Effect of exfoliated MoS2 on the Microstructure, Hardness, and Tribological properties of Copper matrix nanocomposite via hot pressing method

Hossam Mohamed (hossamelkeber@techedu.helwan.edu.eg)
Helwan University https://orcid.org/0000-0003-2571-1741
Ehab Abd-Elhameed
Ahmed I. Ali

Research Article

Keywords: Copper, molybdenum disulfide, Hot compaction, Hardness, wear rate, friction coefficient

Posted Date: March 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1409570/v1

Abstract

This study aims to exfoliate the molybdenum disulfide to flakes and use it in strengthening copper matrix to reduce the rate of mechanical wear and reduce the coefficient of friction, consequently increasing the life of copper composites that are used as self-lubricating bushings. Three samples by mixing for 15 hrs were prepared: pure copper, copper with 10% alumina, and copper with a mixture of alumina and molybdenum disulfide in a ratio of 1:1 (Cu, Cu/10 Al_2O_3, and Cu/ hybrid (10 Al_2O_3-10 MoS_2)). Before adding the hybrid of alumina/MoS_2 with copper, they were mixed for 40 hrs to peel the molybdenum disulfide and cover the alumina particles with it. The Hot-pressing method was used to manufacture prepared samples. The crystal structure of the compositions, microstructure, density, and Raman spectra have been studied. Mechanical properties, including hardness, mechanical wear rate, and coefficient of friction, were investigated for the fabricated pieces. The mixing for 15 hrs improves the exfoliation of the MoS_2 flakes inside the copper matrix. The hardness measurements showed a clear improvement by adding alumina and the mixture of alumina/MoS_2. The copper sample reinforced with the hybrid of alumina/MoS_2 gave the lowest mechanical wear rate and the lowest average friction coefficient of 0.17.

1. Introduction

The loss of energy due to friction associated with the movement of mechanical assembly parts (MMAP) is a fundamental problem in industrial applications. The problem is not only related to the presence of friction but also to the occurrence of mechanical wear, which reduces the service time for the used parts and the need to replace them, and thus the consumption and loss of time for business owners. The primary energy loss due to friction has been estimated to be 30%, and the corresponding financial loss has been evaluated to be in billions [1]. For this reason, we thought of producing self-lubricating materials resisting repeated mechanical loss of parts that results from insufficient lubrication, especially in harsh friction conditions that lubricating fluids are not suitable for it. In order to produce self-lubricating materials, metallic, ceramic, or plastic matrix materials have been used. The most common metallic materials used in this application are copper, silver, gold, lead, tin, and platinum. Since copper has high flexibility that makes it easy to form and has high thermal conductivity, it is widely used in such applications. Nevertheless, copper suffers from poor mechanical wear resistance. Copper matrix composites reinforced with solid lubricants such as graphite, MoS_2, WS_2 have been widely used as self-lubricating in many applications such as bearings and bushings for their low friction coefficient and high wear-resistant properties [2–6]. Molybdenum disulfide is a solid lubricant material. It is similar in its structure to graphite, as it consists of flakes whose atoms Mo and S are linked with a covalent bond, which indicates the strength of the contact between them, as is the case in graphene layers. The MoS_2 can provide lubrication for moving parts such as graphite, especially in a vacuum and dry gas environment. It has a lamellar structure such as graphite formed by many stacked layers. Each MoS_2 layer is composed of a plane of molybdenum embedded between two planes of sulfur atoms by the covalent bonds. Therefore, the strength of every single layer is high as graphene [7–8]. Some studies on copper metal matrix composites strengthened with MoS_2 were performed to improve its tribological performance. Reinforcing the copper matrix with 10 wt% MoS_2 increased the hardness to 89HV with a 32.83% increment. The wear rate dramatically decreased from 0.04 to 0.02 g, and the coefficient of friction reduced to 0.32 µm [9]. Jin-Kun Xiao *et al.* [10] investigated the tribological behavior of Cu- MoS_2 composites. The results confirmed that MoS_2 addition was an effective lubricant for copper matrix composites against steel. The friction coefficient decreased from 0.67 to 0.18 when 20 vol% of the MoS_2 was added. The wear rate of the composites tended to increase at low percentages then reduced as the MoS_2 content increased. Researchers have been tried to improve the properties of the copper-based self-lubricating materials by reinforcing them with ceramic materials such as Al_2O_3, TiC, WC or SiC [11–16]. The presence of ceramic particles in the matrix (bushings) leads to destroying the surface of the shaft (the protected parts) through scratching it. The authors suggested coating the ceramic particles with MoS_2 layers to solve the mentioned problem. Coating the alumina particles by the molybdenum disulfide flakes will cover the sharp edges and reduce their surface roughness and, consequently, the coefficient of friction and mechanical wear. From the authors' point of view, this will improve the strength and resistance of the materials to erosion and thus increase their service life. In addition, maintaining the essential parts required to be protected from mechanical wear (shaft or machine frame).

In this paper author aimed to take advantage of molybdenum disulfide flakes in strengthening copper composites to reduce both the rate of mechanical wear and the coefficient of friction. Farther increase the life of copper composites that are used as self-lubricating bushings. The effect of coating alumina particles with layers of molybdenum disulfide on the microstructure, densification, hardness, mechanical wear, and coefficient of friction of the copper matrix have been studied for applications of self-lubricating applications.

