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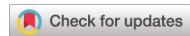
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## Effect of friction stir processing and hybrid reinforcements on copper

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### ABSTRACT

In this research, a copper based surface composite was fabricated through dispersing hybrid composite particles onto its surface through friction stir processing (FSP) technique. Optical micrographs and scanning electron microscopy images indicates finer refinement of grains and particles dispersion into matrix along with its bonding and particle separation. As per the outcomes of microhardness analysis, hardness of the developed surface composite shows increment with increase in dispersion of volume fraction of hybrid particles. Strength of the developed copper surface composite exhibited a positive trend with introduction of hybrid reinforcement particle onto the surface of the composite but yet again ductility reduced. Wear resistance of the composite increased with reinforcement addition and the same was supported through worn out surface morphology. Fluctuations in friction coefficient value reduced with increase in particles, as for the presence in BN particles while the average frictional coefficient value was observed increasing. A reduction in corrosion rate was observed with increase in reinforcement particle dispersion onto copper matrix through FSP.

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### KEYWORDS

Copper; friction; hybrid; microhardness; microstructure; processing; reinforcement; stir; strength; wear

## Introduction

Copper metal with regards to its high formability, plasticity, thermal, and electrical conductivity can be adapted as a highly efficient material but its minimal hardness and wear resistance limits its application to a great extent.<sup>[1]</sup> In awe to this facets, copper metal matrix composites attains great attention in lieu of its enhanced hardness, wear resistance, thermal and electrical conductivity thereby prompting it to be used as an effective material in applications such as heat exchangers, sliding contact, electric switches, marine applications, etc.<sup>[2]</sup> Dispersion of oxides, borides, and carbides as reinforcement particles into the copper matrix induced the hardness value and thereby wear resistance of these developed composite material avails it to be used in structural application accounted for superior mechanical properties. But this dispersion of ceramic particles into copper matrix even though increases hardness and its correlated properties, the bulk properties get affected to a great extent. This scenario forced researchers to develop a new phenomenal development called surface composites were the surface property of the base material gets enhanced with proper dispersion of ceramic particles for a known depth while the rest of the material possess the same property.<sup>[3]</sup> Many fabrication techniques including thermal spraying, laser beam, electron beam, plasma arc spraying, etc., were considered for dispersing ceramic particles homogeneously onto the surface of matrix material but formation of certain detrimental phases degrades the expected property. This phase formation occurs with an evolution of unavoidable high operating temperature, in turn increasing the chances for the matrix and reinforcement particles to react.<sup>[4–6]</sup> Hence to

avoid these phase formation, a surface composite development procedure that works below the melting point of the base matrix material has to be considered and thus friction stir processing (FSP) suits well for the required specs.

Derived from the principle of friction stir welding (FSW), FSP is a solid state process used to alter the microstructure and surface of a material. This works in such a way that a rotating FSP tool with a defined pin and shoulder is allowed to pass over the surface of a work piece along a desired path causing severe frictional heat and plastic deformation thereby evolving microstructure and surface of the material.<sup>[7–9]</sup> As the FSP route takes place within a temperature below the melting point of the base material, chances for reactions between matrix material and reinforcement particles gets reduced thereby minimizing the possibility to form detrimental phases.<sup>[10]</sup> Researches regarding friction stir processed (FSPed) surface composites have proved admissible enhancements in the surface properties including hardness, wear resistance and corrosion behavior of the base matrix material. These eventual engineering technocrats has forced the researchers to try out this procedure mostly for all of the able-bodied, commercialized metals including aluminum, copper, magnesium, titanium, steel, etc.<sup>[11–13]</sup>

Copper metal surface modification through FSP route has been found to be studied quite rare by the researchers worldwide, even though surface modified copper can attribute to be an eminent material. Studies on surface modification of copper metal with dispersing oxides, carbides, CNT's and borides has been found out through literatures but the useful exploitation of nitrides being an advanced ceramic material

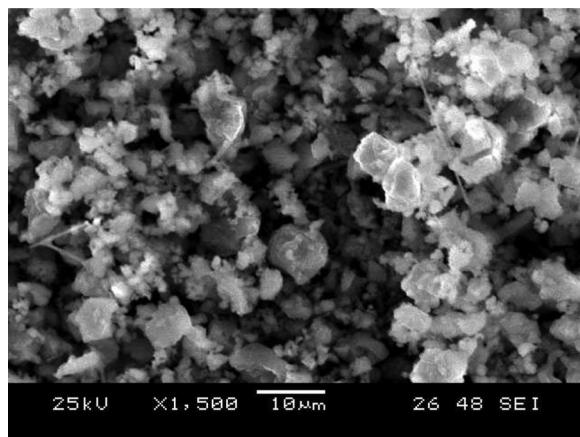
is found minimal.<sup>[14–19]</sup> Aluminum nitride (AlN) and boron nitride (BN) was considered as reinforcement particles by Titus Thankachan et al., for surface modifications of copper matrix and behavior of the same was investigated in detail.<sup>[20–22]</sup> Results showcased encouraging upshots and thus have posed researchers to study the combined effect of AlN and BN particles at equal proportion.

BN, a layer form of material comprises of covalently bonded nitrogen and boron atom stacked together. These particles are found to be hydrophobic and therefore experience an enhanced corrosion resistance behavior. Apart from this, BN has a low frictional coefficient between layers and henceforth is utilized as one of the best lubricating additives.<sup>[23,24]</sup> BN exhibits high thermal conductivity, thermal shock resistance, enhanced electrical resistance, and low thermal expansion which have prepared it to be an important material in various industries. Yet again to these properties, capability of boron particles to absorb neutron in its pure form or as its compound form has enabled itself to find a position in the nuclear industry.<sup>[25,16]</sup> AlN exposes a crystal structure of hexagonal wurtzite and owes high thermal conductivity, electrical resistivity, dielectric breakdown strength besides being nontoxic in nature. This has enabled it to be a candidate material in the electronic industries for substrate and packaging purpose.<sup>[26,27]</sup> Researches that promotes AlN as reinforcement material has been carried over and the attained results were found to be hopeful as it increases corrosion resistance, hardness and strength of aluminum matrix. Effective usage of AlN particles as reinforcement in copper matrix can be a breakthrough in the field of electronic structural application and to the notice it can be stated that copper metal reinforced with AlN-based research is found to be very scarce.

Minimal research has been pointed out by the researchers in copper metal surface processed through FSP and the dispersion of nitride particles into copper metal so as to enhance its surface properties is found to more or less nil. This research highlights the effective property evolution of copper metal when it is dispersed with a set of advanced ceramic particles at equal proportion through FSP. In this research, hybrid composite particles were prepared as reinforcement encompassing equal proportion of AlN and BN particles. Resultant composite particles were reinforced onto the surface of copper matrix for varying volume fraction using FSP route. Effect of these hybrid particles on mechanical and tribological behavior of the developed surface composite was studied and further evaluated. Microstructural characterization through SEM and optical microscope was done so as to explore the particle dispersion, its bonding to matrix material and grain refinement, respectively.

