Characterization and Wear Behaviour of WC-Co Coated Copper under Dry Sliding Conditions

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Keywords:
WC-Co
Copper Coating
Detonation Gun
Tribology
Wear Characterization

ABSTRACT

Pure copper was coated with Tungsten Carbide-Cobalt (WC12%-Co) using Detonation- Gun technique. A coating thickness of 541 μm was obtained and the hardness of WC-Co coated copper surface was 5.2 times greater than the hardness of uncoated surface. The wear properties of coated copper were investigated using pin-on-disc tribometer, where the WC-Co coated copper exhibited higher wear resistance than uncoated copper. Dry sliding wear properties of WC-Co was analysed using Response Surface Methodology by considering the parameters load (10, 20, 30 N), sliding velocity (0.75, 1.5, 2.25 ms⁻¹) and sliding distance (750, 1250, 1750 m). The results indicated an increase in the wear rate with increasing load and velocity, whereas the increase in the distance showed minimal increase in wear rate. The worn surfaces were analysed using Scanning Electron Microscopy to understand the wear mechanism. The result from the presented experiment may find its application in clutch selector fork of automobile transmission and bearings.

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1. INTRODUCTION

Copper being one of the early discovered metal, still finds a wide range of applications in mechanical, electrical, petrochemical, metallurgy, automobile and electronics industries, due to its superior material properties such as good corrosion resistance, ductility, toughness, lubricative, catalytic and a good electrical and thermal conductor [1-3]. Copper alloys due to its superior abrasive resistance and robustness, are widely used in selector forks of transmission and heavy-duty bearings and in automotive moving components [4]. Coatings are currently used in various industries to improve the surface property of the material. An effective and economic method to protect the components from abrasive, erosive, sliding and fretting related wear without reducing wear resistance or other properties is to coat the components with 200–500 μm thick WC-Co coatings [5]. These coatings are made onto a substrate through various coating techniques such as Chemical Vapour Deposition (CVD), Thermal Spraying, Physical Vapour Deposition (PVD)
and Sputtering through which the mechanical properties and wear resistance can be improved and friction can be reduced [6]. From previous literatures, it was concluded that these coatings (WC-Co) were widely used due to their superior combination of properties such as high hardness, toughness and wear resistance [7-10]. It was also confirmed that WC-Co coatings applied on bearings had improved the wear and corrosion resistance and also improved the bearing performance under poor lubricating conditions. It also aided in reducing adhesive wear damages and ultimately reduced any damaging effects produced from vibration effects [11].

The effect of warm spray deposited WC-Co/Cu multilayer coating on the bending strength, fracture behavior and surface hardness was investigated and results confirmed that the coated samples exhibited superior bending strength and surface hardness than monolithic copper. It was also confirmed that the presence of copper aided in higher work of fracture and enhancing the mechanical properties [12]. A comparative study was performed by coating mild steel with WC-17Co and WC-12Co respectively through detonation gun and plasma spray techniques respectively and the abrasive wear rates were determined by varying applied load. The results revealed that detonation sprayed WC-12Co coatings exhibited superior wear resistance than plasma sprayed WC-12Co and WC-17Co coated samples [13]. An enhancement in wear and mechanical properties of AA6063 substrate coated was obtained by coating with WC-Co through detonation gun technique. A thickness of 480 ±10µm was achieved and analysing the morphology of surface confirmed an improvement in tribological properties [10].

The effect of WC particle size on the abrasive wear performance of WC-Co coating sprayed via thermal spray method was studied and results revealed a proportional relationship between abrasive wear and square root of relative carbide size [14]. Studies were made by coating WC-Co on smooth and grit blasted copper surface, wherein the interference region was studied with Transmission Electron Microscope. The results revealed that the interference structure of the coating depended on the morphology of substrate surface [15]. Mild steel pins coated with WC-12%Co displayed three times higher wear resistance than uncoated mild steel pins [16].