2. Materials And Methods

In this study, the as-received molybdenum disulfide powder (MoS_2) of the 1-0.5µm particles size supplied by the DOP ORGANİK KİMYA SAN.VE TİC. LTD ŞTİ, the nano-Al_2O_3 powder with the particle size of 200–500 nm (Hart Minerals), and the copper powder of 1–3 µm (OXFORD Laboratory Reagent; India), were used to fabricate copper matrix nanocomposite for lubricant applications. A die with an inner diameter of 16 mm and 60 mm high fabricated from W320 alloy steel was used for the hot forming process. The outside diameter of the used die was 50 mm.

The Al_2O_3 and MoS_2 with a 1:1 ratio were mixed for 40 hrs to exfoliate the MoS_2 layers and coat the Al_2O_3 particles. *Three copper nanocomposites*: Cu, Cu/10 Al_2O_3, and Cu/ hybrid (10 Al_2O_3-10 MoS_2), were prepared by mechanical alloy milling for 15 hrs. The prepared nanocomposites were cold pressed at 1000 MPa, then heated to 750 ^{o}C for 35 min; after that, hot-pressed at 1000 MPa.

3. Characterizations

The morphology of the fabricated samples has been investigated using Field emission scanning electron microscopy (FE-SEM) (EBS, model Quanta FEG250), The structure of the samples has been investigated using x-ray diffraction. The pattern of X-ray diffraction was measured via the diffractometer (Bruker: D8) through (CuK_{α}; λ ~ 1.540 Å); employed at ~ 40 mA/42 kV. The X-rays were completed through an angular range from 2θ = 10° to 80°. The density of the samples under study have been measured using the Archimedes' route according to MPIF standards 42, 1998. The hardness of the three samples was studied by the Vickers tester (NEMESIS 9100 at 3 kg for 10 sec). The wear rate by the pin on a ring test rig at 2.6 m/sec for 10 min loading time, and different loads (40 and 50N), and coefficient of friction were evaluated.

3. Result And Discussion

3.1 Raman analysis of hybrid (10 Al_2O_3-10 MoS_2) powder

In this study, the number of exfoliated MoS_2 due to the mechanical alloy milling with alumina with a 1:1 ratio was investigated by the Raman analysis, as shown in Fig. 1a. The number of layers have been determined from a distance between two fingerprint peaks (observed at ~ 383 cm^{-1} and ~ 408 cm^{-1} in bulk MoS_2 [17]). With the increasing number of single layers, the mode at ~ 383 cm^{-1} shifts to lower frequencies, and the mode at ~ 408 cm^{-1} changes to higher frequencies (Fig. 1b). The analysis shows that the peaks of the MoS_2 are detected at 378 and 403 cm^{-1} which means an incomplete conversion of MoS_2 to nano-layers at the mentioned weight percentages. No peaks for the Molybdenum trioxides MoO_3 were detected at 820 cm^{-1} according to the reference in Fig. 1c [18], indicating no transition of MoS_2 to MoO_3. In addition to molybdenum peaks, alumina peaks were also discovered.

3.2 X-ray diffraction

The crystal structure of the hot compacted copper nanocomposites was examined by the x-ray analysis, as shown in Fig. 2. In the frits sample, copper and copper oxide of the cubic crystal structures have been detected. The copper oxide peaks does not appear which means the structure is single phase. By adding 10 wt% $Al_2O_{3,}$ the crystal structures transited to tetragonal phase (second sample). One can notes here, the peak of the copper oxide is detectable. While the copper oxide peak was reduced in the third sample due to coating Al_2O_3 particles by the MoS_2 layers. The Molybdenum trioxides MoO_2 was found, which may be formed due to exposing the MoS_2 layers to heat during the production process. The Molybdenum disulfide (MoS_2) and molybdenum trioxide were studied using Raman spectroscopy [18]. Transformation of MoS_2 to MoO_3 has been detected due to the laser intensity effects. The transformation to molybdenum trioxide was interpreted as a function of temperature and atmosphere, revealing an apparent transformation at 375 K in the presence of oxygen. A reduction in the copper peak intensities and an increase in the peaks broadening were detected. Increasing the peak broadening indicates decreasing the copper particles' size due to the mechanical milling for 15 hrs.

3.3 Densification

Figure 3 represents the relative density of the copper matrix nanocomposites. Under the mentioned fabrication condition, the pure copper sample achieved 92.5% relative density. The application of high pressure on cold and hot increased the adhesion between copper particles, which led to the absence of voids, thus achieving a high density of 92.5% at a low temperature of 750 ^{o}C. Because alumina has a low density of 3.95 g/cm^3 compared to copper 8.9 g/cm^3, its addition led to a more down in the density of the copper. The third sample had the same behavior as sample 2. The density of the hybrid $10Al_2O_3$ + $10MoS_2$ (4.505 g/cm^3) is less than the density of copper 8.9 g/cm^3, which led to a decrease in the density of the new compound in general. This reduction can be explained by the fact that the particles of the lighter materials replace the particles of the higher density materials, which leads to a decrease in the density completely. Another factor that could explain the reduction in density of the copper matrix is the formation of pores between the base metal and the supporting material. Also, the formation of oxides CuO and MoO_2 detected from the x-ray analysis may affect the matrix density, as it has a density less than that of the pure metal.

