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Surface Modification of Multiwall Carbon Nanotubes for Metal Matrix Nan composite Applications

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ABSTRACT

MWCNTs first functionalized by using two steps covalent functionalization process. Functionalized MWCNTs coated with copper by using electroless coating process. Three different groups of Cu/MWCNTs nanocomposites with (0.1, 0.5, 1, 2, 3 wt% MWCNTs) were prepared by means of powder technology. The first group contains multiwalled carbon nanotubes as received (Cu/MWCNTs), second group contains functionalized multiwalled carbon nanotubes (Cu/FMWCNTs) while the third group contains coated multiwalled carbon nanotubes (Cu/CMWCNTs). Comparison between these samples show that the coating of MWCNTs was remarkably improve hardness and wear resistance of copper nanocomposite. The improvement in mechanical properties is due to the enhancement in both adhesion with matrix and dispersion ability of MWCNTs. SEM, XRD, FTIR were used to characterize of coating process and Cu/MWCNTs nanocomposites.

Keywords: Carbon Nanotubes, Electroless Plating, Nan composite.

تهيئة سطوح انابيب الكاربون النانوية لملائمة تطبيقات المواد المتراكبة النانوية ذات الاساس المعدني.

الخلاصة

في البداية تم توظيف انابيب الكاربون النانوية باستخدام التوظيف التساهمي وعلى مرحلتين. انابيب الكاربون النانوية الموظفة تم طلاءها بمعدن النحاس باستخدام (Electroless coating process). ثلاث مجاميع من المواد المتراكبة النانوية ذات الارضية النحاسية تم تحضيرها باستخدام تكنولوجيا المساحيق بنسب وزنية مختلفة من انابيب الكاربون النانوية. احتوت المجموعة الاولى على انابيب الكاربون النانوية كما هي واحتوت المجموعة الثانية على انابيب الكاربون النانوية الموظفة بينما احتوت المجموعة الثالثة على انابيب الكاربون النانوية المطلية. بينت المقارنة بيت هذه العينات ان عملية الطلاء قد حسنت وبشكل ملحوظ الصلادة ومقاومة البلا للمادة المتراكبة النانوية. ان التحسن في الخواص يمكن ارجاعه هنا الى زيادة كل من الالتصاق مع الارضية و قابلية التشتت لانابيب الكاربون النانوية. تم استخدام (SEM, XRD, FTIR) لتوصيف عملية الطلاء وكذلك لتوصيف المواد المتراكبة النانوية ذات الاساس المعدني.

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INTRODUCTION

Since first produce of CNTs by SumioIijima [1] in 1991 they get a much of interest due to their high properties. In addition to their remarkable strength, which is usually quoted as 100 times that of steel at one-third of the weight, carbon nanotubes have shown a surprising array of other properties. CNTs conduct heat as efficiently as diamond, conduct electricity as efficiently as copper, yet also be semiconducting depending on chirality [2]. CNTs with these excellent properties have many potential applications, including energy storage and energy conversion devices; sensors; field emission displays; hydrogen storage media; nanometer-sized semiconductor devices, probes [3] and most important high-strength composites especially metal matrix composites [4].

The most important problems of using CNTs in metal matrix composite are the adhesion with the matrices and the homogeneous dispersion of them within the metal matrices {5]. Many attempts were done to overcome these challenges. Using CVD technique to grow CNTs in situ on Al powders has been found to be successful for obtaining powders with good dispersion and adhesion with metal matrix {6].

Improved dispersion and adhesion attained by the molecular level mixing method has been found to lead to an increase in the compressive yield strength by two times in a Cu-10 vol. % CNT composite [7]. Using powder metallurgy method with special technique was also gives good dispersion and adhesion of CNTs with metal matrices [8].The goal of this work is to overcome the challenges that associated with using CNTs as reinforcement in metal matrix composite by using a set of procedures. First MWCNTs coated with metal to improve both dispersion ability and adhesion with metal matrix. Second MWCNTs dispersed within metal matrix using tow step dispersion process which are dispersion in ethanol first and using ball mill process as second dispersion process. Comparison between three groups of samples was done. The first group contains MWCNTs as received; the second group contains functionalized MWCNTs (FMWCNTs) while the third group contains coated MWCNTs with metal (CMWCNTs).

EXPERIMENTAL WORK

Materials:

MWCNTs used in this work were purchased from Cheap Tubes Inc USA. with purity of >99 %, diameter 13-18 nm and length 1-12 µm produced by CVD method and purified by plasma. Copper powder with 99% purity (Alpha Company / Spain) and particle size less than 38 µm is used as a matrix. Sieving method is used to separate copper powder with particle size less than 38 µm.

Work Procedure

Coating of MWCNTs

MWCNTs were coated with copper using electroless plating methods. The coating was in the sequence below:

Functionalization and oxidation

0.5 g of MWCNTs were immersed in 500 ml of mixture of concentrated (HNO_3:$H_2SO_{4)}$ (1:3 by volume) at room temperature and ultrasonicated in high power ultrasonic path (frequency 60 KHz, power 140 W) for 30 min, the solution then was diluted 15 times and filtered in vacuum filtration system using filter papers with 0.2 µm in pore size. MWCNTs were wished many times during filtration using distilled water. Same treatment was repeated using H_2O_2 (30%) [9]. The result was functionalized MWCNTs. FTIR spectra test used to insure that functional groups were attached with MWCNTs side wall.