WC particles of range 5 % to 30 % was mixed with Cu particle and the mixture was made as coating on copper surface by solid-state sintering. It was observed that the wear rate had reduced to 1/17 times to that of un-coated copper [17]. Dry sliding wear tests were performed on uncoated and WC-Co coated mild steel specimens against hardened EN32 steel and WC coated EN32 steel discs. Results revealed superior wear behaviour for WC-Co coated specimens over uncoated specimens. It was also observed that a negative wear behaviour was observed when sliding against EN32 disc whereas, positive wear results were observed when sliding against WC coated EN32 disc [18]. Dry sliding friction and wear behaviour of high velocity oxy-fuel system coated WC-Co coated was studied and results revealed constant friction co-efficient values for the WC-Co/alumina pair whereas, specific wear rate had increased with increasing carbide grain size and decreased with increasing temperature. It was also concluded that the formation of dense tribo film aided in reducing the dry sliding wear rate at elevated temperatures [19]. A comparative study on the abrasive wear properties of thermally sprayed WC-Co coating and hard chrome coating was performed and results confirmed better micro hardness and abrasive wear resistance for carbide based coatings than hard chrome coatings. This was mainly due to dense coating structure of WC-12Co coating [20]. Mechanical, tribological and tribo-corrosion performance analysis of thermally sprayed WC-Co based coatings was performed and it was confirmed that the abrasion resistance of the coating had comparable performance to that of sintered cerments. It was also concluded that the unlubricated and lubricated wear resistance of these coatings to be better with minimal friction co-efficient values [21].

An extensive literature study was conducted to find the economical and best available coating technique. Of all available methods, the detonation gun technique was concluded as the best (economic aspect) and facilitated multilayer and thick coating formation through thermal spraying [22]. From the literature survey conducted, it was confirmed that the
tribological behaviour of WC-Co coated copper substrate was not fully investigated. Therefore, this study deals with the synthesis, characterisation, hardness and tribological behaviour of WC-Co coating on copper substrate.

2. EXPERIMENTAL PROCEDURES

The experimental procedures for coating, hardness test and dry sliding wear tests are explained in the following subsections.

2.1 Specimen preparation

Pure copper (Cu) of dimension 100x100x20 mm was taken for coating and its characterisation and composition were determined before the coating process. Figure 1a depicts the SEM image of pure copper substrate specimen. Fig. 1b depicts the elemental composition of the copper specimen as obtained through Energy-dispersive X-ray spectroscopy (EDS). Figure 1c represents the X-ray diffraction (XRD) analysis. It was confirmed that the specimen considered for study was purely copper.

2.2 Coating characterisation and deposition

Tungsten Carbide-Cobalt powder with 86 % of WC and 12 % of Co of size 20 µm was chosen as the coating particulates. Detonation gun technique was employed to coat the substrate material as it facilitated thick and multilayer thermal coating. D-Gun apparatus consists of a barrel, where the fuel gas acetylene and oxygen were injected at high rates together along with the coating powder WC-Co and the barrel was fired using the spark plug. The mixture was heated and accelerated towards the substrate at high velocity of 650 ms\(^{-1}\) to 700 ms\(^{-1}\) and a temperature of 3250 °C. Due to high kinetic energy of the mixture hitting the substrate, a dense bond was formed between substrate and coating. Nitrogen gas was injected after every detonation and it removed any material waste and unburned gas out of the chamber and also acted as the carrier gas. Detonation took place several times a second. A coating thickness of about 100 µm can be obtained from a single coating of the mixture. Hence, the coating process was repeated five more times to get a coating thickness of approximately 500 µm. The spray parameters are provided in Table 1.

The coated surface was finished with the cloth wheel polishing and was observed through scanning electron microscope (SEM). EDS
analysis was performed to obtain the elemental composition of coating after fabrication process. The specimen coated with WC-Co revealed a composition of 46.83 %, 26.34 %, and 7.21 % of Tungsten, Carbon and Cobalt respectively. Analysis of SEM image (Fig. 2a) inferred a tight and uniformly packed structure and the EDS pattern (Fig. 2b) revealed the elemental composition of the coated substrate surface.

![SEM image of WC-Co coated surface](image)

![EDS pattern of WC-Co coated surface](image)

**Fig. 2.** (a) SEM and (b) EDS of WC-Co coated surface.

### 2.3 Coating hardness and thickness

Vickers micro hardness study (model: Mitutoyo HV-110A-B10) was performed as per ASTM 384 standards. Hardness test was performed on the coated surface using a diamond Indenter, wherein a load of 0.95 N with a 10 second dwell was applied. Three indentations were performed for each test, at three different locations to measure the hardness. Hardness of coated surface and uncoated copper surface was observed. The average of the obtained hardness values was considered as the micro-hardness of the specimen.

Thickness of coating of coated specimen was measured, following the standards ASTM B487-85 using metrological optical microscope (model: Leica DM4000M). The surface was polished by placing the coated surface and polishing wheel normal to each other with minimal pressure applied on specimen. The specimen was etched with Murakami’s solution (20ml HNO₃ + 20ml HF + 60ml H₂SO₄) for one minute to differentiate the substrate and coating. The specimen was then placed under the microscope to measure the thickness.