3.4 Microstructure

Figure 4 shows the morphology of the fabricated Cu, Cu/10 Al_2O_3, and Cu/ (10 Al_2O_3-10 MoS_2) nanocomposites. The pure copper sample shows complete diffusion between some particles of copper. A black areas on the grain boundaries represent the copper oxide was formed, which may be due to perform the hot forming process in un-controlled atmosphere. Due to adding 10 wt% alumina to the second sample and milling for 15 hrs, a refining of copper particles is observed. The particles refining may also due to the applying pressure before and after heating. According to the microstructure, this process can be classified under severe plastic deformation processes. The black areas that represent the copper oxide is increased due to the reaction between copper and alumina. The third sample showed high diffusivity of molybdenum flakes with the copper matrix. The microstructure proven the separation of molybdenum in the form of flakes. The MoS_2 layers in the last image d appeared transparent and takes the horizontal position.

3.5 Hardness

The effects of 10 nano-Al_2O_3 and hybrid (10 Al_2O_3-10 MoS_2) on the hardness of the copper matrix are shown in Fig. 5. The copper matrix recorded 96.1 HV, nearly equal to the common value of copper 100 HV. Reinforcing the copper with 10 wt% nano-Al_2O_3 increased the hardness to 150.47 HV, Which is equivalent to a 56.5% improvement in the hardness of pure copper. The high hardness of alumina and reasonable distribution of it with the copper matrix are the main reasons for achieving this improvement. Also, applying the pressure before and after heating had a significant effect, where it reduced the particles size under high shearing processes and increased the adhesion between inter-particles. Adding the MoS_2 to the Al_2O_3 by 1:1 ratio and mixing them with copper by the mechanical alloy milling for 15 hrs participated in Peeling MoS_2 into flakes as shown in the microstructure in the last image (d). Due to exfoliating MoS_2

into layers, the third sample recorded 175.45 HV, which is equivalent to an increase in the hardness by 16.6% compared to the Cu/10 Al_2O_3 sample, and by the rise of 82.57% compared to the pure copper sample.

3.6 Wear rate

The wear rate of the hot-pressed copper nanocomposites at 40 and 50N for 10min is shown in Fig. 6. The results show that the wear rate was decreased by reinforcing the copper matrix with 10 wt% nano-Al_2O_3 and hybrid (10 Al_2O_3-10 MoS_2), respectively. Adding 10 wt% Al_2O_3 to the copper matrix reduced the wear rate by 52.72% and 80.9% when the hybrid was added. The presence of MoS_2 layers with the copper matrix and its accumulation on the surface of the disc during contact with the pin facilitate the pin sliding and consequently reduce the wear rate. Also, increasing the strength of the fabricated copper material due to reducing the particles size during forming processes and the separation of MoS_2 into layers were participated in reducing the wear rate. The wear behavior of copper matrix composites was evaluated to determine the optimal additive content of MoS_2 with copper [19]. 40 vol% of MoS_2 was added in the step of 10. Due to the formation of a continuous lubricating film on the worn surface of composites contain MoS_2 above 20 vol% a decrease in the wear rate was observed. On the other hand, the wear rate was increased by increasing the load due to increasing the contact area between the pin and disc.

3.7 COF

Figure 7 shows the friction coefficient of Cu, Cu/10Al_2O_3, and Cu/ (10Al_2O_3 -10MoS_2) nanocomposites under 50N applied load. The COF curves of Cu composites are shown in Fig. 7a. It can be observed that pure copper exhibits a significantly high COF with an extensive range of inconstancy with increasing time. Integrating Al_2O_3 and hybrid (Al_2O_3-MoS_2) with the copper matrix effectively decreases the COF. The COF curves were dropped and became more stable with the addition of 10 wt% nano-Al_2O_3 and combination (10Al_2O_3-10MoS_2), respectively. The high and oscillate COF of pure copper may be due to the severe adhesion and strain hardening of pure copper at the surface of the contacting pairs. The reduction in COF may be related to the accumulation of the MoS_2 layer on the sliding surface, which acts as a solid lubricant and consequently prevents direct contact between the frictional surfaces. The variation of average COF versus the Cu, Cu/10Al_2O_3, and Cu/ (10Al_2O_3-10MoS_2) is plotted in Fig. 7b. The average COF was decreased by adding alumina and molybdenum disulfide to the copper matrix. The COF starts at 0.2318 for the pure copper and then dramatically reduces by adding alumina to 0.2059. The addition of hybrid (10Al_2O_3-10MoS_2) reduced the COF to 0.17 by 26.66% reduction compared with the pure copper.

Conclusion

In this research, three copper-based samples were prepared: pure copper, copper supported by 10% alumina, and copper supported by a mixture of alumina/MoS_2 by 1:1 ratio. First, alumina/ MoS_2 mixture were mixed for 40 hours. The support materials were mixed with copper for 15 hours using alumina balls by a ratio of 1:10 powder to balls. The mechanical milling process was performed similarly for pure copper. All powder composites were produced by hot pressing method. This was established by filling the mold with powder, cold pressing it at a pressure of 1000 MPa, then heating to 750 for 35 mins and pressing immediately at 1000 MPa. The density of the fabricated samples was measured by the Archimedes method. The microstructure, chemical composition, hardness, mechanical wear rate and coefficient of friction were studied, and the results were as follows:

1. The copper composites were successfully fabricated at 750 °C for 35 minutes by the hot pressing technique.
2. The Raman analysis show that, molybdenum disulfide did not convert to layers, because the proportion of molybdenum disulfide involved in the mixing process was high.
3. The X-ray analysis show that some oxidation of copper was formed, because the manufacturing process took place in uncontrolled atmosphere.
4. The density was decreased by adding both alumina, as well as a mixture of alumina/ MoS_2.
5. The mixing of alumina with copper for 15 hours and cold-hot pressing led to a reduction in the size of the particles, as indicated by the microstructure.
6. The microstructure of the Cu/ (Al_2O_3-MoS_2) sample shows that the MoS_2 was separated into flakes due to mixing it with copper for 15 hours.
7. The hardness was improved by adding alumina as well as (Al_2O_3-MoS_2), and the last sample recorded 175.45 with an improvement of 82.57% compared to the pure copper sample.
8. The mechanical wear rate was decreased, and the sample containing (Al_2O_3-MoS_2) recorded 2.6 mg compared to 22 mg for copper at 50 Newton load.
9. The coefficient of friction decreased by adding alumina and hybrid (Al_2O_3-MoS_2), and the last sample recorded 0.17 compared to 0.23 for pure copper at a load of 50 N.