Sensitization

Functionalized MWCNTs were immersed in aqueous solution of 0.1 M $SnCl_2$ + 0.1 M HCl (aged for 72 h) at room temperature, and sonicated for 30 min by the same ultrasonic bath used above. MWCNTs were separated from the solution by using centerfugation method with 4000 rpm for 10 min, the product washed with distilled water and then dried at 90ºC.

Activation

Sensitized MWCNTs were immersed in aqueous solution of 0.0014 M $PdCl_2$ + 0.25 M HCl at room temperature. The same procedures of ultrasonication, centerfugation, wishing and drying that used in sensitization process were repeated.

Coating

Activated MWCNTs were immersed in electroless path (table1) for 3 min under ultrasonication [10], here ethanol was used for washing to decrease any possible to oxidation. XRD and SEM were used to characterize coating process.

COMPOSITE PREPARATION

Dispersion of MWCNTs within Metal Matrix

MWCNTs were dispersed in 50 mL of ethanol ultrasonically for 10 min and then copper powder was added to solution [11]. Mechanical agitation was used simultaneously with ultrasonication by using mechanical stirrer with 600 rpm in rotation speed. The solution was also heated to 60 ºC to evaporate ethanol. The process continued until most of ethanol evaporated. Samples were then dried at 90 ºC and ball milled in ceramic container using ceramic balls. The process parameters were (1:10 ball to powder ratio, 200 rpm rotation speed, 0.5 ml of ethanol is added as process controlling agent (PCA) [81] and 5 h in time).

The mixed powders may have oxides therefore it was reduced by using H2 at 400 °C for 1 h in quartz tube at tube furnace [12].

Compaction and Sintering

The samples were compacted under uniaxial compaction force 100 kN for 30 sec using hydraulic press. Sintering was done in tube furnace using quartz tube attached from outlet with water bubbler and with Ar flow meter from inlet. First temperature was raised to 100 ºC for 1 h and then raised to 900 ºC for 2 h. All sintering process was achieved under pure Ar atmosphere with 350 ml/min in flow rate. SEM was used to characterize composite material.

Hardness Test

Vickers hardness was measured for all samples using Vickers hardness apparatus (HLNSOLDT WETZLAR). A 200 g in weight was tested for 10 sec.

Wear Test

Wear under dry sliding condition was also measured using pin on disk wear apparatus. The test parameters were (1 kg in weight, 15 min in time, 3.7 m/sec at sliding speed and 35 HRC in disc hardness).

Results and Discussion

Functionalization of MWCNTs

To make insurance, XRD was taken for purchased MWCNTs and is shown in Figure (1). In this pattern there are two main beaks (25.886º and 43.09º). Pure graphite displays a sharp characteristic peak at 26.6º, corresponding to the (0 0 2) diffracting plane. Graphite also displays other peak at 44.5º corresponding to the (1 0

0), (1 0 1) crystallographic planes. For MWCNTs, the shape, width and intensity of these peaks were modified to lower value of 2θ due to the high curvature and high strain energy resulting from small diameters of MWCNTs [12].

FTIR spectrum (Figure 2) shows clearly the presence of C=O at 1633.71/cm, –OH at 3437.16/cm and C–C at 1172.72/cm .C–C refers to sigma bond that exists between carbon atoms in MWCNTs side wall, while C=O and –OH bonds refer to presence of each of hydroxide (–OH) and carboxylic (–COOH) functional groups on the MWCNTs walls [13].

Coating of CNTs by Metal Nanoparticles

SEM image Figure (3) shows a continuous and approximately homogeneous coating layer is successfully deposit on MWCNTs surface. From Figure 3 we can determine the diameter of coated MWCNTs (115 -135 nm), so we can calculate that the coating layer is about 50 – 60 nm in thick.

XRD of the coated MWCNTs with copper Figure (4) shows two diffraction beaks for copper nanoparticles metal (43.25º for (1 1 1) plane and 50.42º for (2 0 0) plane) [14]. The pattern also displays other two peaks in (36.45º, 38.71º) these tow diffraction peaks are for nanocrystalline copper (II) oxide (Cu_2O) and copper oxide (CuO) [15]. In order to reduce Cu_2O and CuO on MWCNTs, the MWCNTs was heated in H_2 at 400 ºC for 1 h. The XRD pattern does not display any MWCNTs diffraction peak which proves a continuous copper layer deposition.

Dispersion of MWCNTs within Matrix

Figure (5) shows the SEM image of Cu/0.5 wt% MWCNTs powder, In this image, it's easy to note that MWCNTs are well imbedded in copper particles during ball mill process.

Figure (6) shows the SEM image of Cu/2 wt% CMWCNTs powder after mixing process, the image shows clearly the homogeneous dispersion of CMWCNTs on the copper particle.