### 2.4 Pin-on-disc wear test

The coated side of the copper substrate was subjected to dry sliding wear with pin-on-disc tribometer (DUCOM) following ASTM standard G99. Specimens were cut to 10x10x20 mm wherein the 10x10 mm cross-section with coated edge was placed in contact against the rotating sliding disc (EN 31). The track diameter was set as 80 mm. The disc was periodically cleaned before and after each experiment to remove any debris and burrs present on the counterface and to ensure smooth and total contact with the disc. The load was applied through the potentiometer setup in the tribometer. The surface was cleaned after the experiment using acetone and an optimal surface finish was given to specimen by removing burs and ensuring the removal of stuck impurities. The specimen was weighed in an electronic weighing machine of tolerance ±0.001 g before and after each experiment. Each experiment was repeated thrice and the average of the wear rate is given in Table 3. Wear rate was calculated using the equation 

\[ W = \frac{M}{\rho D} \]

wherein \( W \) is wear rate in mm³/m, \( \rho \) is density in g/mm³ and \( D \) is the sliding distance in m.

The experiments to be performed was generated using a mathematical model developed using Response Surface Methodology (RSM). Central composite design was chosen to generate the experiments. The input parameters were chosen considering the system limitations. The parameter range selected were as follows, applied load (10 to 30 N), sliding velocity (0.75 to 2.25 ms⁻¹) and sliding distance (750 to 1750 m) with an increment of 10 N, 0.75 ms⁻¹ and 500 m respectively.
2.5 Response surface methodology

Response surface methodology (RSM), a statistical and mathematical method in design of experiments (DOE) is a diligent and systematic approach in optimising influencing parameters such as velocity, sliding distance, and load over the wear rate of the coated specimen. This method is very well suitable when a response or set of responses are influenced by a set of predefined variables. It also helps in ranking and analysing the amount of influence of those variables over responses. Minitab 17 statistical software was used to generate the set of experiments to be performed based on the chosen process parameters which are load, velocity and distance. The selected parameters and its levels are shown in Table 2. The table of experiments generated and the corresponding results as obtained from experiments performed are shown in Table 3.

| Table 2. Parameters layout. |
|-----------------------------|
| **Factors** | **Levels** |
| Load | 10 N | 20 N | 30 N |
| Velocity | 0.75 ms⁻¹ | 1.5 ms⁻¹ | 2.25 ms⁻¹ |
| Distance | 750 m | 1250 m | 1750 m |

3. RESULTS AND DISCUSSION

3.1 Evaluation of coated thickness and specimen’s hardness

WC-Co coating thickness of 541±17 μm was observed under metallurgical microscope, which is shown in Fig. 3.

![Fig. 3. Coating thickness of WC-Co.](image)

The hardness of uncoated copper substrate was observed as 338.2 HV, whereas WC-Co coated surface showed a hardness of 1735.8 HV with an increase of nearly 5.2 times the hardness of uncoated specimen. This was mainly due to the superior bonding strength (>70 MPa) developed between coating and substrate on fabrication. Uniform WC-Co coating on copper substrate also aided in promoting better load bearing capacity. The roughness of WC-Co coating on copper substrate was measured as 5.96 – 6.4 Rₐ.

3.2 Evaluation of wear resistance

The WC-Co coated surface was subjected to dry sliding wear test and the results are tabulated in Table 3. The analysis was carried out using Response Surface Methodology technique using MINITAB 17 statistical software. Density of WC-12%Co coated specimen and uncoated copper substrate was calculated as 13.7 g/cm³ and 8.96 g/cm³ through gas pycnometry.