## Materials and Methods

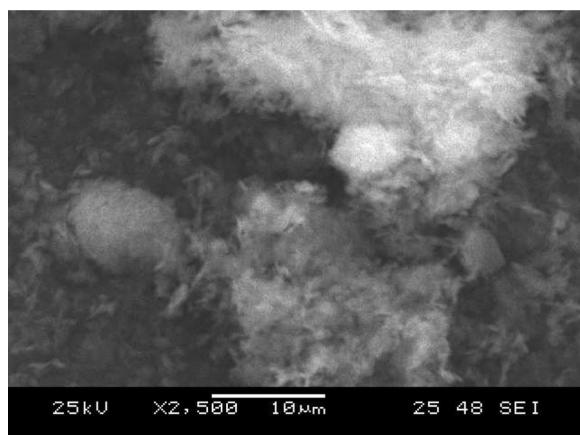
Pure copper or else known as electrolytic copper of plate form ( $150 \times 50 \times 8$  mm.) were used in this research as the base material. Two micron size particles, AlN ( $10 \mu\text{m}$ ) and BN ( $01 \mu\text{m}$ ) acquired from Sigma-Aldrich was considered as the reinforcement particles in this study. SEM morphology of the acquired powders is as shown in Figs. 1 and 2, respectively. The acquired standalone AlN and BN particles are dispersed



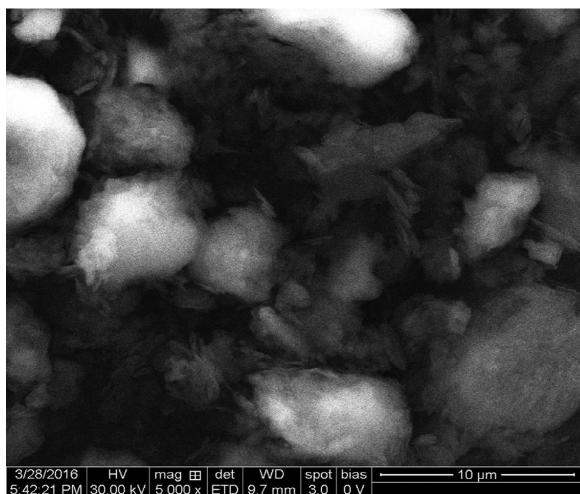
**Figure 1.** SEM micrograph for AlN.

into each other at equal proportion so as to attain an AlN-BN composite powder by a chemical-mechanical blending technique. AlN and BN powders of same proportion say 1:1 ratio is mixed with an chemically inert solution, acetone in this research through a mechanical stirrer separately. The so attained individual solutions are then blended to each other through mechanical stirring in a beaker wherein one solution is poured into another in a drop by drop manner. The stirring continues for a period of an optimized time at an optimized speed. Received blended solution is dried in atmospheric condition and the resultant particles attained is the hybrid composite (50% AlN + 50% BN) as per research requirement. The attained composite particles were undergone for microstructural characterization so as to monitor the dispersion of each particle into another and the chemical analysis of the same was performed through EDS spectrum.

Microstructural characterization of the acquired hybrid composite powder is depicted in Fig. 3 which demonstrates the mixing of AlN and BN particles to one another. It can be observed from figure that the breaking down of particles has happened slightly. Result for the chemical evaluation of the attained AlN-BN composite powder is provided in the form of EDS spectrum and the same is as depicted in Fig. 4. It illustrates the presence of aluminum (Al), boron (B), and



**Figure 2.** SEM micrograph of BN particles.



**Figure 3.** SEM micrograph of hybrid AlN-BN composite powder.

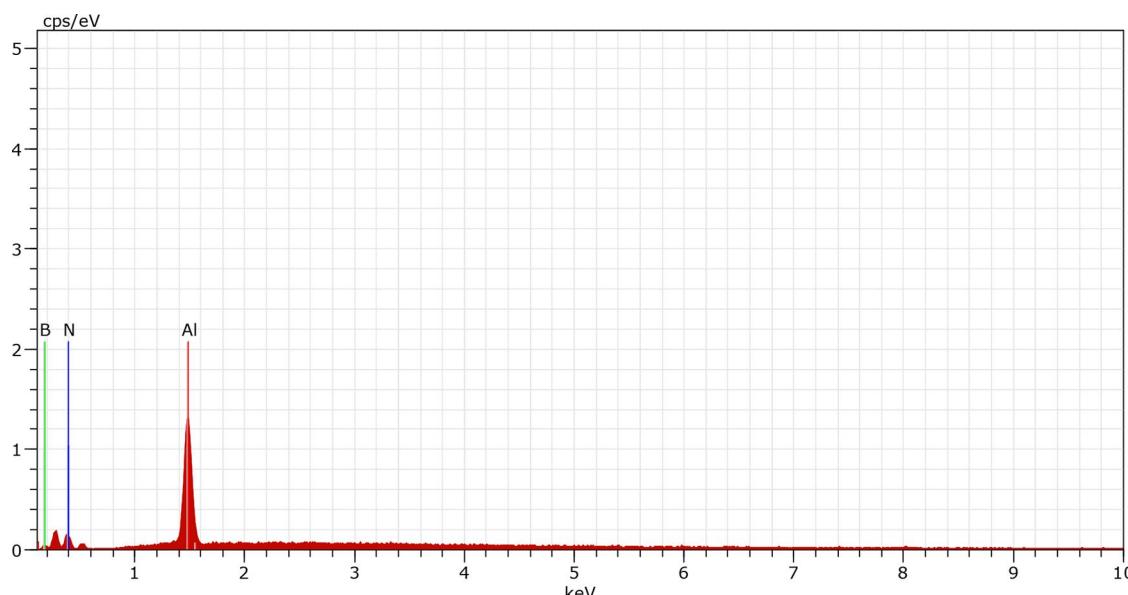
nitrogen (N) element in more or less equal proportion stating the dispersion of AlN and BN particles in equal proportion.

Surface composite development through FSP technique involves a groove cutting in the middle of the copper plate into which the reinforcement particles will be stowed. The dimensions of the groove plowed in the middle of the plate are administered based on the volume fraction of reinforcement that is stuffed inside the cut. The volume fraction of hybrid composite powder considered in this study are 5, 10, and 15 based on which the grooves are cut on the copper plate engaging a wire cut EDM for dimensions 0.3, 0.6, and 0.9 mm, respectively, for a constant depth of 5 mm. Into the above said groove hybrid reinforcement composite particles are stowed and compacted. A pinless FSP tool is allowed to pass above the reinforcement filled grooves so as to avoid the scattering of the particles during the FSP route. This compacted hybrid reinforcement composite particles is dispersed onto the surface of the copper matrix material through friction stirring

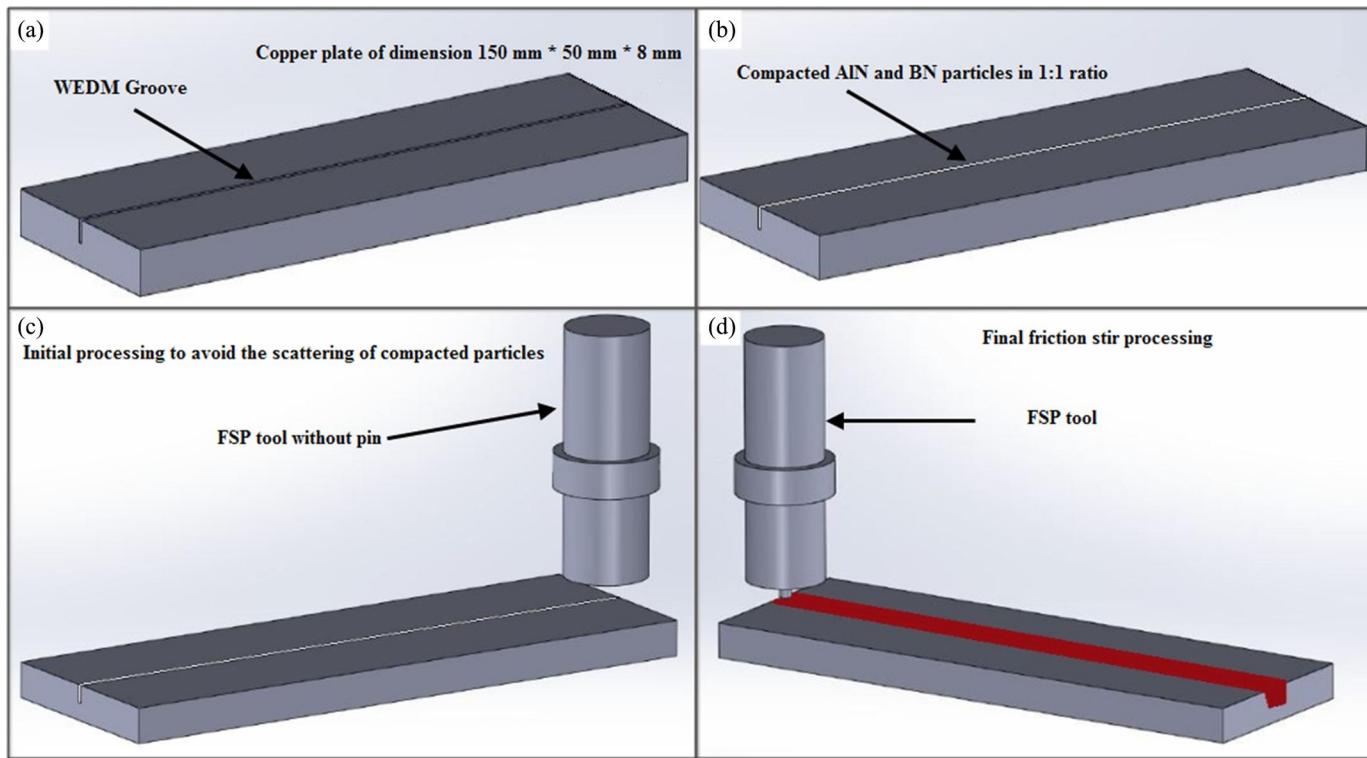
with a double tempered H13 steel made FSP tool. The procedure for FSP process is provided as [Fig. 5](#) which gives a clear schematic representation.