Declarations

Funding

No funding was received for this work.

Acknowledgement

Authors thank staff of production technology department - Faculty of Technology and Education - Helwan University, Cairo, Egypt, for their cooperation

Conflict of interest (No Conflict of interest related to this work**)**

Availability of data and material (data transparency)

Not applicable

Code availability (software application or custom code)

Not applicable

Ethics approval (include appropriate approvals or waivers)

Not applicable

Consent to participate (include appropriate statements)

Not applicable

Consent for publication (include appropriate statements)

Not applicable

References

1. Holmberg K, Andersson P, Erdemir A (2012) Global energy consumption due to friction in passenger cars. Tribol Int 47:221–234
2. Cho KH, Hong US, Lee KS, Jang H (2007) Tribological properties and electrical signal transmission of copper–graphite composites. Tribology Letter 27:301–306
3. Ma XC, He GQ, He DH, Chen CS, Hu ZF (2008) Sliding wear behavior of copper-graphite material for use in maglev transportation system. Wear 265:1087–1092
4. Moustafa SF, El-Badry SA, Sanad AM, Kieback B (2002) Friction and wear of copper-graphite composites made with Cu-coated and uncoated graphite powders. Wear 253:699–710
5. Huang S, Feng Y, Liu H, Ding K, Qian G (2013) Electrical sliding friction and wear properties of Cu-MoS2-graphite-WS2 nanotubes composites in air and vacuum conditions. Mater Sci Eng A 560:685–692
6. Cao H, Qian Z, Zhang L, Xiao J, Zhou K (2014) Tribological behavior of Cu matrix composites containing graphite and tungsten disulfide. Tribol Trans 57:1037–1043
7. Scharf TW, Prasad SV (2013) Solid lubricants: a review. J Mater Sci 48:511–531
8. Kovalchenko AM, Fushchich OI, Danyluk S (2012) The tribological properties and mechanism of wear of Cu-based sintered powder materials containing molybdenum disulfide and molybdenum diselenite under unlubricated sliding against copper,Wear290–291106–123
9. Hossam M, Yehia A, Abu-Oqail MA, Elmaghraby, Omayma A, Elkady (2020) Microstructure, hardness, and tribology properties of the (Cu/MoS_2)/graphene nanocomposite via the electroless deposition and powder metallurgy technique. J Compos Mater 0(0):1–12
10. Xiao J-K, Zhang W, Liu L-M, Zhang L, Zhang C (2017) Tribological behavior of copper-molybdenum disulfide composites. 15:61–71Wear384–385

11. Abd-Elwaheda MS, Sadouna AM, Elmahdy M (2020) Electroless-plating of Ag nanoparticles on Al_2O_3 for enhanced mechanical and wear properties of Cu–Al_2O_3 nanocomposites”. J mat Res Technol 9(6):13749–13758
12. H. M. Yehia “Microstructure, physical and mechanical properties of the Cu/ (WC-TiC-Co) nano-composites by the electro-less coating and powder metallurgy technique”,Journal of Composite Materials, 53, pp.1963–1971
13. El-Kady O, Yehia HM (2019) Fathy. N. Preparation and characterization of Cu/ (WC-TiC-Co)/graphene nano-composites as a suitable material for heat sink by powder metallurgy method. Refract Met Hard Mater 79:108–114
14. Yehia HM, Nouh F, El-Kady O (2018) Effect of graphene nano-sheets content and sintering time on the microstructure, coefficient of thermal expansion, and mechanical properties of (Cu /WC –TiC-Co) nano-composites. J of Alloys and Compounds 764:36–43
15. Elmaghraby MA, Yehia HM, Elkady OA, Abu-Oqail A (2018) Effect of Graphene Nano-Sheets Additions on the Microstructure and Wear Behavior of Copper Matrix Nano-Composite,Journal of Petroleum and Mining Engineering, Pp.124–130,
16. Yehia HM, El-Tantawy A, Ghayadb IM, Eldesoky AS, El-kady O Effect of zirconia content and sintering temperature on the density, microstructure, corrosion, and biocompatibility of the Ti-12Mo matrix for dental applications,J. of mater. Research and Tech.9 (2 0 2 0)8820–8833
17. Hong, Li et al (2012) From Bulk to Monolayer MoS_2: Evolution of Raman Scattering. Adv Funct Mater 22:1385–13907
18. Bret C, Windom WG, Sawyer DW, Hahn (2011) A Raman Spectroscopic Study of MoS2 and MoO3: Applications to Tribological Systems. Tribol Lett 42:301–310
19. Jin-Kun, Xiao (2017) Tribological behavior of copper-molybdenum disulfide composites,Wear,V. 384–385,61–71

