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Investigation and characterization of Copper-Fly ash-Tungsten hybrid composites synthesized through P/M process

S Thanga Kasi Rajan 1,3, A N Balaji 2, G R Raghav 2, K J Nagarajan 1 and S C Vettivel 1

1 Department of Mechanical Engineering, Kamaraj College of Engineering and Technology, Near Virudhunagar, K.Vellakulam, Madurai-625701, Tamil Nadu, India
2 Department of Mechanical Engineering, K.L.N College of Engineering, Madurai-630612, Tamil Nadu, India
3 Department of Mechanical Engineering, Chandigarh College of Engineering and Technology, Chandigarh-160019, India

E-mail: stkrajan@gmail.com and balajime@yahoo.com

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Abstract

This research paper describes the enhancement of mechanical, wear and corrosion behaviour of the Copper (Cu) matrix composite by reinforcing Fly ash (FA) and Tungsten (W). The main objective of this study was to reduce the weight and cost of the hybrid composites. The weight percentage of low density material (FA) was kept constant at 6% and samples were prepared by the addition of W in weight percentages of 3, 6 and 9 in the Cu matrix. The characterization of the hybrid composites was studied using a Scanning Electron Microscope (SEM) and Energy-dispersive spectroscopy (EDS). The micrographs revealed the uniform distribution of W and FA in the Cu matrix. From the mechanical characterization, it was identified that there is an increase in microhardness and compressive strength with the addition of W particles. It can be understood that the W particles occupy substitutional type reinforcement and FA particles occupy interstitial type reinforcement in the Cu matrix. The Wear behavior and its mechanism were studied using worn surface SEM micrographs. It was observed that the lowest specific wear rate was recorded for the hybrid composition of Cu-6FA-9W. Electrochemical polarization test and Electrochemical Impedance Spectroscopy (EIS) study revealed that Cu-6FA-9W shows higher corrosion resistance in both 1 N HCl (256.593 × 10^{-4} \ \text{Ω cm}^2) and seawater media (219.855 × 10^{-4} \ \text{Ω cm}^2) than pure Cu.

1. Introduction

The composite material is made of a mixture of two or more distinctly different insoluble materials. [1]. The main objective of adding reinforcement was to improve the desired properties of the base material based on suitable applications. Copper (Cu), magnesium, titanium and aluminum-based composites are commercially and widely used composite materials. Among which, Cu is considered to be one of the most dominant nonferrous materials that find extensive applications in cooling system applications, electrical contacts, heat sink applications, antifriction, antiwear and semiconductor devices [2]. The addition of single reinforcement especially Cu-W composite materials finds application in welding electrodes, high voltage electric contacts, and microelectronic materials [3–6]. Similar kinds of other popular reinforcing materials such as B4C, Ti & TiO2, WC, TiC, [7–11] etc, promised to increase the thermal conductivity, electrical conductivity, hardness, and wear resistance.

At present, industry demands to reduce the weight and cost of the material without sacrificing its mechanical, electrical, tribological and thermal properties. The demand even extends up to finding the machining characteristic of the composite material and cost of fabrication etc, [12]. One factor which reduces the cost of fabrication is to reinforce the low cost material. Some of the low density reinforcement materials which are widely used in copper are MoS2, SiC, Al2O3, graphite, and Fly Ash (FA) [13–18].

The addition of low density material has certain advantages and disadvantages. For example, MoS2 is one of the solid lubricants mainly added with Cu to improve the machinability of the material but it undergoes reaction with the base material and also acts like a poor lubricant [19]. Similarly, the addition of Al2O3 increases the
hardness but reduces the compressive strength of the material due to the localized softening of the material [20]. Very few works of literature are available for using FA as reinforcement. The FA is a waste byproduct obtained by the burning of coal in thermal power stations. It is available in plenty. The major Chemical ingredients present in FA are SiO₂, Al₂O₃, MgO, CaO, Fe₂O₃, and other oxide particles. The density of the FA is low (less than 1 g cm⁻³). Christie & Tensing [21] studied and described a few engineering properties of FA. Surabhi 2017 [22] explained the utilization of FA in India in various sectors such as Agriculture, Concrete, road and embankments, Bricks and tiles, reclamations etc.

Several researchers were started to utilize FA. Balamurugan et al [15] discussed the various process and influencing parameters in the fabrication and tribological behavior of Cu-FA composite material. The major problem encountered in addition to FA in the copper matrix is its density (volume fraction). The density and compressive strength of the Cu-FA composite material decreases with an increase in percentage addition of high volume fraction low density FA reinforcement. The reason and mechanism of decrease in compressive strength of the composite material were explained with the concept of grain deformation and Boundary Slip [23]. The major cause for the decrease in the compressive strength of Cu-FA was identified as boundary slip [24].