Surface composite development through FSP was performed using a CNC milling machine with displacement controlling facilities. The FSP tool utilized in this research had a shoulder and pin diameter of 20 and 6 mm, respectively, with a pin length of 5 mm. Based on the particle nature and quantity, the rotating speed and traverse feed were optimized and in this research 1000 rpm and 30 mm/min, respectively were considered for FSP techniques so as to attain a sound surface composite. To study the microstructural depiction of the developed surface composite, a cross section of the sample cut perpendicular to travel direction as shown in [Fig. 6](#) was considered. Optical microscope (OM) and SEM images were investigated so as to get a deeper knowledge on the developed surface composites. Optical micrograph gives clear cut knowledge on the effect of stirring over matrix material, grain refinement and effect of hybrid reinforcement particles while SEM micrographs helps in studying the dispersion of particles, its uniformity over the matrix and bonding developed between matrix and particles. Microstructural characterization is advisable only after the preparation of samples based on the metallographic standards and in this study, the specimens were polished as per the same using varying grades of emery sheets and velvet disc polisher using diamond paste. Thus polished specimens were then etched and then characterized for its microstructural variations. Etchant prepared with an optimized proportion of 2.5 g FeCl<sub>3</sub>, 15 ml H<sub>2</sub>O<sub>2</sub>, and 100 ml distilled water was considered in this research and the same was exposed to the polished sample specimen for a time period of 8 s.

Incorporation of advanced ceramic particles such as AlN and BN onto copper matrix surface can affect the hardness of the developed surface composites to a large extent. Again, the stirring mechanism exerted during FSP process may lead



**Figure 4.** EDS spectrum of hybrid composite (50% AlN + 50% BN) powder.

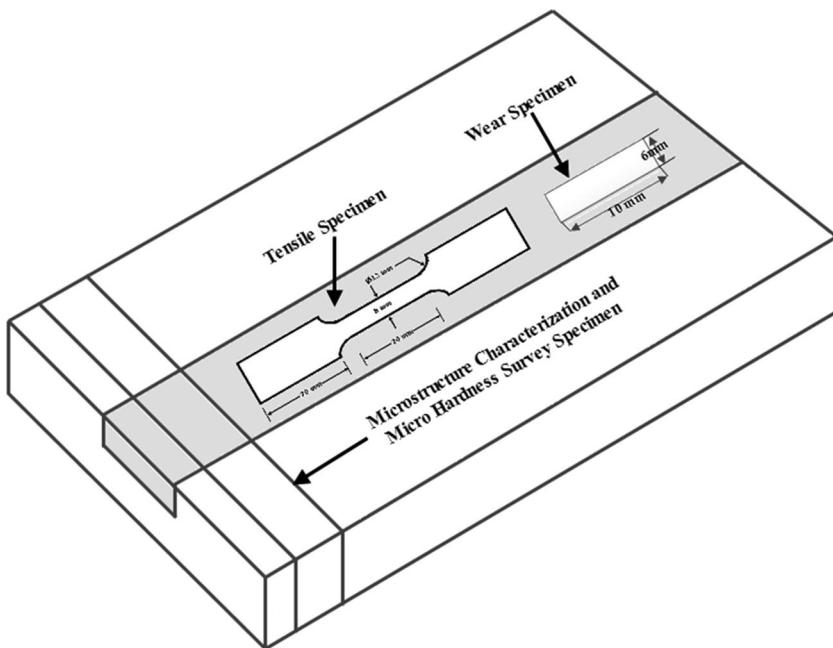


**Figure 5.** Schematic representation of FSP technique: (a) copper plate of appropriate dimensions is taken and WEDM groove is plowed in the middle of the plate, (b) hybrid reinforcement is stowed into the groove, (c) initial processing to avoid scattering of the powders during FSP, and (d) final stirring process.

to a variation in the hardness value and henceforth a survey over the hardness was performed. Vickers microhardness maps for the developed surface composites were generated based on a polished cross section cut perpendicular to the processing direction at a load of 50 g for 15 s. Mechanical strength of developed copper surface composites was investigated through an Instron electronic tensile machine with a strain

rate condition of  $10^{-5} \text{ s}^{-1}$  at ambient temperature condition. Fractured surface of the failed copper surface composites were examined through SEM to study the mechanism behind the failure.

Tribological characteristics of the developed set of copper surface composites were evaluated through dry sliding technique using a pin on disc apparatus at room temperature.



**Figure 6.** Schematic representation of different testing specimens.

Rectangular pin specimens of dimensions  $6 \times 6 \times 10$  mm as shown in Fig. 6 was cut using WEDM from the center of the FSPed zone of the developed copper surface composites samples and the same was ground on emery sheets to avoid the debris and irregularities on surface. The rotating counterpart disc were made of hardened chromium steel and the tests were performed in dry sliding condition for a constant sliding distance of 1000 m at a sliding velocity of 2 m/s. Load exerted by the pin on the rotating counterpart disc is kept to be of a constant value at 30 N. The pins after the wear test were cleansed with acetone solution and weighed to evaluate the weight loss in a weighing balance to an accuracy of  $\pm 0.01$  mg. The frictional coefficient value between the pin and rotating counterpart disk plotted against the sliding distance is evaluated by acquiring the frictional force through WINDUCOM 2010 system software. The wear mechanism of the developed surface composites were studied based on the SEM morphology of worn out surfaces.

Electrochemical characterization of developed copper surface composites was performed after polishing the specimens as per standards. Copper surface composites were considered as the working electrode of the electrochemical cell; platinum counter electrode and a calomel reference electrode were also used along with it. 3.5% NaCl electrolyte solution was used as the corrosion medium so as to study the corrosive behavior of developed specimens. Potentiodynamic polarization of developed copper surface composites was conducted thrice for results confirmation and based on the attained Tafel plot, corrosion rate was evaluated.