Figures

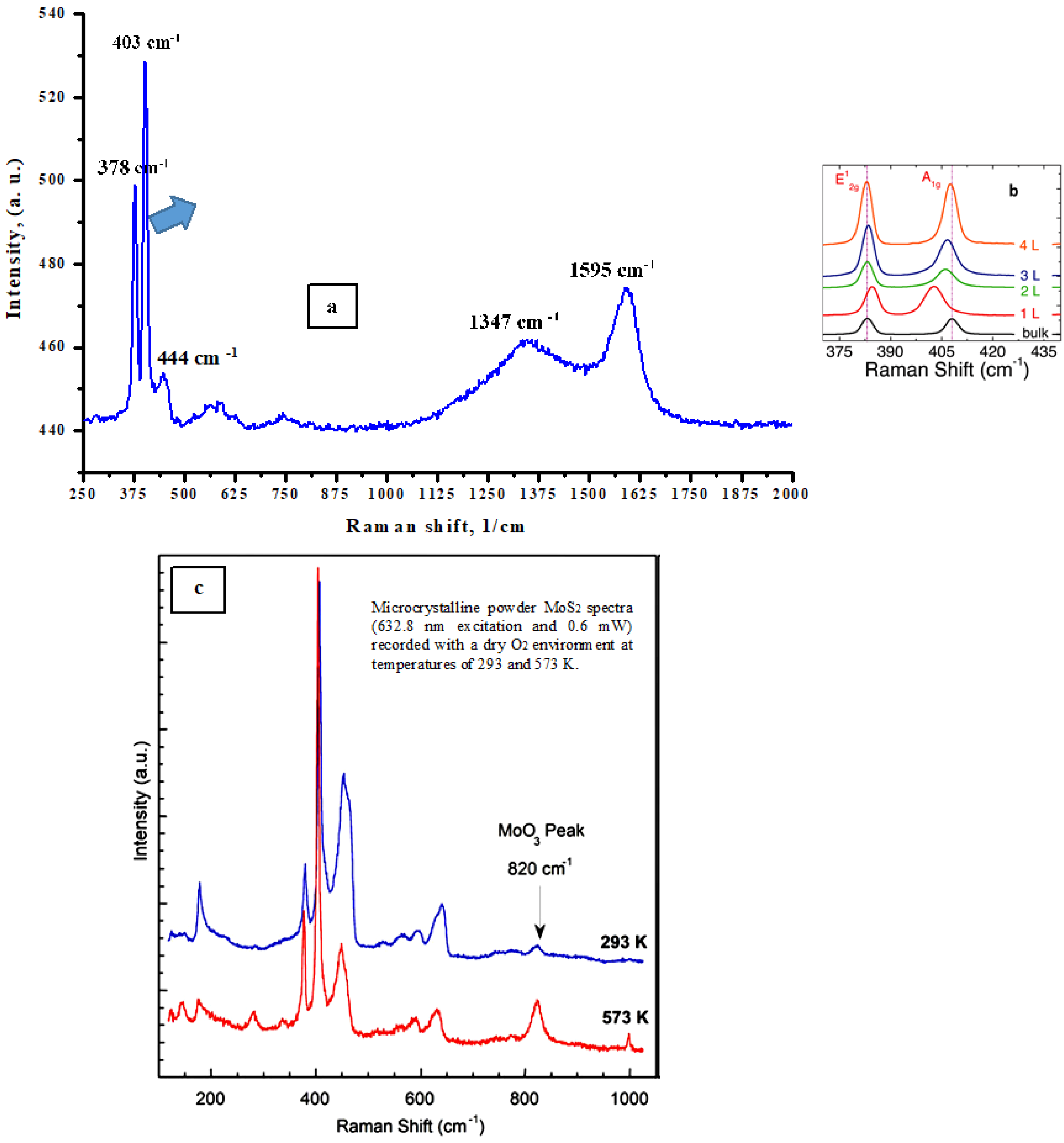

Figure 1

Raman analysis of the hybrid ($10MoS_2$-$10Al_2O_3$)