| Table 3 Experimental Results. |
|-------------------------------|
| **S.No** | **Load (N)** | **Distance (m)** | **Velocity (ms⁻¹)** | **Wear Rate (mm²m⁻¹)** |
|-------|-------------|-----------------|------------------|---------------------|
| 1     | 10          | 1750            | 0.75             | 0.00000767          |
| 2     | 10          | 750             | 2.25             | 0.0000894           |
| 3     | 20          | 1250            | 1.5              | 0.0001073           |
| 4     | 30          | 750             | 2.25             | 0.0001193           |
| 5     | 20          | 1250            | 1.5              | 0.0000984           |
| 6     | 10          | 1250            | 1.5              | 0.0000805           |
| 7     | 30          | 1750            | 0.75             | 0.0000958           |
| 8     | 30          | 1750            | 2.25             | 0.0001150           |
| 9     | 20          | 1750            | 1.5              | 0.0001022           |
| 10    | 20          | 1250            | 2.25             | 0.0001163           |
| 11    | 10          | 1750            | 2.25             | 0.0000958           |
| 12    | 20          | 1250            | 1.5              | 0.0000984           |
| 13    | 20          | 1250            | 0.75             | 0.0000715           |
| 14    | 30          | 1250            | 1.5              | 0.0001163           |
| 15    | 30          | 750             | 0.75             | 0.0000894           |
| 16    | 10          | 750             | 0.75             | 0.0000596           |
| 17    | 20          | 750             | 1.5              | 0.0001044           |
| 18    | 20          | 1250            | 1.5              | 0.0000984           |
| 19    | 20          | 1250            | 1.5              | 0.0000894           |
| 20    | 20          | 1250            | 1.5              | 0.0001073           |

3.3 Influence of process parameters on wear rates

The effect of applied load, sliding velocity and sliding distance on wear rates of the specimen are discussed below. Representations in 3D plots are shown in Fig. 4.

3.3.1 Effect of load

From Fig. 4b and 4c, it was inferred that the increment in load led to a linear increase in material loss. Lower loads (10 N) contributed to
minimal wear rate. It was concluded that with increasing load to 20N, a uniform increase in wear rate had occurred and at a maximum load of 30N, maximum wear rate was observed. The trend observed was in accordance with Archard's law, which stated that the material loss observed was linearly proportional to the increasing applied load. The increase in load led to higher contact pressure at the interface point between pin and counter face which generated higher friction values. Higher friction coefficient led to rise in temperature which additionally contributed to increase in wear rate by the plastic deformation of pin material. Hence, wear rate increased with increase in applied load [23].

3.3.2 Effect of sliding distance

As shown in Fig. 4a and 4c, wear rate displayed minimal dependency on sliding distance as it increased. At minimum sliding distance, minimal wear was observed. As sliding distance increased from 500 m to 1500 m, a slight increase in wear rate was observed. As sliding distance increased further, the pin surface experienced continuous deformation due to continuous rotatory motion. This led to the rise in temperature at the interface between pin and counter face, which slightly increased the rate of plastic deformation. This also resulted in an increase in hardness due to work hardening, which resisted the wear of the sample. Hence, Archard's law was obeyed here, which confirmed that volume loss was inversely proportional to hardness. Oxide formation (WO$_2$) at high temperature due to increasing sliding distance also contributed to the wear resistant property. The oxide layer formation behaved as a tribo-film on the specimen, resisting the wear formation and produce minimal wear.

3.3.3 Effect of sliding velocity

As shown in Fig. 4a and 4b, wear rate increased uniformly with increase in sliding velocity. At initial velocity (0.75 ms$^{-1}$), the contact between mating parts were subjected to ploughed appearance on the surface which produced micro-cracks and produced minimal wear rate, due to high bonding strength. As the velocity increased (0.75 to 2.25 ms$^{-1}$), the shear stress between the specimen and the disc increased, which in turn led to higher ploughing effect forming numerous and larger cracks, eventually leading to plastic deformation of pin material. This induced more rupture of the surface and thus producing higher wear rate.

![Graphs](a)![Graphs](b)![Graphs](c)

**Fig. 4** Plot of wear influence parameters (a) distance and velocity, (b) load and velocity, (c) load and distance.

3.4 Numerical modelling for wear rate

The numerical model was developed by Analysis of Variance (ANOVA) with the confidence level of 95% taking the different parameters such as load, distance and velocity into consideration. It was also comprehended from the regression
equation (Equation 1) that, sliding distance does not create any deviation in the wear rate, as all the coefficients for sliding distance was zero. 

Regression equation

Wear rate (mm\(^3\)m\(^{-1}\)) = 
-0.000012 + 0.000003 \text{ Load} + 0.000066 \text{ Velocity} 
-0.000013 \text{ Velocity} \times \text{Velocity} \tag{1}

Table 4. Coded Coefficients.