## Results and Discussion

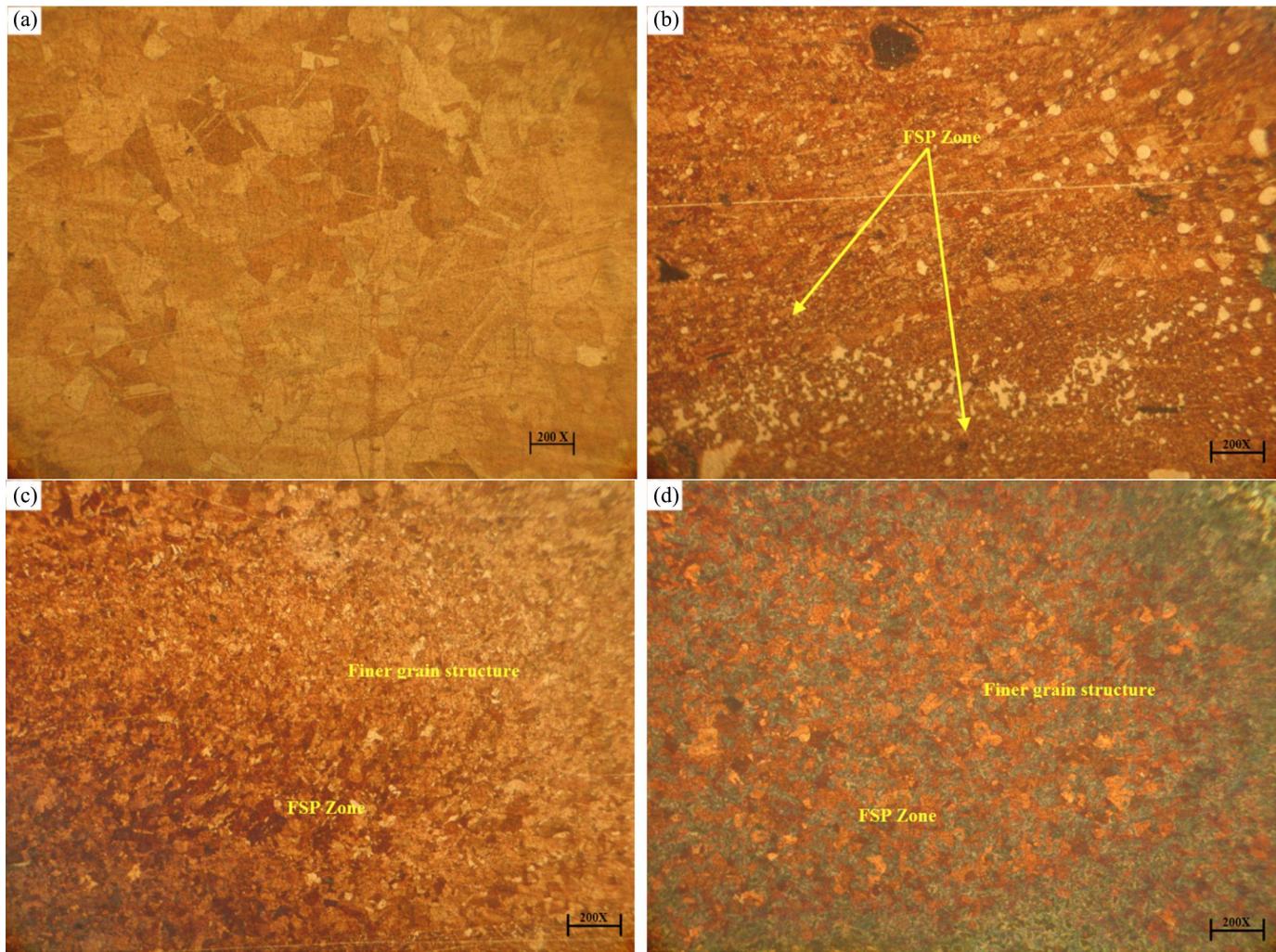
Optical microscopy of copper and the processed samples with 5, 10, and 15 vol% of hybrid composites (50% AlN + 50% BN) are shown in Fig. 7 in which 7a illustrates optical micrograph of pure copper while 7(b-d) exemplifies optical micrographs of FSPed copper surface composites with varying reinforcement percentages. Optical micrograph demonstrates significant differences in grain size and its structure between unprocessed copper and FSPed copper composites. A tremendous decrease in size of grain size can be observed when compared with unprocessed copper samples and the same can be attributed to the rigorous stirring of FSP tool. FSP route generates high temperature as a function of friction created between copper and FSP tool plastically deforming work piece and a stirring action through FSP pin in the semi molten work piece breaks down grain size to a smaller size. Grains of unprocessed copper metal exhibits coarse size with annealing twins present in it, while surface composites reinforced with hybrid reinforcement particles demonstrates recrystallized fine grains with nil existence of annealing twins. Phenomenon of dynamic recrystallization occurs as a function of FSP creating new nucleation sites resulting in smaller grain size. Furthermore, dispersion of hybrid particles into copper matrix which includes AlN and BN particles in equal weight proportion also helps in reducing grain size of the surface composites to a large extent. This mechanism of grain size reduction with particle dispersion is a result increased privileged sites for initiating recrystallization.

As per Zener-Hollomon strictures in MMCs, decrement in reinforcement particle's size reduces grain size of the matrix and the same can also be considered as an interpretation of grain size; as sizes of AlN and BN particles varies wherein BN has minimal grain radii which gets dispersed into copper matrix thereby reducing grain size again. Minimal size of BN particles increases the quantity of particles that owe to be dispersed onto surface which also restricts grain size growth to a larger extent.

Microstructural evaluation through SEM shows the dispersion of particles into copper matrix as portrayed in Fig. 8. SEM images describes the dispersion of hybrid reinforcement onto copper matrix and the inter distance between particles was found to be decreasing with respect to increase in volume fraction. Uniformity of particles along the matrix can be observed through SEM images and increase in particles can be notified with respect to increase in volume fraction. In refer to the SEM micrographs a good bonding between reinforcement particles and copper matrix was observed which is inferring to severe plastic deformation caused as a function of vigorous stirring action offered by FSP tool and the same can also be accounted to the irregularities of dispersed hybrid reinforcement particles. A clean interface is observed between reinforcement particles and matrix material without voids that explains good bonding formed in the developed surface composites. This clear interface with nil voids and reaction products may enhance the micro hardness and wear properties of the developed copper surface composites which can be attributed to stirring action and ample material flow.

Microhardness values in terms of Vickers hardness on the cross-sectional specimen of FSPed copper surface composites is as shown in Fig. 9 through which an easy identification of increase in hardness value on the FSP zone can be observed. A variation in microhardness value is observed in stir zone as a result of uniform dispersion of hybrid reinforcement and any unusual increase in hardness value can't be observed which clearly exemplifies that agglomeration of particles through the measured area is nil. The same characteristics can be achieved for the whole surface for the optimized set of traverse feed and tool rotation speed.

From microhardness mapping of the developed copper surface composite reinforced hybrid reinforcement particles, an enhanced hardness for surface is observed in FSP stir zone which can be attributed to many mechanisms of FSP route along with the uniform dispersion of advanced ceramic particles including AlN and BN. The presence of fine ceramic particles such as AlN and BN in copper matrix inhibits the growth of grain boundary thereby reducing the grain size of the developed set of composites, in turn increasing hardness of the composite material. Yet again the thermal behavior of copper matrix, AlN and BN particles are differential in nature which leads to a quench hardening effect and also the strain misfit between the particles and copper matrix leads to work hardening of the developed composite material. This quench and work hardening effects on the stir zone together accounts for a tremendous increase in microhardness of the developed set of surface composites. FSP route initiates a vigorous plastic deformation and thus breaking down the grain size leading to