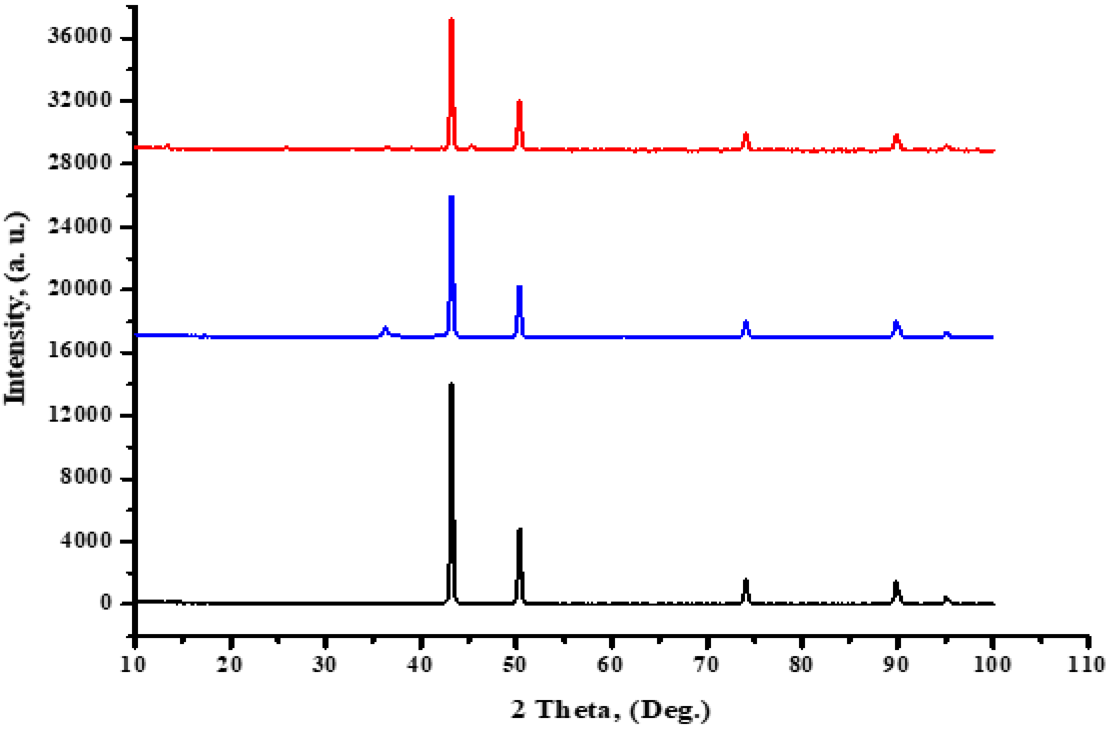

Figure 2

X-Ray patterns of copper nanocomposites fabricated by hot compaction

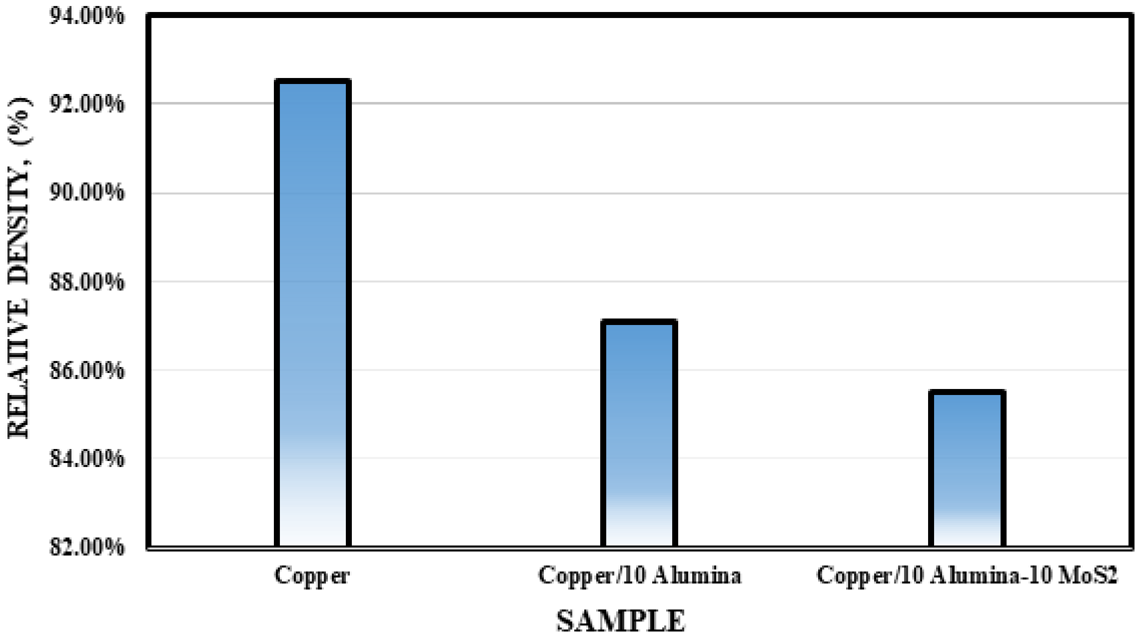

Figure 3

Relative density of fabricated capper nanocomposites