| Term           | Coef  | SE Coef | T-Value | P-Value | VIF |
|----------------|-------|---------|---------|---------|-----|
| Constant       | 0.000100 | 0.000002 | 42.36   | 0.000   |     |
| Load           | 0.000013 | 0.000002 | 6.14    | 0.000   | 1.00|
| Distance       | 0.000002 | 0.000002 | 1.08    | 0.308   | 1.00|
| Velocity       | 0.000014 | 0.000002 | 6.55    | 0.000   | 1.00|
| Load* Distance | -0.000003 | 0.000004 | -0.64   | 0.538   | 1.82|
| Distance* Distance | 0.000002 | 0.000004 | 0.54    | 0.601   | 1.82|
| Velocity* Velocity | -0.000007 | 0.000004 | -1.71   | 0.117   | 1.82|
| Load* Distance | -0.000003 | 0.000002 | -1.09   | 0.300   | 1.00|
| Load* Velocity | -0.000000 | 0.000002 | -0.00   | 1.000   | 1.00|
| Distance* Velocity | -0.000003 | 0.000002 | -1.09   | 0.300   | 1.00|

3.5 Data adequacy

Data adequacy of specific wear rate was checked by plotting the residuals as normal probability plot through regression analysis. It was observed that the error was minimal, as all the residuals fell near the straight line as shown in Fig. 5a. All the residual values fell between 0.000012 to -0.000012 when residual was plotted with observation order and there was no unpredictable pattern observed as shown in Fig. 5b.

3.6 SEM and XRD analysis

Worn surfaces were subjected to SEM analysis to determine the wear mechanism. At a minimum load of 10 N (Fig. 6a) with the sliding distance of 1750 m and velocity of 0.75 ms\(^{-1}\), the specimen displayed presence of minimal micro voids.

Fig. 6 SEM of worn surface at minimum and maximum load condition (a) 10 N, (b) 30 N.
These micro voids were due to the removal of uneven surface coating and some oxide layer formation was observed due to the heat developed at higher sliding distance during the contact between disc and pin. With increase in applied load to 30 N (Fig. 6b) and by maintaining the other two parameters constant, an increase in wear was observed which led to the formation of wear debris and delamination over the surface. This was mainly due to an increase in friction force as a consequence of increment of load. It was observed that the formation of oxide layer occurred during higher sliding distances.

At the initial sliding distance of 750 m (Fig. 7a) at a constant load of 30 N and the velocity of 2.25 ms$^{-1}$, minimal wear was observed due to the less contact time between the pin and the disc, but as sliding distance increased to 1750 m (Fig. 7b) maintaining the other two parameters, the wear gradually increased due to the increase in the contact duration. More oxide layer formation was observed due to the heat generated at the pin counterface interface during the contact. For a longer duration, the oxide layer formed aided in reducing the wear, but the variation in distance does not show a notable disturbance in wear rate. XRD analysis (Fig. 8) for the maximum load, sliding distance and sliding velocity of 30 N, 1750 m and 2.25 ms$^{-1}$ respectively was done and the result showed the formation of WO$_2$ at 36.1, 75.4 and 76.3 degrees with the presence of WC (JCPDS card No. 51-0939) and Co (JCPDS card No. 15-0806).

![Fig. 8. XRD of surface at maximum sliding distance.](image)

![Fig. 7 SEM of worn surface at minimum and maximum sliding distance condition (a) 750 m, (b) 1750 m.](image)

![Fig. 9. SEM of worn surface at minimum and maximum sliding velocity condition (a)0.75 ms$^{-1}$, (b) 2.25ms$^{-1}$.](image)
At minimum sliding velocity condition of 0.75 ms\(^{-1}\) (Fig. 9a) with load and the sliding distance of 10 N and 750 m respectively, mild shallow ploughings were observed. At these parametric combination, minimum wear was observed which was confirmed through the mathematical regression model generated by RSM method. With increasing velocity to 2.25 ms\(^{-1}\) (Fig. 9b) at constant load and sliding distance, deeper and larger ploughed surfaces were observed, which increased the shearing force between the pin and the disc.

4. CONCLUSION

WC-Co coating was successfully coated on copper substrate through detonation gun technique. SEM analysis confirmed closely and tightly packed ceramic particles, and EDS confirmed the presence of 46.83 %, 26.34 %, and 7.21 % of Tungsten, Carbon and Cobalt respectively. Hardness of uncoated substrate was observed as 338.2 HV, whereas coated substrate displayed a hardness of 1735.8 HV. Dry sliding wear test performed on coated specimens revealed applied load and sliding velocity as significant process parameters influencing the wear rate, whereas sliding distance had minimal influence on the wear rate of the specimen. Optimal parametric combination for minimal wear rate was concluded as 10 N, 750 m and 0.75 ms\(^{-1}\) for load, distance and velocity respectively. The result of the present work may find its application in selector fork or bearing of the vehicle transmission.

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