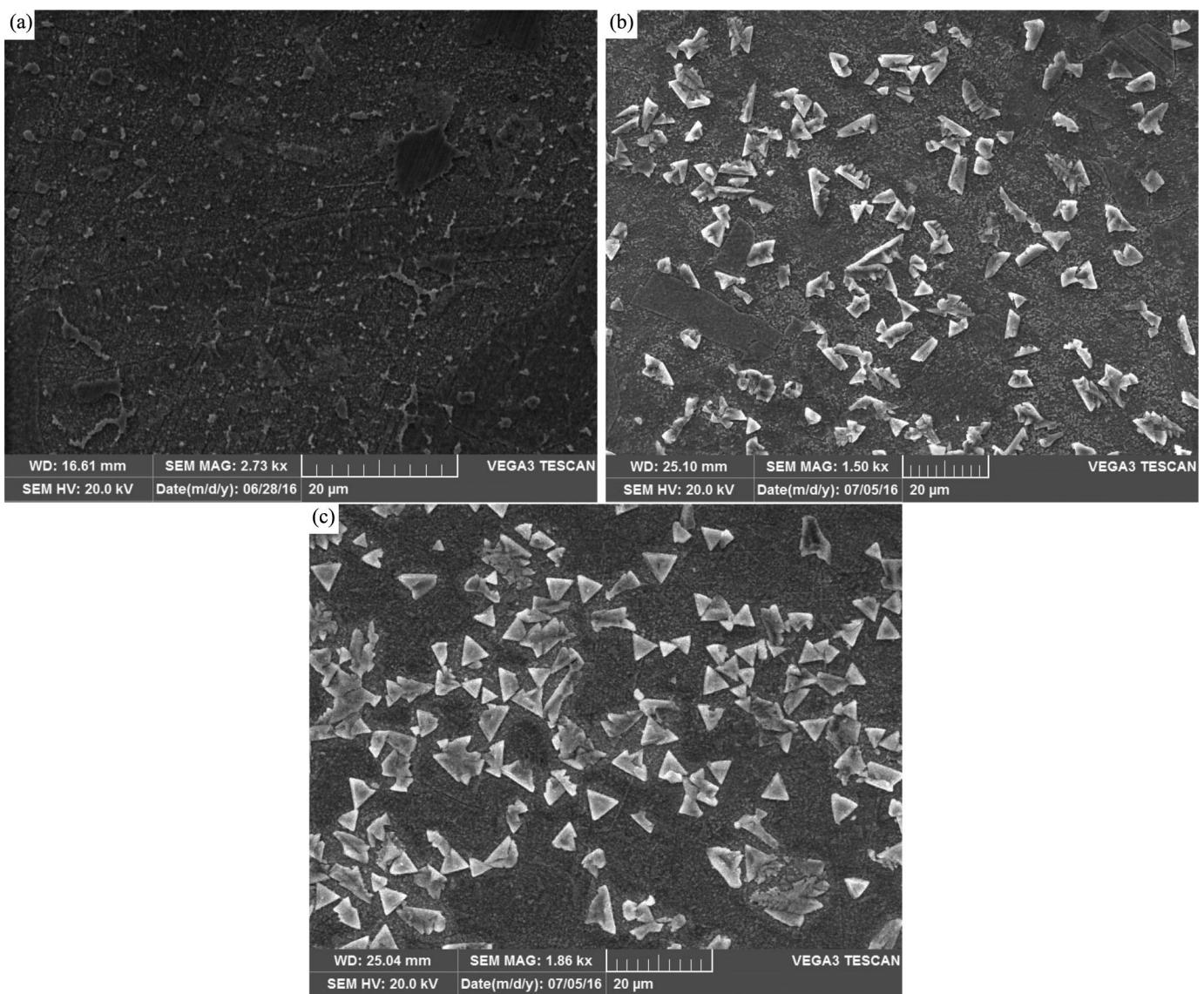
**Figure 7.** Optical micrographs of (a) reference copper metal, (b) Cu+ 5% hybrid reinforcement, (c) Cu+ 10% hybrid reinforcement, and (d) Cu+ 15% hybrid reinforcement.

dynamic recrystallization. This phenomenon of grain size reduction increases the hardness of the developed copper surface composite and the same is well established as Hall-Petch relationship.<sup>[28]</sup>

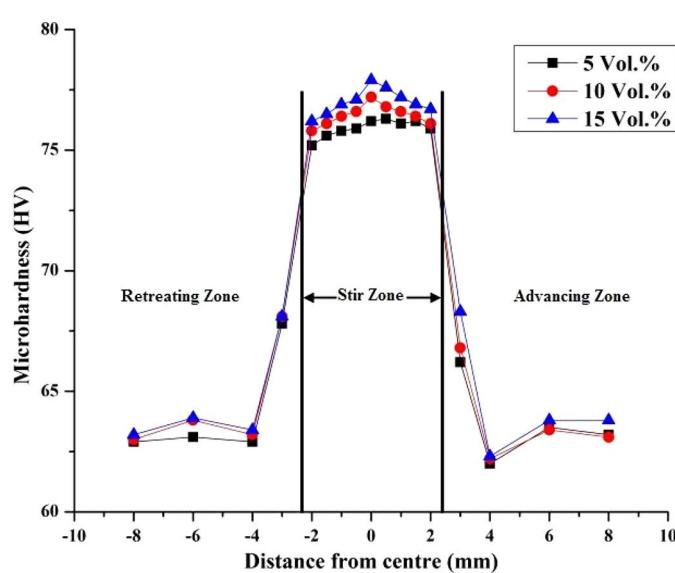
Copper surface composites with varying vol% of hybrid composite as reinforcement was prepared under an optimized traverse feed of 30 mm and tool rotation speed of 1000 rpm, the same was tested for tensile properties includes ultimate tensile strength (UTS), yield strength (YS), and percentage elongation (% E). Tensile properties of the developed copper surface composites tested under a strain rate of  $10^{-5} \text{ s}^{-1}$  is as provided in Table 1 in which the tensile properties of surface composites tend to increase with introduction of reinforcement particles and ductility triggers a negative trend. Strength of the material is governed by many metallurgical parameters along with manufacturing aspects and in this research the metallurgical aspects that has to be considered includes grain size reduction, dislocation density and bonding that exists between reinforcement particle and matrix materials. From results a clear view of tensile behavior express a reduction in strength value by reinforcement particles introduction when compared with as received copper and the same can be explained with

crack initiation mechanism as the susceptibility of crack development at the interaction point between reinforcement particles and copper matrix with dispersion of hybrid reinforcement. Yet again an increase in tensile strength was notified with increase in the varying vol% of hybrid reinforcement particles that gets dispersed onto the copper matrix. This conflicting result of increase in strength with introduction in varying vol% of reinforcement particles can be well attributed to the mechanism of grain size reduction with particle dispersion. In spite of this the varying size of particles both AlN and BN leads to a reduced grain structure formation hindering the growth of grain boundaries which thereby increase the strength of developed copper based surface composites.

Over again an increase in yield strength is notified with increase in particle volume introduction which can be well endorsed to an increased hardness property of the developed surface composite material beside with its grain size diminution. Ductility of developed copper surface composites tends to decrease with introduction of hybrid reinforcement particles as dislocation movement of the material gets decreased with AlN and BN particle presence.



**Figure 8.** SEM micrographs of (a) Cu+ 5% hybrid reinforcement, (b) Cu+ 10% hybrid reinforcement, and (c) Cu+ 15% hybrid reinforcement.