Considering all the above factors, it was observed that FA, when used as single reinforcement in Cu matrix, decreases the compressive strength. Hence it is required to go for the concept of addition of second reinforcement material called hybrid composite material [25] in Cu-FA for enhancing the material properties. Among the various choice of second reinforcement materials such as Ti, TiO₂, B₄C, WC, etc, W is considered to be one of the most attractive materials [26] as it finds much application in electronic, aerospace and defense field. Hence W was chosen as secondary reinforcement material for this study.

The method of fabrication of the hybrid composite material(Cu-FA-W) is another important parameter that highly influences the material properties. The most common techniques used are solid phase processing and liquid phase processing. Though liquid phase processing (casting) is suitable for mass production, it has certain disadvantages such as the non-uniform distribution of reinforcements, the reaction of reinforcement with the matrix phase, the formation of oxides and the segregation of reinforcement etc. [27]. In this study, the Powder metallurgy process was used for the fabrication of preforms and uniform distribution of reinforcement was achieved.

Based on the literature review and demand to reduce the weight and cost of the composite material with improved strength, it is necessary to find the characterization, mechanical, tribological and corrosion behavior of Cu-FA-W composite material. Also, it is observed that no research study was carried out to find the effect of the addition of high density W and low density FA in the Cu matrix to form Cu-FA-W hybrid composite material.

Hence the present study aims to fabricate Cu-FA-W composite material with a weight percentage of Cu-6%FA-3%W(Cu-6FA-3W), Cu-6%FA-6%W(Cu-6FA-6W), Cu-6%FA-9%W(Cu-6FA-9W) and pure Cu through powder metallurgy process. Here the percentage reinforcement of FA is kept constant. A detailed characterization of the samples was done using a Scanning Electron Microscope (SEM) and EDS Dispersive Spectrum (EDS). The mechanical behavior was studied using the Vickers hardness and compressive test. The Wear behavior using the pin on disc apparatus. The Effect of addition of W on the Specific wear rate (SWR) and the Coefficient of Friction (COF) was determined for the sliding speed of 1 m s⁻¹, 2 m s⁻¹, 3 m s⁻¹ and sliding load of 10 N, 15 N, and 20 N for the constant sliding distance of 2000 m. The corrosion study was studied using Electrochemical workstation in 1 N HCl and seawater as an electrolyte.

2. Materials and methods

2.1. Materials used

Pure electrolytic Cu powder of grade EC1 and W powders with test reports were procured from M/s Metal Powder Company (P) Ltd, Tirumangalam, Madurai, Tamilnadu, India. In this study, Cu was used as a matrix and W & FA was used as reinforcement material. Table 1 shows the various characteristics of electrolytic Cu and W powder as given in the test report by M/s Metal Powder Company (P) Ltd, Tirumangalam, Madurai. The FA was collected from the Electrostatic precipitator, Tuticorin Thermal Power Station, Tuticorin, Tamilnadu, India.

Cu with a purity level of 98.6% and W with a purity level of 97.6% was used. The average particle size of both Cu and W powders was less than 45 μm shown in table 1. The chemical composition present in the FA materials that were already discussed in our previous article and it was SiO₂–66.13%, Al₂O₃–30.36%, Fe₂O₃–0.42%, CaO–1.39%, MgO–1.70% [24].

2.2. Sample preparation

Cu, W and FA powders were precisely weighed individually using the digital balance of precision 0.1 mg. The weight percentage of FA was kept constant at 6% throughout this study and the weight proportion of W at 3%, 6% and 9% respectively. The material composition of the hybrid composites is Cu-6FA-3W, Cu-6FA-6W and Cu-6FA-9W. The weighted powders were mechanically blended in a mortar for 2 h to ensure uniform mixing of the powders. The blended powders were preheated in a muffle furnace under an inert atmosphere to a
temperature of 250 °C for removing the moisture content if any. The preheated samples were then compacted in a 10 mm cylindrical split die to a pressure of 550 MPa. Before compaction the walls of the die were well lubricated using graphite. The green compacts were then sintered to 900 °C for 1 h as suggested by balamurugan et al[15].

2.3. Characterization of Cu-FA-W hybrid composites
SEM and EDS Characterization with the mapping of all elements present in the hybrid Cu-FA-W composite material was taken using SEM with EDS attachment. The EDS micrograph shows the various elements present in the hybrid mixture and mapping shows the distribution of various elements present in the hybrid mixture.

