *Cu*-Sn after FW sliding, (g) *Cu* after SW sliding, (h) *Cu-Sn* after SW sliding for 2772 m at the applied pressure of 1.02MPa and the sliding speed of 0.513 ms^{-1}

In case of FW sliding, the worn out surface micrographs (3rd row of fig. 6) indicate again less rough surfaces compared to dry sliding (2nd row of fig. 6). Here, worn surfaces show the improved morphology to a remarkable level and there is no appearance of cracks also. Moreover, the protective role of the oxidation film is distinctive here to cover the grooves and delamination of worn out surface. It gives an indication for the consequence of COF and the wear rate variations for dry and FW sliding conditions. In SW sliding condition, the wear tracks being displayed on the worn out surface are distinctly smoother than dry condition and even FW wet condition. Moreover, very limited number of debris and grooves are noticeable in limited areas only. In addition, some dark areas are visible as a consequence of lubrication and cooling in presence of SW. The concentrations of heat, development of localised stress and shear friction have been reduced in FW and SW environments, which have resulted in averting the crack generation and propagation. However, the wear mechanism is changed in SW sliding condition from that of FW. Actually, the erosion corrosion has occurred in contact of corrosive SW. Though, the oxidation film was formed initially but subsequently broken down, and the wear debris was generated. But most of the tiny debris/particles have been washed away by SW during the sliding process for which micrographs have been observed to be smooth.

4. Conclusions

Wear behavior studied for pure *Cu* and *Cu-Sn* alloy in dry, FW wet and SW wet environments provides following concluding remarks:

(a) *Cu* with micro-hardness of 60.71 HV and *Cu-Sn* alloy with micro-hardness of 68.42 HV have displayed the average dry sliding wear rate of 0.58 µg/N.m and 0.44 µg/N.m, respectively. So, the presence of tiny amount of *Sn* has increased the hardness and the wear resistance of *Cu* materials to a significant level, and 'the harder the wear resistant' has been matched with the results.

(b) Wear rates of *Cu-Sn* alloy in FW and SW environments have been found to be 44% and 39% less than that of dry sliding condition, respectively.

(c) COF values of both *Cu* and *Cu-Sn* alloy have shown non-linearly increasing trends at the initial stage and finally reached to some steady state level for all three sliding environments. Improvements have also been observed for COFs in FW and SW sliding conditions compared to dry sliding for which average COF of *Cu-Sn* alloy is 9% and 16.5% less than that of dry sliding.

(d) The harder material (*Cu-Sn* alloy) shows the lower values of COF and the softer material (pure *Cu*) displays the higher COF values over the whole range of sliding, which confirms the inverse relation of friction coefficient with material hardness.

(e) Micrographs have indicated the adhesion wear mechanism along with abrasion for *Cu* based materials during sliding.

5. References

[1] Davis, J.R. (Eds), Copper and Copper Alloys. *ASM Specialty Handbook Series,* ASM International, Materials Park, Ohio 44073-0002, USA, 2001.

[2] Tyler, D.E., Black, W.T., Introduction to Copper and Copper Alloys. In *ASM Handbook Volume 2*, 1990: 216-240.doi.org/10.31399/asm.hb.v02.a0001065

[3] Sun, S. Chang, X. Chen, G.J., Zhi, Y.C., The Influence of Material Properties on the Hydrodynamic Performance of Propeller. *Advanced Materials Research* 1120: 1356-1362 (2015).

[4] Collini, L. (Ed), *Copper Alloys – Early Applications and Current Performance – Enhancing Processes,* InTech Janeza Trdine 9, 51000 Rijeka, Croatia, 2012.

[5] Villena, M., Greve, F., On resource depletion and productivity: The case of the Chilean copper industry. *ResourcesPolicy* (2018). doi:10.1016/j.resourpol. 2018.10.001

[6] Cui, J., Forssberg, E., Mechanical recycling of waste electric and electronic equipment: a review. *Journal of Hazardous Materials* 99(3): 243–263 (2003). doi: 10.1016/s0304-3894(03)00061-x

[7] Rahman, M.M., Ahmed, S.R., Kaiser, M.S., Behavior of work hardened SnPb-solder affected copper on corrosion resistance in pH varied environments. *European Journal of Materials Science and Engineering,* 5(4) (2020) (in press)

[8] Samuelsson, C., Björkman, B., Copper Recycling. In *Handbook of Recycling*. Elsevier Inc., 2014: 85–94. doi:10.1016/b978-0-12-396459-5.00007-6

[9] Bateni M. Ashrafizadeh F. Szpunar J. Drew R.A. Improving the tribological behavior of copper through novel Ti–Cu intermetallic coatings. *Wear* 253(5-6): 626–639 (2002). doi:10.1016/s0043-1648(02)00143-6

[10] Zeren A. Feyzullahoglu E. Zeren M. A study on tribological behavior of tin-based bearing material in dry sliding. *Materials & Design* 28(1): 318–323 (2007). doi:10.1016/j.matdes .2005.05.016

[11] Equey S. Houriet A. Mischler S. Wear and frictional mechanisms of copper-based bearing alloys. *Wear* 273(1): 9–16 (2011). doi:10.1016/j.wear.2011.03.030

[12] Kumar P S. Manisekar K. Subramanian E. Narayanasamy R. Dry Sliding Friction and Wear Characteristics of Cu-Sn Alloy Containing Molybdenum Disulfide. *Tribology Transactions* 56(5): 857–866 (2013). doi:10.1080/10402004.2013.806685

[13] Fujita M. Fujii S. Eguchi H. Hagino G. Friction and Wear Property of Copper Alloys for Plain Bearing. *Tribology Online* 10(5): 366-376 (2015). doi.org/10.2474/trol.10.366

[14] Archard J F. Contact and Rubbing of Flat Surfaces. *Journal of Applied Physics*, 24(8), 981–988, (1953). doi:10.1063/1.1721448

[15] Kato K. Wear in relation to friction – a review. *Wear* 242(2): 151–157 (2000). doi.org/ 10.1016/S0043-1648(00)00382-3

[16] Kapoor A. Franklin F J. Tribological layers and the wear of ductile materials. *Wear* 245(1-2): 204–215 (2000). doi:10.1016/s0043-1648(00)00480-4