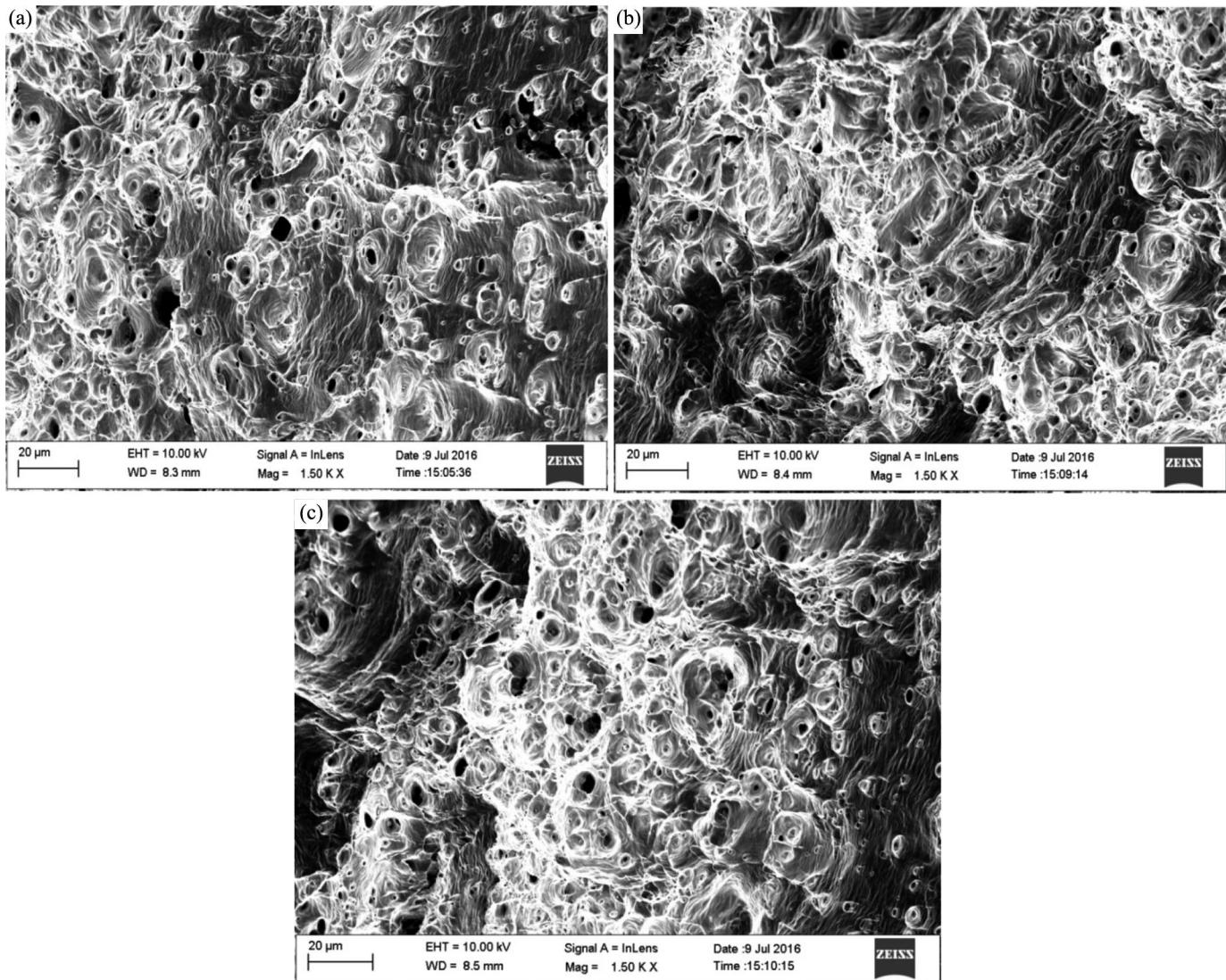


**Figure 9.** Microhardness mapping results.

Fractographs for fractured surfaces of tensile specimens are shown in Fig. 10, which portrays fracture surface of surface composites with 5 vol% of hybrid composite and the failure described a ductile manner in which pimples and dimples of uneven size and distribution can be observed. These formations of dimples are resultants of nucleation, growth, and coalescence of micro voids that are formed due to the presence of AlN and BN particles as cracks initiates and propagate at the matrix reinforcement interfaces in the case of composite materials. SEM images notify that with introduction of these hybrid particles, the pimples and dimples reduce and a clear state of surface is distinguished presenting

**Table 1.** Tensile properties of copper base and surface composites.

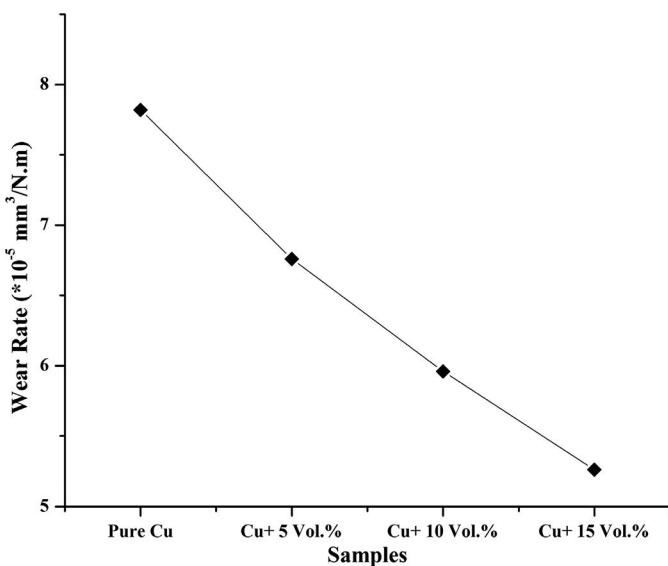
Samples	UTS (MPa)	YS (MPa)	% El
Copper as received	218	125	19.4
Cu with 5 vol% hybrid reinforcement	172.6	98.3	10.15
Cu with 10 vol% hybrid reinforcement	179.4	100.5	8.93
Cu with 15 vol% hybrid reinforcement	183	104.5	7.22



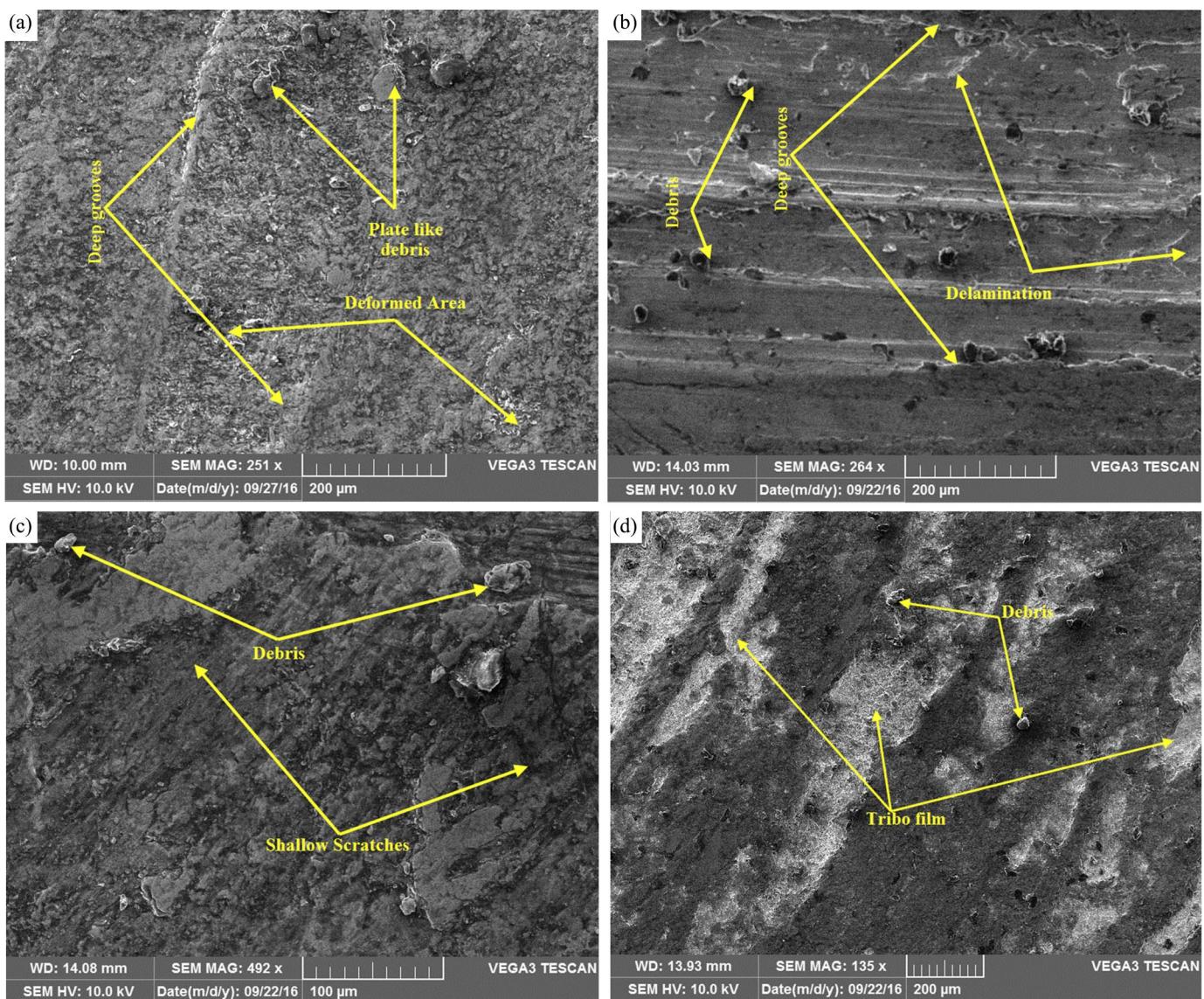
**Figure 10.** SEM micrographs of fractured surface of (a) Cu+ 5% hybrid reinforcement, (b) Cu+ 10% hybrid reinforcement, and (c) Cu+ 15% hybrid reinforcement.

the brittle nature of the developed set of composites. Figure 10c shares the knowledge that ductility of the developed copper surface composites reduced to a great extent with particle introduction as fracture surface is devoid of these dimples to a large extent.

