Wear and Friction Study of Centrifugally Cast Functionally Graded Cu-Ni-Si Alloy and Composite

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A B S T R A C T
The functional grade composite Cu-11Ni-4Si/10wt.%TiC along with Cu-11Ni-4Si alloy was stir cast, followed by horizontal-centrifuge cast technique. Cast sample was prepared at a dimension Φout 100 x Φin 85 x 100 mm. A comparative analysis for non-lubricated slide tribology at inner wall zone (1-5 mm), middle wall zone (5-10 mm) and outer wall zone (10-14 mm) of composites and alloy, was performed utilizing pin-on-disc tribometer. Observed a proportional raise in wear and friction with rise in applied loads and slid distances. For alloy and composite, a slight decline in wear was seen at medium velocity; showing a gradual deduction in friction with rise in slid velocity, while alloy wear showed a linear growth. Rate of increase in wear response with respect to change in distance was less prominent, compared to its response with load. Worn surfaces analysis of composite using Scanning Electron Microscope showed the presence of Mechanically Mixed Layers, which reduced friction at higher slid velocities resulting in lower wear. The phase formations and presence of oxides were confirmed by X-ray diffraction (XRD) and Energy dispersive spectrometers (EDS) results respectively.

1. INTRODUCTION
Aggressive demand for automotive and aviation composites with exceptional strength-weight ratio, have created a rapid boom in its research and development over past few years. Composites with these potential for extensive application leads to large economy savings, also reducing the environmental pollution [1]. Conventionally used monolithic materials always faced the challenge to achieve desirable combinations of properties like strength, stiffness and density [2]. Design and development of Metal Matrix Composites (MMCs) through proper processing methods, reinforcements, machining, testing and analysis leads to enhanced hardness, wear performance, and corrosion resistance compared to pure metal or alloy [3]. The most relevant objective in designing MMCs is to utilize the right combination of process attributes [4]. Particle size of reinforcements always had an impact during the fabrication process, as those larger sized particles were mostly settled by gravity.
segregation [5]. Particle distribution in the matrix during centrifugal casting is strongly dependent on stirring speed and time, slurry viscosity, process temperature, wetting, solidification rate, and reduction of gas entrapment which leads to cast defects [6]. Concept of functionally grading has been introduced recently for enhancing the properties of MMCs through its various techniques and materialistic factors. This facilitates material development for performing specific functions at the least cost [7-8]. Utility of Functionally Graded MMCs for tribological applications requires detailed research on its gradient structure, as it has a greater influence on component development for specific functions due to its gradient properties [9]. The gradient properties of Functionally Graded Materials (FGM) are predominantly achieved by the desired distribution of hard ceramic particles in the matrix [10]. Centrifugal casting method is the most economical technique preferred for the fabrication of FGMMC, combining both rotating speed as well as centrifugal force for producing a gradient structure [11]. Fabrication of FGM also requires proper selection of a matrix element that could withstand extreme working conditions and hold the reinforcements in position [12].

Selection of copper as matrix material owes superior properties and possess proven applicability that range from household to aviation applications. But the low hardness and poor wear performance of pure copper limits its applicability [13]. Reinforcement of copper with ceramic particles (carbides and borides) meets the primary concern of tribology in several rotary or sliding applications [14]. Wear resistance of copper composite reinforced with 53 vol. % WC produced by microwave sintering process exhibited improved anti-wearing as hard WC particles strengthened the copper matrix, but Chandrakanth et al. observed that WC induced brittle nature which is highly not recommended for high speed applications. Whereas, Li et al. reported that addition of TiC (15 wt.%) as a reinforcement to copper matrix produced by microwave sintering showed 25 % improved wear resistance during electrical sliding applications, as no interfacial de-bonding or cracks were observed under microstructural analysis [15-16]. Apart from the material characteristics, always a combination of influential factors also governs the frictional response of a material [17]. Chen et al. reported that formation of tribo-films restricted wear up to an appreciable level of 50 % for Cu+Gr(10wt%)+ BN(10wt%) [18].

An elaborated research over the existing literatures revealed that a lot of unexplored areas over tribology application of copper still exists. Cu-Ni-Si alloy reinforced with ceramics under horizontal centrifugal casting is a novel combination ever researched particularly with TiC. Zonal analysis of mechanical and tribological performance of the developed composite along the composite wall establishes a new analytical approach on functionally grading. This technology also open-ups a future scope for hybrid ceramics in copper matrix, manufactured with a single production process. So, an in-detail study has been performed focusing non-lubricated slide performance of Copper+Ni+Si alloy and its graded composite enforced with TiC for a specific functionality. Also, it’s utility for mobility industry including engine and transmission components were researched [19], by computing the comparison of wear and friction values of composites with alloy.