2.4. Density and hardness measurement
The actual density of the hybrid mixture was calculated according to the ASTM: B9632–13 using Archimede’s principle. The hardness of the Cu-FA-W was determined using Vickers hardness tester as per ASTM E384 for a load of 3 kgf and dwell time of 10 s. Before the test to be carried out, the surface of the samples was well polished and average of 5 hardness readings on the surface of the specimen was determined [28].

2.5. Compression test
The Compression test was conducted to find the mechanical behavior of the samples as per the ASTM E9–89 standard using a computerized universal testing machine with a feed rate of 1 mm/minute[24]. The Compression test was carried out for all the samples with the help of mirror polished die sets. Graphite was used for lubrication. The best load bearing capacity was obtained for the aspect ratio of 0.8 than other ratios [29]. The dimensions of the samples are of length L = 8 mm and diameter d = 10 mm (L/D = 0.8). The end surface of the samples was kept normal to the surface of the fixture.

2.6. Wear test
The Cylindrical performs of 10 mm diameter Cu-6FA-W (3%, 6%, 9%) were tested using pin-on-disc wear tester apparatus (Ducom, model No: ED-201, Bangalore, India) using ASTM G99 standard. The wear tests were conducted for three normal loading conditions (10 N, 15 N and 20 N), three sliding speeds (1 m s⁻¹, 2 m s⁻¹ and 3 m s⁻¹) and sliding distances of 2000 m. The other parameters such as track dia of 60 mm and counter disc material made of EN 31 steel of 64 HRC was used. The surfaces of the preforms and counter disc were well grounded and cleaned before conducting the experiment using SiC emery paper of different grades and acetone. [1].

2.7. Potentiometric polarization test
The Corrosion test was conducted on the prepared Cu-FA-W hybrid composite material using the Electrochemical workstation of model: Biologic Sp-150. Tafel extrapolation curves and EIS tests were conducted in 1 N HCl and seawater media as per the procedure is given in the article [24, 30, 31]. Seawater was taken from Rameshwaram, Tamil Nadu, India.

| Table 1. Characteristics of electrolytic Cu powder of Grade EC1 and W powder. |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Characteristics | UOM Test method | Specification | Test value |
| Sieve Analysis: Characteristics of Cu powder | | | |
| + 75 μm | % | 10 Max | 0.27 |
| − 75 + 45 μm | % | IS5461 | Balance | 4.20 |
| − 45 μm | % | 90.0% min | 95.40 |
| Flow | Sec/50 g | ASTM B-213 | NIL | NIL |
| Apparent density | g/cc | ASTM B-417 | 1.2–1.7 | 1.4312 |
| Acid Insoluble | % | ASTM E-194 | 0.1 Max | NIL |
| Cu Content | % | ASTM E-53 | 98.3 min | 98.6 |
| Characteristic of W powder | | | |
| Sieve Analysis passing through 45 μm | % | ASTM D–185 | 98.5 min | 99.00 |
| Fisher Number (By FSSS) | % | ASTM B–330 | 4.0 max | 3.90 |
| Hydrogen Loss | % | ASTM E-159 | 2.0 max | 1.9065 |
| Chemical Analysis Other metallic impurities | % | AAS | 1.0 max | 0.1640 |
| Purity | % | | 97.0 min | 97.92 |
3. Results and discussion

3.1. Characterization of Cu-FA-W hybrid composite

Table 1 infers that fine grained electrolytic copper of size less than 45 $\mu$m with a purity level of 98.6% was used as a matrix. The particle shape and size of the FA were already tested and given in our previous article. It was observed that FA particles are spherical in shape with an average size of around 8 $\mu$m and the particle size ranged from 2 to 10 $\mu$m [24]. Fine graded W powders of size less than 45 $\mu$m with a purity level of 97.92% were used as another reinforcement.

Figure 1. SEM with EDS Mapping of Cu-6FA-3W, (a) Sem of Cu-6FA-3W, (b) EDS of Cu-6FA-3W, (c) mapping of Copper (d) tungsten (e) Oides (f) Aluminiunm (g) Iron (h) Silicon.