Dry sliding wear rate of the developed surface composites was evaluated through a pin on disc apparatus and the same was compared with as received copper to appraise the effectiveness of hybrid reinforcement particles and friction stir processing after effects. Wear rate of developed copper surface composites decreased with increase in introduction of advanced ceramics AlN and BN particles which is as shown in Fig. 11. Reinforcement of hybrid particles into copper matrix upholds the wear exerted and thereby avoids the direct contact of copper matrix and rotating counter disc. Again these particles inhibit the growth of grain size and at the same time increase the hardness of developed surface composites. According to Archard, hardness of a material inversely affects its wear rate property as with increase in hardness value of a material the wear rate of the same shows a decrement. So with introduction of these hybrid reinforcements, hardness of the



**Figure 11.** Wear rate values for pure copper and its surface composites.



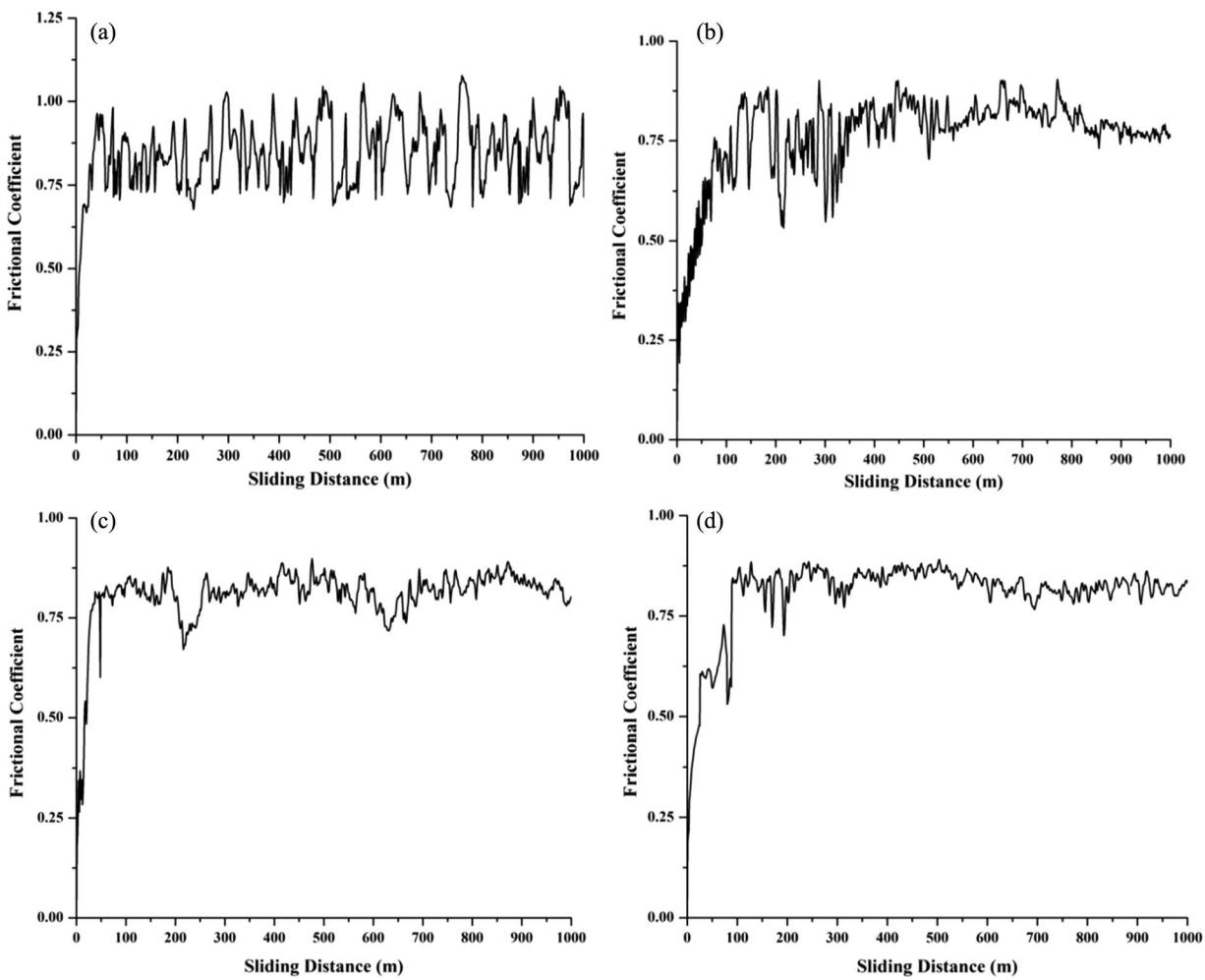
**Figure 12.** Wear surfaces morphology of (a) reference copper metal, (b) Cu+ 5% hybrid reinforcement, (c) Cu+ 10% hybrid reinforcement, and (d) Cu+ 15% hybrid reinforcement.

copper surface composites increases thereby reducing the wear rate value. BN particles, a self-lubricating kind of material when dispersed into copper matrix provides a self-lubricating effect to the developed surface composites when forced to undergo through wear effect. This self-lubricating effect of BN particles dispersed creates a tribolayer over the surface reducing wear rate of the developed surface composite. Copper being a ductile material undergoes severe plastic deformation during wear test as the matrix material softens as a result of high temperature created due to sliding over the counter disc. Softening of the matrix material leads to locally welding of copper matrix on disc counterpart and with further sliding large material removal takes place increasing the wear rate of the material. This phenomenon of material removal is termed as adhesive wear mechanism and the same can be observed in Fig. 12a.

With introduction of hybrid particles onto the copper surface, the ductility of developed surface composite decreases

reducing adhesive wear to a great extent which thereby reduces wear rate values. The same can be observed from SEM micrographs 12(b–c) that with introduction of hybrid particles, plastic deformation based grooves tends to get reduced henceforth declaring a reduction in wear rate of developed surface composites. A tribolayer formation can be observed for 15 vol% hybrid reinforcement dispersed sample which may be an after effect of BN presence, a well-considered self-lubricating material.