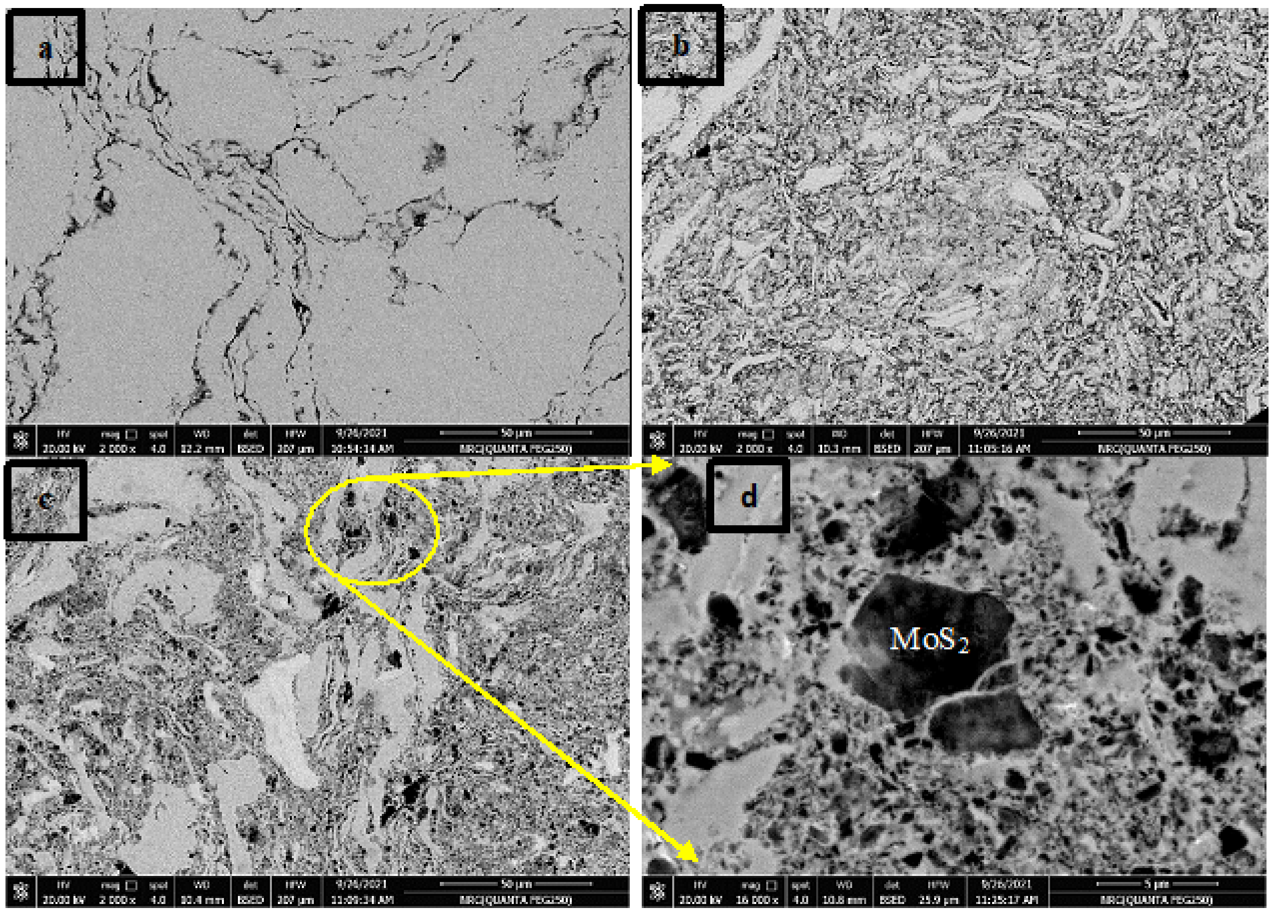

Figure 4

Microstructure of the hot pressed copper matrix nanocomposites

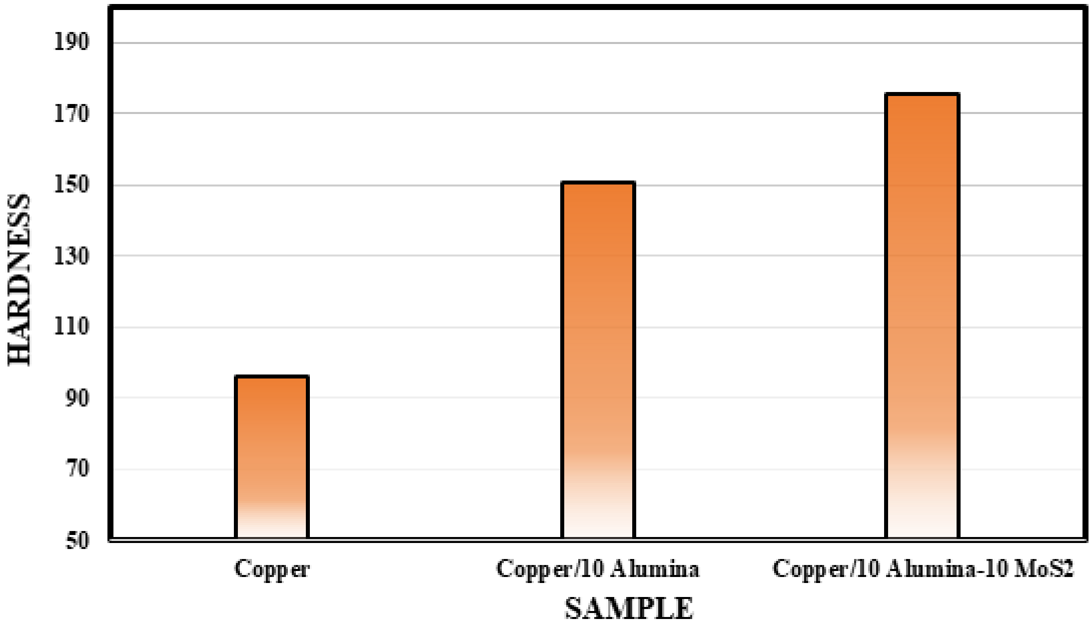

Figure 5

Hardness of hot pressed samples