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Figures 1 (a)–(h), 2 (a)–(h) and figures 3 (a)–(h) explains SEM with EDS mapping of Cu-6FA-3W, Cu-6FA-6W and Cu-6FA-9W hybrid composite material respectively. It confirms the presence of various elements such as Cu, W and oxides of Al, Si and other oxide particles such as Fe, Ca and Mg and their distribution in the matrix phase. As stated earlier, the main elements present in FA are oxides of Al and Si. Other oxide particles also present but their percentage was very low. From the SEM with EDS mapping, it is observed that there is no agglomeration of reinforcement particles and also evidences the uniform distribution reinforcements (W & FA) in the Cu matrix.
Figure 3. SEM with EDS Mapping of Cu-6FA-9W, (a) Sem of Cu-6FA-9W, (b) EDS of Cu-6FA-9W, (c) mapping of Copper (d) tungsten (e) Oxides (f) Aluminium (g) Iron (h) Silicon.

Table 2. Sintered Density, Porosity and relative density of fabricated hybrid composites.

| Sl. no | Material composition | Theoretical density (g/cm³) | Actual density (g/cm³) | Relative density (%) | Porosity (%) |
|-------|----------------------|-----------------------------|------------------------|---------------------|--------------|
| 1     | Cu                   | 8.96                        | 8.342                  | 93.1                | 6.9          |
| 2     | Cu-6FA-3W            | 8.7926                      | 8.160                  | 92.8                | 7.2          |
| 3     | Cu-6FA-6W            | 9.1028                      | 8.493                  | 93.3                | 6.7          |
| 4     | Cu-6FA-9W            | 9.413                       | 8.848                  | 94                  | 6            |
3.2. Density and hardness

Table 2 shows the theoretical, actual, relative density and porosity of the Cu-FA-W hybrid composite material. The density of Cu is 8.96 g cm$^{-3}$, FA is 1 g cm$^{-3}$ and W is 19.3 g cm$^{-3}$. The theoretical density was calculated by the rule of mixture. The theoretical density of Cu-6FA-3W decreases when compared to the Cu and then the density value increases as the percentage reinforcement of W increases. The main reason for this decrease in
density is due to addition of 6% of low density FA and 3% W. The reason is in good agreement with Thanga Kasi Rajan et al [24] and Balamurugan et al [15] reported that the addition of FA in Cu matrix decreases the relative density of the composites. The increase in addition of reinforcement obviously increases the porosity of the

Figure 7. (a)–(c) Effect of Sliding Velocities on SWR of Cu-FA-W hybrid composites at different loading conditions.
fabricated samples in P/M process as FA is in large volume compared to W. The density increases when the percentage addition of W increases. It was observed that the porosity of Cu-6FA-3W increases since FA is in large quantity and volume addition of W is small. When the W addition % increases, the porosity value slightly decreases due to addition of high density W.

Figure 4 reveals the Vickers hardness value of Cu-FA-W hybrid composite material. The hardness value of the Cu-FA-W increases as the % reinforcements increase. The major reason for the increase in hardness was the presence of metallic oxides in FA and W particle which prevents the material dislocation and thereby deformation. Also the average size of the Cu and W were almost equal in size of around 45 μm and FA is around 8 μm. The W was a high density and hard material whereas FA was a low density spherical shaped solid inert material and volume of FA was larger as compared to W. During compaction process, the needle shaped Cu matrix wound around the W and FA particles. FA particles are smaller in size which would slide or move and occupies the intergranular space between the Cu and W particles which results in increase in hardness. Dinaharan et al [32] reported that incorporation of FA in metal matrix (irrespective of matrix material such as Aluminium, Copper and Magnesium) improve the microhardness due to oorwan strengthening which increases the resistance for dislocation. Another reason for increase in hardness is increase in % reinforcement of W particles which could resist the material dislocation. Moreover, both the reinforcements W and FA have good wettability with Cu as suggested by Vettivel et al (2013) [1]. From table 2, the low Porosity values of our samples indicate the good wettability. The increase in hardness value confirms the good bondage and physical structure of Cu-FA-W hybrid composite material.

Figure 5 reveals the compressive strength of the Cu-FA-W composite material. It was observed from the graph that the increase in addition of % reinforcement of W increases the compressive strength of the composite material. The compressive strength of the composite material depends on the effective compaction and bonding strength between the matrix and reinforcement phases. But here, the difference in particle size of matrix and reinforcement plays a major role in the increase in compressive strength of the Composite material.

The Cu and W particles were of sizes around 45 μm form substitutional type reinforcement whereas the size of FA particles was 8 μm which forms interstitial type reinforcement. As discussed earlier in hardness that the
bonding between the reinforcement phases and matrix is good due to good wettability. The distribution of matrix and reinforcements were represented schematically in figure 6. Hence the applied compressive load causes the grain boundary to withstand to a larger extent and prevents the boundary to slip. This load transfer is mainly due to the transfer of load from reinforcements to the matrix and vice versa. As the % reinforcement of W increases, the compressive strength also increases. At the same time the FA was comprised of oxides particles which piled off from the matrix and trying the boundary to slip. As the load increases the W particles act as a barrier and shears off the matrix and induces plastic deformation along with the boundary slip. It was in good agreement with Lin et al (2004) [23] who explained the mechanism of plastic deformation especially effect of particle size in compression load for the composite prepared by P/M process. Also better compressive strength was obtained when compared to Cu-FA composites [15, 24].