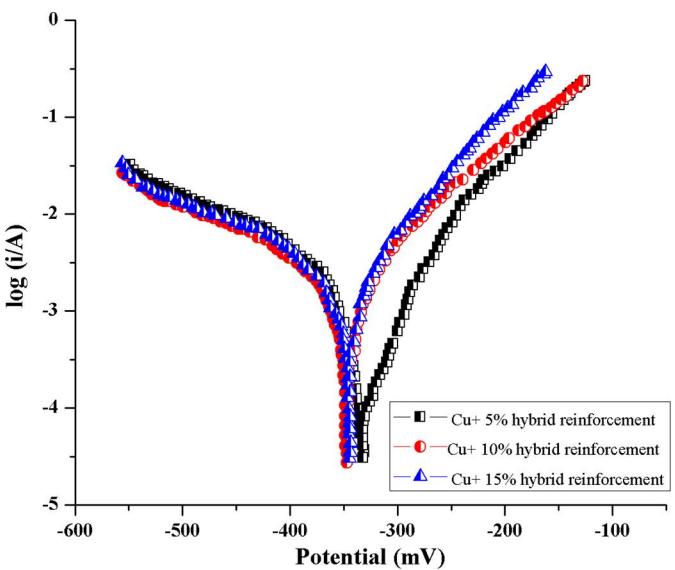
Frictional coefficient variation of pure copper and its surface composites for a sliding distance of 1000 m are as shown in Fig. 13 through which it can be stated that a high fluctuation of frictional coefficient value is notified. This large fluctuation in frictional coefficient value for copper reference material can be attributed for the intensive cohesive action that exists between copper and rotating counterpart during the sliding action. With introduction of hybrid reinforcement particles fluctuation on frictional coefficient



**Figure 13.** Variation of friction coefficient with sliding distance for (a) reference copper metal, (b) Cu+ 5% hybrid reinforcement, (c) Cu+ 10% hybrid reinforcement, and (d) Cu+ 15% hybrid reinforcement.

value tends to decrease as cohesive action that takes place between ductile copper matrix and rotating counterpart decrease. With sliding, hybrid reinforcement particles get exposed to the rotating counterpart thereby reducing actual contact area of the matrix material and steel disc thereby reducing the cohesive behavior and in turn the frictional fluctuation. Reduction of fluctuation while considering surface composites can yet again be attributed for the presence of BN particles which creates a lubricating layer thereby reducing friction created between composite specimens and rotating counterpart. Average frictional coefficient value of surface composites exposed an increased value when compared with reference copper metal. This phenomenon of increase in frictional coefficient value can be stated as an end effect of friction created due to the presence of hybrid particles that gets exposed to the disc during sliding procedure and offers a high resistance toward surface sliding.

In saline conditions (3.5 wt% NaCl), corrosion reaction of copper metal takes place mainly through cathodic and anodic reactions. Evolution of hydrogen ions or the formation of passive oxide layer takes place during cathodic reaction, while metal dissolution or ion formation takes place during anodic

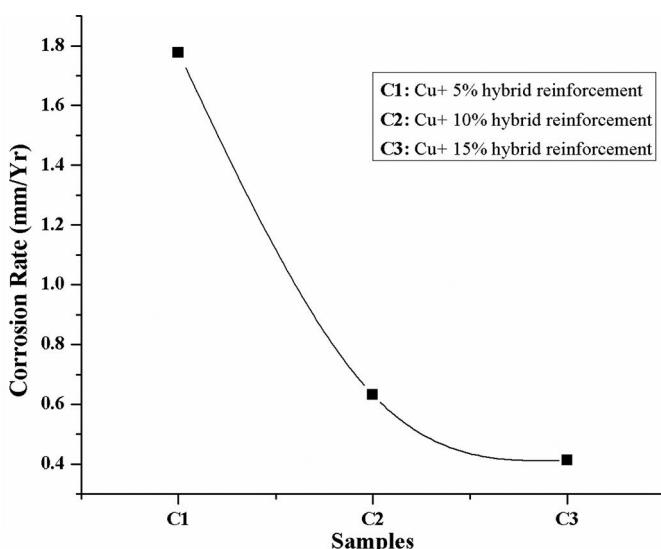


**Figure 14.** Tafel plots for copper surface composite reinforced with hybrid reinforcement particles at varying fractions.

reaction. Pure copper forms copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) layer over the surface of copper substrate reducing the contact area between the substrate and electrolyte, which inhibits the flow of metal ions from copper substrate to corrosive electrolyte by creating an protective barrier. Formation of these oxide layer decrease the corrosion current density by diminishing the flow to ion and it is a known fact that corrosion current density is directly proportional to corrosion rate. Hence decrement in corrosion current density improves the corrosion resistance of copper metal substrate. During corrosion reaction, copper ion formations takes place as an after effect of anodic reaction. These copper ions react with chlorine ions present in saline electrolyte and form cuprous chloride as the corrosion product. Formation of copper ions results in corrosion current density increment thus decreasing the corrosion resistance of copper substrate.

Tafel plot, attained from the electrochemical studies is effectively used to analyze the corrosive behavior of the test samples and the attained results for the developed copper surface composites are as provided in Fig. 14. In this plots, shifting of corrosion potential toward anodic region implies the occurrence of anodic reactions while shifting of potential toward cathodic region resembles the occurrence of cathodic reaction. The corrosion potential in the attained polarization curves for the developed surface composites demonstrated a positive side shift with respect to increase in reinforcement addition confirming the occurrence of anodic reaction. It can be observed from Fig. 15, that the corrosion rate of the developed copper surface composites exhibits a declining trend with respect to increase in hybrid reinforcement additions. This reduction in corrosion rate with respect to particle dispersion can be attributed for the (i) grain size reduction that takes place during FSP and (ii) the presence of hybrid reinforcement particles viz. AlN and BN particles, which inhibits the corrosion rate of developed composite.

During FSP, the grain size of the developed copper surface composites reduces significantly increasing the grain boundary



**Figure 15.** Corrosion rate of the developed copper surface composites reinforced with varying fractions of hybrid reinforcement particles.

region which helps in resisting the dissolution of the matrix metal. The presence of AlN and BN particles as reinforcement also improves the corrosion resistance of the developed copper surface composites in a positive trend.

Aluminum and nitrogen atoms are the major constituent of AlN particle. When these particles come in contact with aqueous electrolyte it form alumina or aluminum di oxide ( $\text{Al}_2\text{O}_3$ ) which is a well-known corrosive resistance ceramic particle. When these hybrid copper surface composites is immersed in electrolyte, the presence of aluminum in AlN particle tends to form a passive alumina layer over the composite surface which inhibits the flow of electron by avoiding the substrate to electrolyte contact. Likewise presence of nitride ions increases the resistance of metal again pitting corrosion. During electrochemical reaction, these nitrogen ions dissolve in corrosive electrolyte and forms  $\text{NH}_4^+$  which diminishes the pit formation that occurs due to the oxidation of metal surface thereby restricting the degrading of the material. BN particles being an insulating material prohibit the electron transport during electrochemical reactions which inhibits the corrosion current density thereby protecting the material from degrading. Thus it can be concluded that the dispersion of hybrid reinforcement particles onto the surface of copper matrix through FSP can increase the corrosion resistance of developed copper surface composites.

## Conclusion

Copper-based surface composites reinforced with hybrid composite particles which enfolds AlN and BN particles in equal proportion was fabricated successfully through friction stir processing method. Results deduced from experiments are as follows:

1. Microstructural characterization of FSPed copper surface composite with varying vol% of hybrid composites exhibited a superior dispersion of hybrid particles and a good bonding between matrix material and reinforcement particles were observed with a clear interface.
2. FSP route on the copper surface refined the size of grains and dispersion of hybrid reinforcement particles enclosing AlN and BN particles of equal proportion reduced the grain size further more.
3. Dispersion of hybrid reinforcement through FSP route onto the surface of copper matrix induced increase in hardness value in awe to distribution of AlN, BN particles along with dynamic recrystallization.
4. Enhancement in ultimate and yield strength of the developed surface composites was observed with respect to an increase in particle introduction, while ductility of the same showcased a negative trend.
5. Wear rate resistance improvisation was demonstrated by copper surface composites with increase in introduction of hybrid reinforcement particles and the worn out surfaces proved a reduction in adhesion wear mechanism. Average friction coefficient values tend to increase as AlN particles offers high resistance to surface sliding.
6. Corrosion resistance of the developed copper surface composites demonstrates an increasing trend with respect to dispersion of hybrid reinforcement particles.

The presence of AlN particles develops an oxide layer which reduces the corrosion rate while BN particles inhibits the conduction of current thereby reducing the corrosion rate of the developed surface composites.

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