2. SELECTION OF MATERIAL AND PRODUCTION METHODOLOGY

Cupronickel alloys showed improved tribo-mechanical properties when alloyed with silicon (0.2-12 wt.%) [20]. Copper alloyed with TiC(10 vol.%) & Gr(5 vol.%) by microwave processing technique showed a superior anti-wearing [21]. TiC as a hard ceramic reinforcement showed better wettability and bond strength with cupronickel alloys making it most suitable for automotive industry especially for manufacturing mechanical seals, atomization nozzles, valves etc. Copper alloy (11 wt.% of nickel, 4 wt.% of silicon) when reinforced with TiC (10 wt.%) using stir casting and horizontal centrifuge cast technique showed a density of 8.26 g/cm3; which was later subjected to tribo-study in comparison with the graded functional alloy.

Alloy constituents (Nickel and Silicon) were melt with Copper in a furnace in the presence of inert gas which prevent unwanted reaction between the constituent elements. Preheated (200 °C) TiC (10 μm) was then mixed with alloy melt. The
mixture was well stirred (150 rpm/5 minutes) within the crucible. The temperature gradation was controlled by the warming process of centrifuge mould (350 °C) using a pre-heater. The molten melt was then directly poured into a rotating centrifuge mould at optimal rotation speed (900 rpm) for effective distribution. Upon cooling, the cast was well formed as a shell cylinder of dimension Φout100 x Φin85 x 100 mm.

3. EXPERIMENTATION

Dry sliding tribology performance was experimentally analysed according to ASTM G99 standard, on a Pin over disc tribo-tester maintaining the same track diameter (90 mm) throughout the experimental cycles. Proper contact of slid pin with the rotating disc (Fig. 1) ensured efficient load transfer.

![Composite Specimen](image)

**Fig. 1.** Pin-on-disc tribometer.

The experimentation is based on comparison between three zones: inner wall zone (1-5 mm), middle wall zone (5-10 mm) and outer wall zone (10-14 mm) of composites and alloy. Each pins (sample of 10x10 mm fixed to 35 mm tall steel tube of 10 mm outer diameter) were tested three times under varied parametric combinations ranging from load (15-55 N), slid distance (500-2500 m) and slid velocity (0.75-3.75 m/s) and its average value was plotted for wear rate and Coefficient of friction (COF). Test pins were weight measured before and after each cycle of experiment. Wear and COF of the alloy and graded composite were compared along with a detailed study on the effect of variable tribo-parametric combinations.

4. CONTRIBUTION OF LOAD ON WEAR

Wear and friction at various wall zones of both composite and alloy were plot (Figs. 2a and 2b) for different loads at unvaried speed (2.75 m/s) and slid distance (1000 m). Both showed a general trend of proportional increase as expected by Archard’s law, except in few conditions where it showed a slight decline in wear at uncontrolled test parameters. Inner wall zone with TiC had (Fig. 2a) the maximum anti-wearing at lowest friction (Fig. 2b). This proportional raise in tribo-properties, was due to the exertion of pressure by the minimum load range (15-25 N). Above this range, a non-proportionate rise was seen (until 55 N). This was enabled by the stable hard particle presence present at the inside wall zone. These particles takes up the load and distributes among them even at extreme test parameters. But alloy (inner zone) showed the maximum wear and friction performance, followed by middle and outer. The decline in fine grain formations, towards the inside wall zone facilitated this. Wear at the inside composite showed 250 % enhancement after reinforcement.

![EFFECT OF LOAD ON WEAR RATE](image)

(a)

![EFFECT OF LOAD ON COF](image)

(b)

**Fig. 2.** a) Wear rate across wall zones of composite and alloy under varied load condition; b) Coefficient of friction across wall zones of composite and alloy under varied load condition.
4.1 CRACKS AND DELAMINATION

Micro-level cracks were seen (Fig. 3a) in the outer alloy SEM, at minimum load (15 N), with slid velocity (0.75 m/s) and slid distance (500 m) maintained unchanged. These points towards meagre wear at this region. As the load raised (till 55 N), these hair like splits (Fig. 3b) were seen growing as surficial skin peeling and tears.

Also the analysis carried out on the worn pins made out of inner wall zone (Fig. 4a) of composite at minimum load (15 N), revealed the digging of small grooves. Those observations classified the tribology of this region as minimum wear, whereas deep grooves and major delamination observed (Fig. 4b) along the worn pin surface (made from inner wall zone of composite) at high load (55 N) depicted higher wear. As both wall zones showed features like crack propagation, mode of wear changed from mild to severe. Fatigue loads creates surface splits and material detachments causing a change from oxidation/adhesion mode of wear towards de-lamination.