3.3. Wear analysis

3.3.1. Effect of Sliding velocity on specific wear rate

Figures 7(a)–(c) represents the effect of the sliding velocity of Cu-FA-W hybrid composite material at different compositions under various loading conditions of 10 N, 15 N and 20 N with a constant sliding distance of 2000 m. From figures 7(a)–(c), it was inferred that pure Cu has the highest specific wear rate compared to other compositions. When the % addition of reinforcements was increased to Cu-6FA-3W, there was a drastic reduction in specific wear rate. Further addition of 3% W has not much influence on specific wear rate. When the % of W reached 9% the specific wear rate started increasing.

Figures 8(a)–(d) shows the SEM micrographs of the worn surface of pure copper at load 10 N and 20 N with respect to sliding velocities of both 1 m s\(^{-1}\) and 3 m s\(^{-1}\) respectively. Similarly, figures 9(a)–(d), 10(a)–(d) and figures 11(a)–(d) show the respective worn surface analysis of Cu-6FA-3W, Cu-6FA-6W and Cu-6FA-9W hybrid composites. SEM micrographs of the worn surface were used to find the wear mechanism of the fabricated hybrid Cu-FA-W composite material.

Copper is a soft ductile material that initially has a higher specific wear rate and undergoes severe plastic deformation. It was in good agreement with the worn surface images as shown in figures 8(a)–(d). It also
evidences that when the velocity increases the contact time between the pin and the counter disc decreases. Hence severity in the plastic deformation has somewhat reduced at increased velocity. At the same time when the load increases the plastic deformation also increases and it is observed that at higher velocities, the subsurface delamination with plastic deformation was observed. The SEM images evidence the same and shown in figure 8.

The addition of % reinforcements of FA and W reduces the specific wear rate of the hybrid composite material. There was a drastic reduction in the SWR of the composite. The reason for this reduction in SWR may be due to the addition of high density W which occupies substitutional type reinforcements whereas the addition of low density high volume FA occupies the voids and the intergranular space of Cu-W composite material forms Cu-FA-W hybrid composite material. As discussed earlier in compressive strength (figure 6) that the load transfer capacity of the fabricated samples increases and initially it piles off the FA particles and forms abrasive wear.

Figures 9(a)–(d) confirms that the abrasive wear of Cu-6FA-3W composite material. Initially, at low velocity, the abrasive wear was more. When velocity increases, the time of contact decreases and abrasion was reduced. At the same time when the load increases, some of the reinforced particles are piled out which was observed in figures 9(b) and (d).

Further addition of 3% W does not much influence on the specific wear rate. Figure 10 shows the worn surface analysis of Cu-6FA-6W. (a) at load 10 N and sliding velocity 1 m s\(^{-1}\), (b) at load 10 N and sliding velocity 3 m s\(^{-1}\), (c) at load 20 N and sliding velocity 1 m/s and (d) at load 10 N and sliding velocity 3 m s\(^{-1}\).

Figure 10. Worn surface analysis of Cu-6FA-6W, (a) at load 10 N and sliding velocity 1 m s\(^{-1}\), (b) at load 10 N and sliding velocity 3 m s\(^{-1}\), (c) at load 20 N and sliding velocity 1 m/s and (d) at load 10 N and sliding velocity 3 m s\(^{-1}\).
material shears off the matrix causing plastic deformation along with surface delamination and ploughing. It finds good agreement with Lin et al. (2004) who explained the influence of the particle size of the dispersion phase which was represented schematically from figure 6. Figures 11(a)–(d) shows the SEM micrographs of Cu-6FA-9W and confirms that the plastic deformation was observed to be high at increased load and higher velocities. At higher velocities, some surfaces are piled off which confirms the adhesive wear with delamination.

3.3.2. Effect of sliding velocity on CoF

Figures 12(a)–(c) shows the effect of sliding velocity on CoF of the Cu-FA-W composite material at different normal load conditions and at a constant sliding distance of 2000 m. It was observed from the graph that the increase in sliding velocity from 1 m/s to 3 m/s reduces a smaller decrement in CoF for all compositions and at all loading conditions.