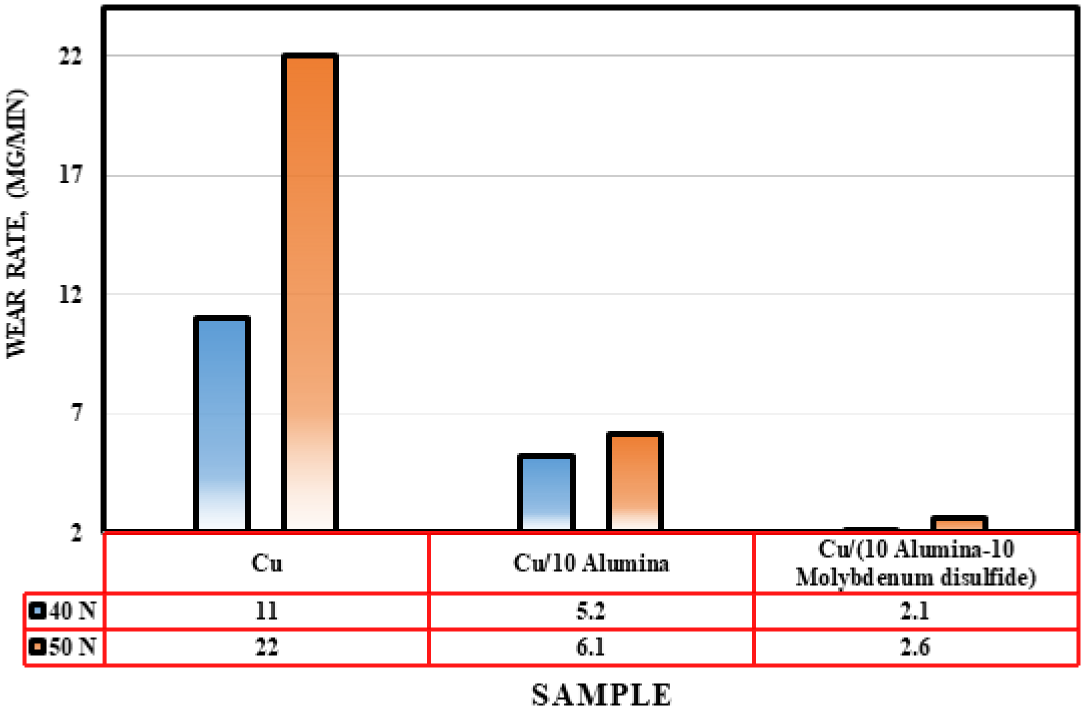

Figure 6

Wear rate of hot pressed copper nanocomposites at 40 and 50N

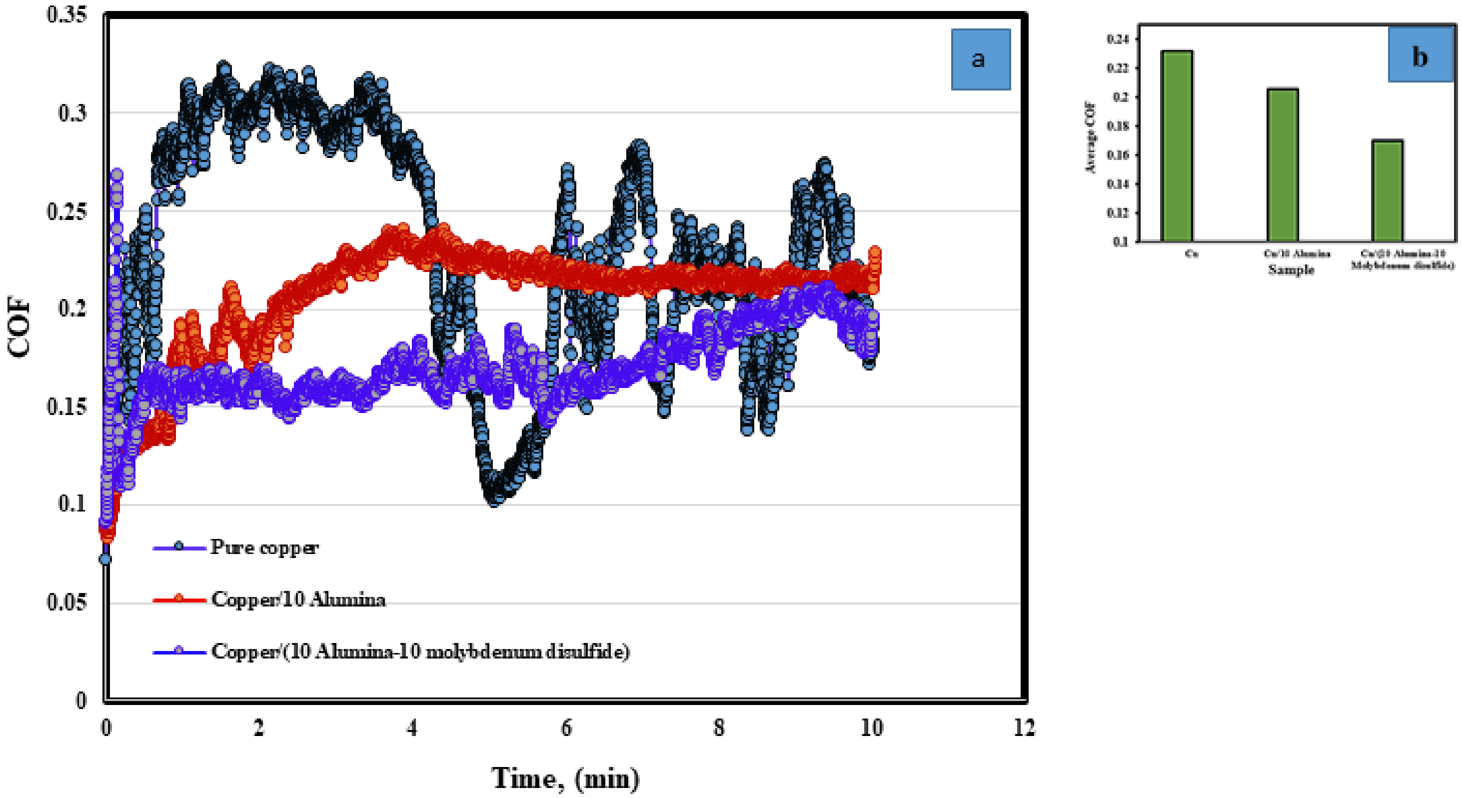

Figure 7

Friction coefficient of hot pressed copper nanocomposites at 50N