Mu et al. [22] reported a similar tribology observation during their SEM analysis on Yttrium based copper composites with 26 % higher wear rate than the composite developed through this research.

5. CONTRIBUTION OF SLIDE DISTANCE ON WEAR

Impact of slid distance on tribology of all three zones of graded functional alloy and its composite were (Fig. 5a) studied. Trend analysis showed that the inner alloy underwent superior wear than it's outer. The slow cooling duration produced fine granular structure at the outer zone. Rich presence of particles, efficiently transferred load at inner. The inside alloy of its
coarser structure and minor particle distribution, showed major wear comparative to all zones of the alloy and composites. High particle presence, nullify the risk of high wear during slide even at high interface frictional temperature. The inside composite (43 %) and alloy (71 %) had a betterment in wear performance, than the outer alloy.

Friction had a direct influence over tribology. Zones of composite (Fig. 5b) experienced lower friction to those of alloy. Especially, the inside wall of composite quantified 44 % and 67 % lower friction than it’s outside and of alloy respectively. Major presence of hard ceramic (TiC) towards the inside wall, enhanced anti-wearing than that of the outside. Inside alloy quantified 22 % lower friction than the inner wall of alloy. Comparing all zones, the inside alloy revealed highest friction as a result of absence of reinforcements. The resistance due to plastic deformation induced during cyclic stresses were found responsible for this trend.

5.1 Flake Formation

SEM detailing (Fig. 6a) was done over the wear test pin made out from outer wall of alloy, at low slid distance (500 m), maintaining other parameters (3 m/s, 25 N) unchanged. Small flake pull outs were found as a sign of low wear. Raise of slid distance (up to 2500 m), caused dimples of shear and bigger flakes (Fig. 6b) broke out from out-wall.

Flakes formed at fine grain wall, as cracks wrapped around the grain due to high bond strength. The mechanism of pinning points impeding further dislocation propagation along the grain boundaries were reported by Prabhu et al. [23] during his experimental analysis on Cu/SiC + Gr hybrid composites. Slow cooling
promotes fine grain structure thereby bringing improvement in the bond strength.

5.2 DEBRIS AND GROOVES

SEM detailing (Fig. 7a) over the worn pins made out of the inner composite (worn at short slid distance (500 m) and fixed parameters of 3 m/s and 25 N) showed shallow groove formations revealing minimum wear. When the slid distance was raised (up to 2500 m), superficial delamination and tribo-debris (Fig. 7b) occurred over the exterior layer.

6. CONTRIBUTION OF SLIDE VELOCITY ON WEAR

Impact of slid velocity on wear of all zones of alloy has been analysed (Fig. 8a) along with its composite, using line-graph.

Delayed solidification or slow cooling rate observed along the outer zone resulted in its better wear resistance than the inner and middle zones. Middle zone acts as a transition zone, where the change in temperature is found minimum resulting in a moderate solidification rate. This showed better anti-wearing than the inner. Middle and inner composite had an initial deduction in wear (till 4 m/s) and later, a further rise. Detached debris at the worn interface, which were vulnerable to atmospheric oxidation was responsible for this. The frictional heating during sliding promoted the oxidation of the
surface. The removal of the oxide fragments led to increase in wear rate. The same phenomenon was also seen for outer composite, but at a lower speed (3 m/s). Similar phenomenon was also observed in AZ91/ SiCp 10 % composites where greater the amount of SiCp reinforcements, more compact is the oxide film that protects the surface from metallic wear. Of all zones, the inner composite showed least wear (43 % lower to that of outer and 60 % lower to inner alloy).

Friction increased (Fig. 8b) with rise in slide velocity, for all wall regions of alloy. Raised speed condition induced elastic strain, that disrupted the oxidized layer. This layer plays a protecting role to prevent the bulk matter from severe adhesive wear. This promoted higher friction for alloy tested at similar conditions. Deduction in friction was observed for all three wall zones of composite, during rise in slide velocity. This was due to the presence of interfacial wear debris at suitable friction temperature and pressure conditions. These conditions also stimulates the formation of low friction tribolayer over the tribo-surface. As an effect, a slippery action is observed along the sliding interface, which minimized the friction coefficient. The inner wall of composite revealed the minimum COF compared to all other wall zones, also showing 66 % deduction of the same.