Pure copper subjected to severe plastic deformation has low CoF when compared to other compositions because of adhesive wear. When the % reinforcements increased to Cu-6FA-3W, the CoF also increases due to more FA particles are pulled out and causes abrasive wear. Also for lower velocities, the abrasive wear rate was more and for higher velocities, the abrasive wear rate was less. The reason behind this mechanism was more FA particles are piled out and these particles are smaller and spherical in shape which results in increases in CoF at lower velocities.

The same trend was observed at Cu-6FA-6W for all sliding speeds. Further addition of 3% W decreases the CoF due to a decrease in specific wear rate. The W particle present in the matrix induces plastic deformation which causes adhesive wear and hence decreases in CoF. The increase in specific wear rate increases the volume of the Cu-6FA-9W and hence CoF decreases.

3.4. Corrosion Studies

3.4.1. Electrochemical corrosion analysis

The electrochemical potentiodynamic polarization corrosion analysis of Cu-FA-W composites in 1 N HCl and seawater were calculated using an electrochemical workstation. Figure 13 elaborates the potentiodynamic
polarization behaviour of Cu-FA-W hybrid composites. The Tafel extrapolation method was utilized for exploring the Corrosion Current ($I_{\text{Corr}}$), polarization resistance ($R_p$) and Corrosion potential ($E_{\text{Corr}}$) as revealed in table 3.
From the table 3, we could understand that the corrosion current density of Cu-6FA-9W (−1.22 mA/cm²) hybrid composite has reduced considerably than that of pure Cu (−0.80 mA cm⁻²) in 1 N HCl solution. Further the corrosion potential (Ecorr) of Cu-6FA-9W (−0.07 V) has reduced than the pure Cu (−0.156 V) which substantiates the increase in corrosion resistance. The polarization resistance of the Cu-FA-W composites in HCl has enhanced from 34.938 × 10⁻⁴ Ω cm² for pure Cu to 256.593 × 10⁻⁴ Ω cm² for Cu-6FA-9W
composites. Similarly, for seawater, the polarization resistance of Cu-FA-W has enhanced from $142.428 \times 10^{-4}$ Ω cm$^2$ for pure Cu to $219.855 \times 10^{-4}$ Ω cm$^2$ for Cu-6FA-9W. The corrosion potential ($E_{corr}$) also reallocated to the positive side from $-0.160$ V for pure Cu to $-0.070$ V for Cu-6FA-9W hybrid composite material. The corrosion resistance seems to be more or less similar for all the hybrid composites.

It can be also be noted that there are signs of passivation in cathodic curves for all samples in both HCl and seawater. This enhancement in corrosion resistance is endorsed owed to the addition of non-corrosive FA and W reinforcements. Also the improved hardness and relative density enhanced the Corrosion resistance of the Cu-FA-W composites.

3.4.2. EIS of Cu-FA-W Hybrid Composite in HCl Medium

EIS spectroscopy was engaged to explore the corrosion behaviour of Cu-FA-W hybrid composites in the 1 N HCl acidic medium. Figure 14 shows the characteristic two layered semi-circular arcs. It was observed that there was no perfect capacitance mechanism. Hence constant phase element was introduced in the equivalent circuit. Table 4 shows the 3 resistance systems of R1, R2 and R3 which represent solution resistance, single layer and double layer resistance respectively of FA and W dual reinforcements. R3 represents the charge transfer resistance ($R_{ct}$). The increase in ($R_{ct}$) value represents the increase in corrosion resistance due to the addition of W in the hybrid composites. This evidenced that Cu-6FA-9W exhibits higher corrosion resistance.

![EIS graph of Cu-FA-W hybrid composites in 1 N HCl medium and its equivalent circuit.](image)

**Table 4. Charge transfer resistance data by EIS fitting.**

| S.No | Specimen     | R1 kΩ | R2 kΩ | R3 kΩ |
|------|--------------|-------|-------|-------|
| 1    | Cu-6FA-3W    | 0.5   | 0.66  | 2.19  |
| 2    | Cu-6FA-6W    | 0.78  | 0.84  | 2.47  |
| 3    | Cu-6FA-9W    | 0.7   | 0.77  | 2.57  |
4. Conclusion

Thus Cu-FA-W hybrid composite material with compositions of Cu-6FA-3W, Cu-6FA-6W, Cu-6FA-9W was successfully fabricated through P/M method. EDS with mapping was used to characterize the hybrid composite and Archimedes principles for density measurement, Mechanical behavior using Vickers hardness and wear behavior using the pin on disc apparatus. The effect of the addition of W on SWR and CoF was determined for the sliding speed of 1 m s\(^{-1}\), 2 m s\(^{-1}\) and 3 m s\(^{-1}\) and sliding load of 10 N, 15 N, and 20 N for the sliding distance of 2000 m. The results are furnished and given below:

- EDS with mapping confirms the uniform distribution W and FA (various elements of oxides in FA) in the Cu matrix and reveals that there was no agglomeration of reinforced particles.
- Initially, there was a weight reduction in hybrid composite material for Cu-6FA-3W and further addition of W increases the weight of the hybrid composite. The porosity of the hybrid composite increases initially and then decreases as wt% of W increases.
- Vickers hardness of the Cu-FA-W hybrid composite increases with % addition of W reinforcement. The presence of W particles resists the material dislocation and FA particles occupy the voids between Cu and W results in an increase in resistance to penetration and deformation.
- The compressive strength of the Cu-FA-W hybrid composite material increases with an increase in the addition of W reinforcement. The mechanism observed that the W particle forms substitutional type reinforcement and transfer the load to adjutant Cu or W particle causing the grain boundary to withstand for the applied compressive load.
- The particle size of matrix and reinforcements influences for the increase in hardness and compressive strength of the Cu-FA-W hybrid composite material.
- SWR of the Cu drastically decreases with an increase in addition of reinforcements (Cu-6FA-3W) and an increase in COF confirms the transformation from plastic deformation to abrasive wear. Cu-6FA-6W does not influence much in SWR and COF compared to Cu-6FA-3W.
- For Cu-6FA-9W hybrid composite, the SWR value increases and shows the transition from abrasive wear to adhesive wear. The W particle present in it shears off the matrix and hence the plastic deformation. The decrease in COF confirms the same.
- The corrosion resistance of the hybrid composite increases with an increase in % reinforcement of W in both acidic and seawater mediums. The EIS study confirms the same.

ORCID iDs

S Thanga Kasi Rajan  @  https://orcid.org/0000-0003-1555-3436
A N Balaji  @  https://orcid.org/0000-0002-7008-6116
G R Raghav  @  https://orcid.org/0000-0001-6028-3979
S C Vettivel  @  https://orcid.org/0000-0003-3719-1050

References

[1] Vettivel S C, Selvakumar N and Leema N 2013 Experimental and prediction of sintered Cu-W composite by using artificial neural networks Mater. Des. 45 323–35
[2] Zhan Y Z, Shi X B and Xie H F 2006 Microstructural investigation on antifriction characteristics of self-lubricating copper hybrid composite Mater. Sci. Technol. 22 368–74
[3] Chen P, Shen Q, Luo G, Li M and Zhang L 2013 The mechanical properties of W-Cu composite by activated sintering Int. J. Refract. Met. Hard Mater 36 220–4
[4] Liu R, Hao T, Wang K, Zhang T, Wang X P, Liu C S and Fang Q F 2012 Microwave sintering of W/Cu functionally graded materials J. Nucl. Mater. 431 196–201
[5] Shu-dong L, Jian-hong Y, Ying-Li G, Yuan-dong P, Li-ya L and Jun-ming R 2009 Microwave sintering W-Cu composites: analyses of densification and microstructural homogenization J. Alloys Compd. 473 5–9
[6] Zhou Y, Sun Q X, Liu R, Wang X P, Liu C S and Fang Q F 2013 Microstructure and properties of fine grained W-15 wt% Cu composite sintered by microwave from the sol-gel prepared powders J. Alloys Compd. 547 18–22
[7] Yener T, Altınsöy İ, Yener S C, Celebi Efe G F, Ozbek İ and Bindal C 2015 An evaluation of Cu-B_{4} C composites manufactured by powder metallurgy Acta Phys. Pol. A 127 1045–7
[8] Zhang E, Li S, Ren J, Zhang L and Han Y 2016 Effect of extrusion processing on the microstructure, mechanical properties, biocorrosion properties and antibacterial properties of Ti-Cu sintered alloys Mater. Sci. Eng., C 69 760–8
[9] Nageswaran G, Natarajan S and Ramkumar K R 2018 Synthesis, structural characterization, mechanical and wear behaviour of Cu-
TiO2-Gr hybrid composite through stir casting technique J. Alloys Compd. 768 733–41
[10] Kumar Singh M, Kumar Gautam R, Prakash R and Ji G 2018 Mechanical and corrosion behaviors of developed copper-based metal
matrix composites IOP Conf. Ser.: Mater. Sci. Eng. 330 012021
[11] Akhtar F, Askari S J, Shah K A, Du X and Guo S 2009 Microstructure, mechanical properties, electrical conductivity and wear behavior
of high volume TiC reinforced Cu-matrix composites Mater. Charact. 60 327–36
[12] Rajkumar K and Aravindan S 2011 Tribological performance of microwave sintered copper TiC-graphite hybrid composites Tribol. Int.
44 347–58
[13] Grandin M and Wulkund U 2018 Wear phenomena and tribofilm formation of copper/copper-graphite sliding electrical contact
materials Wear 398–399 227–35
[14] Thanga Kasi Rajan S, Balaji A N, Narayansamy P and Vettivel S C 2018 Microstructural, electrical, thermal and tribological studies of
copper-fly ash composites through powder metallurgy 66 935–40
[15] Balamurugan P and Uthayakumar M 2015 Influence of process parameters on Cu–Fly ash composite by powder metallurgy technique
Mater. Manuf. Processes 30 313–9
[16] Rajkovic V, Bozic D and Jovanovic M T 2008 Properties of copper matrix reinforced with nano- and micro-sized Al2O3 particles 459
177–84
[17] Moazami-Goudarzi M and Nemati A 2018 Tribological behavior of self lubricating Cu/MoS2 composites fabricated by powder
metallurgy Transactions of Nonferrous Metals Society of China. 28 946–56
[18] Efe G F C, Ipek M, Zeytin S and Bindal C 2016 Fabrication and properties of sic reinforced copper-matrix-composite contact material
Materials in Technologie, 50 585–90
[19] Furlan K P, de Mello J D B and Klein A N 2018 Self-lubricating composites containing MoS2: a review Tribol. Int. 120 280–98
[20] Panda S, Dash K and Ray B C 2014 Processing and properties of Cu based micro-and nano-composites Bull. Mater. Sci. Indian Academy
of Sciences. 37 227–38
[21] Freedas Christy C and Tensing D 2010 Greener building material with flyash Asian Journal of Civil Engineering. 12 87–105 https://www.
sid.ir/en/Journal/ViewPaper.aspx?ID=185369
[22] Journal I and Chemistry A 2017 Fly ash in India : generation vis à-vis Utilization and Global perspective Int. J. Appl. Chem. 13 29–52
https://www.rupublication.com/ijac17/ijacv13n1_03.pdf
[23] Lin Y C, Li H C, Liu S S and Shie M T 2004 Mechanism of plastic deformation of powder metallurgy metal matrix composites of Cu-Sn/
SiC and 6061/SiC under compressive stress Mater. Sci. Eng., A 373 363–9
[24] Thanga Kasi Rajan S, Balaji A N, Ragav G R and Vettivel S C 2019 Compression and corrosion behaviour of sintered copper-fly ash
composite material Compression and corrosion behaviour of sintered copper-fly ash composite material Mater. Res. Express 6 046554
[25] Ramesh C S, Noor Almuez R, Majeelbu M A and Abdullah M Z 2009 Development and performance analysis of novel cast copper–SiC–
Gr hybrid composites Mater. Des. 30 1957–65
[26] Dong L L, Ahangarkani M, Chen W G and Zhang Y S 2018 Recent progress in development of tungsten–copper composites: fabrication,
modification and applications Int. J. Refract. Met. Hard Mater 75 30–42
[27] Maji P, Diwe R K and Basu B 2009 Enhancement of wear resistance of copper with tungsten addition (≤ 20 wt %) by powder
metallurgy route J. Tribol. 131 041602
[28] Razaq A M, Majid D, Ishak M and Basheer U 2017 Effect of Fly Ash Addition on the Physical and Mechanical Properties of AA6063
Alloy Reinforcement Metals. 7 477
[29] Vettivel P, Selvakumar S C and Vijay Ponraj N 2012 Mechanical behaviour of sintered Cu–5%W nano powder Composites, Procedia
Engineering, 38 287–90
[30] Ragav G R, Balaji A N, Muthukrishnan D, Sruthi V and Saijith E 2018 An experimental investigation on wear and corrosion
characteristics of Mg-Co nanocomposites Mater. Res. Express 5 66523
[31] Ragav G R, Balaji A N, Selvakumar N, Muthukrishnan D and Saijith E 2019 Effect of tungsten reinforcement on mechanical,
tribological and corrosion behaviour of mechanically alloyed Co–25C Cermet nanocomposites Mater. Res. Express 6 116546
[32] Dinaharan I and Akinlabi E T 2018 Low cost metal matrix composites based on aluminium, magnesium and copper reinforced with fly
ash prepared using friction stir processing Composites Communications 9 22–6