6.1 MECHANICALLY MIXED LAYER

SEM detailing on the worn pin surfaces made out from the outer wall zone of alloy and the inner wall zone of composite, at intermediate velocity (2.25 m/s) keeping other parameters (1000 m, 15 N) unchanged; displayed features (Fig. 9a) of moderate wear. Intermediate velocity was selected for analysis, as it showed a meagre rise in wear rate compared to low velocity (0.75 m/s). Non-uniform oxidation and flake formations were seen over the worn pin surface made from the outer alloy at this selected combination of parameters. Phase formations at the interface of alloy constituents have provided a strengthening effect, safeguarding the materials from severe wearing. As the velocity raised (till 2.75 m/s), wear value was seen to slightly climb up in its rate. This was also influenced by growing surficial heat at the slid interface, acting responsible for deformations due to plastic behaviour (Fig. 9b).

While at the inner composite, oxidation was observed (Fig. 10b) more vigorous (at 3 m/s) due to the more compact layer formation from the added contributions from the reinforcement particles. Debris agglomerate and cluster to get oxidized. But this oxide layer formation (Fig. 10a) is not to the extreme such that it is capable of restricting wear at low velocity (0.75 m/s). This is due to insufficient working conditions that promotes oxidation. The thickness of tribo-layer increases with increase in the rate of oxide formation. Increase in friction by 10 % were observed with accumulation of debris, during the tribo-study performed by Kaushik et al. [26]; where the load distributing role of debris during sliding, under non lubricated work conditions were also revealed. The minor presence of carbon in the EDAX results (Fig. 11a) of alloy test pin surface reveals the accumulation of debris promoting
third body abrasion. Presence of Cu, Ni, Si spikes affirms the purity of the alloy composition.

Fig. 10. Impact of tribo-velocity on worn pin surface made out of inner wall zone of composite at a) 0.75 m/s; b) 3 m/s.

The amount of oxygen (at atomic level) along the worn pin of composite surface (at optimum tribo-condition) was evaluated through EDAX analyses (Fig. 11b) under standard SEM parameters (keV, working distance and probe current).

This ensured the presence of oxide formation which obstructed the direct slide between the matrix with pin tribo-face, facilitating deduction in wear by 35.6%. Apart from the matrix composition (Cu, Ni, Si spikes), the presence of Fe reveals the hardness of the developed composite, as it causes the third body abrasion by removing material from the counter body.

7. MINIMUM WEAR

SEM detailing of the worn surface of inner wall zone of composite, at an optimum parametric combination of applied load (15 N), slid distance (500 m) and slid velocity (3 m/s) shows (Fig. 12) features of minimum wear like shallow grooves and tiny scratches. Optimum parametric combination resulted in an average wear rate of 0.0035mm³/m which was 15.6% lower to those observed by Kaushik et al. [26]; during the tribo-tests on Al 6082–SiC.

Fig. 11. EDX result for the test surfaces of a) alloy and b) composite pin.

Fig. 12. Worn pin surface made out of the inner composite at optimum tribo-conditions.
XRD analysis (Fig. 13) demonstrated the presence of phases like α-Cu (64.7 %), Cu$_3$Ti$_2$ (11.6 %), Cu$_{15}$Si$_4$ (10.2 %), and Cu$_2$O (7.2 %) for the analysis carried out for specimen of inner composite worn at optimum condition. These phase formations promoted strengthening, which facilitated reduction in wear during extreme tribological parametric conditions. The Cu$_2$O (cuprite) had the major contribution towards the MML formations which were responsible for the reduction in wear during medium velocities.

8. CONCLUSION

Functional development and wear study of graded alloy and copper composite mixed with titanium carbide at three different zones (inner, middle and outer) concludes that:

1) Tribo-analysis of composite zones revealed that inner zone of the composite showed 60 % wear in comparison with alloy, due to its high rigidity under the presence of hard ceramic TiC. Graded alloy and composites observed a climbing trend where wear and friction raised proportionately with load, as slight deformation due to plasticity was introduced under high pressure-interfacial friction heating.

2) For higher slid velocities, all zones of graded alloy showed a proportionately rising wear and friction; whereas for composites deduction in both wear (35.6 % at medium velocities) and friction (30.2 % at high velocities) were seen in comparison with the average rate of wear. This was promoted by the minimal friction oxidized interfacial layer thickened of the contributions from both the interactive surfaces; whose presence was asserted by the XRD results.

3) Extended slid distance resulted in a linearized gradual rise of wear and friction, for all tested zones of both graded alloy and its composites. This impacted tribology by the cyclic scrapping of disc debris over the tested pin surface.

Comparitive exploration of the investigation outputs showed the tribological behavior of functionally developed copper composite graded with TiC, and its alloy. Interpretation of outcomes, recommends the developed TiC graded composite for slide applications in various domain applications like cylinder inner lining, bearing components, horizontal or vertical slid guide bars etc.; as its inner wall zone had the maximum anti-wearing property.

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