Copper / MWCNTs Composites

A comparison between Cu/ as received MWCNTs (MWCNTs), Cu/ Functionalized MWCNTs (FMWCNTs) and Cu/coated MWCNTs (CMWCNTs) composites is shown in Figure (7).

In Figure (7) a and b the clustering of MWCNTs is easily seen, the clustering seems to be more intense in Cu/ FMWCNTs composite. For Cu/ CMWCNTs as shown in Figure (7) c, the CMWCNTs are very well dispersed in copper matrix composites. Thus, coating process enhances the dispersion process. Very good dispersion on CMWCNTs gives good adhesion of CMWCNTs. This will lead to good improvement in mechanical properties of the composite.

Hardness

The hardness measurements of Cu/ MWCNTs composites materials are plotted versus wt % of MWCNTs as shown in Figure (8). In general, the hardness increases almost linearly with increasing the MWCNTs wt % up to a certain MWCNTs wt %.

For Cu/MWCNTs nanocomposites, the hardness increases with increasing the weight fraction of MWCNTs up to 0.5 wt% of MWCNTs. When the 0.5 wt% of MWCNTs is reinforced, the hardness of Cu/MWCNTs nanocomposites is 112 kg/mm2, which is about 2.2 times higher than that of Cu without MWCNTs. For Cu/FMWCNTs nanocomposites, the hardness increases with increasing the weight fraction of FMWCNTs up to 0.1 wt% of FMWCNTs. When the 0.1 wt % of MWCNTs is reinforced, the hardness of Cu/FMWCNTs nanocomposites is 101 kg/mm2, which is about 2 times higher than that of Cu without MWCNTs. For Cu/CMWCNTs nanocomposites, the hardness increases with increasing in the weight fraction of CMWCNTs up to 2 wt % of CMWCNTs. When the 2 wt % of CMWCNTs is reinforced, the hardness of Cu/CMWCNTs nanocomposites is 140 kg/mm2 , which is about 2.7 times higher than that of Cu without CNTs.

The enhancement of hardness by MWCNTs reinforcement is originated from the high interfacial strength at Cu/MWCNTs interface and the homogeneous distribution of MWCNTs within Cu matrix. Cu/CMWCNTs nanocomposites gives the highest value of hardness (140 kg/mm2). This is explained by the fact that CMWCNTs are very well dispersed with the copper particles (Figure 6) and there good adhesion between CMWCNTs and copper particles (Figure 7 c) at least up to 2 wt%. After 2 wt% , the dispersion process is affected by the fact that the number of individual CMWCNTs becomes very large after this limit and this fabrication process becomes ineffective. This is in agreement with the work of Kim et al [16].

Wear Resistance

of Cu/ MWCNTs composites materials are plotted versus wt % of MWCNTs as shown in Figure 9. In general, the wear rate of Cu/ MWCNTs nanocomposites decreases with MWCNTs % up to certain wt% of MWCNTs and then starts to increase. The wear rate of Cu/ MWCNTs nanocomposites decreases with MWCNTs% up to 0.5 wt% and then starts to increase. Under dry sliding wear condition, the wear resistance of Cu/ MWCNTs nanocomposites is 1.6 times higher than that of pure copper metal at 0.5 wt % MWCNTs. For Cu/ FMWCNTs nanocomposites , under dry sliding wear condition, the wear resistance of Cu/ FMWCNTs nanocomposites is 1.34 times higher than that of pure copper metal at 0.1 wt % FMWCNTs. For Cu/CMWCNTs nanocomposites, under dry sliding wear condition, the wear resistance of Cu/ CMWCNTs nanocomposites is 3.5 times higher than that of pure copper metal at 2 wt % CMWCNTs. The variation in the wear rate with MWCNTs wt % is consistent with the hardness measurement. Increasing wear resistance that is achieved by adding MWCNTs as reinforcement occurs by two different effects, first is the strengthening effect of MWCNTs which attaches the grains to each other and prevents flaking a way of copper grains. The second effect of MWCNTs as reinforcement is the self-lubricant ability or the low coefficient of friction of MWCNTs which decreases metal to metal contact. The first effect directly depends on dispersion of MWCNTs within the matrix and the adhesion between MWCNTs and the matrix; these two factors are enhanced remarkably by coating of MWCNTs with metals (copper here). During wear process the pure Cu surface flakes away, the worn chips are formed by peeling of Cu grains near the worn surface. However, in case of Cu/MWCNTs nanocomposite, the Cu grains are not easily peeled from the worn surface because of the pinning of Cu grains by the homogeneously implanted MWCNTs across Cu grains in Cu/MWCNTs nanocomposites. Also the MWCNTs exposed to the worn surface during wear process can act as a lubricating carbon film owing to its low friction coefficient. Therefore, the wear rate of Cu/MWCNTs nanocomposites is remarkably decreased with increasing the wt% of MWCNTs due to the effect of homogeneous distribution of MWCNTs in Cu matrix and low friction coefficient of exposed MWCNTs on the worn surface. Therefore, the wear rate of Cu/ MWCNTs nanocomposites is remarkably decreased with increasing wt% of MWCNTs due to the effect of homogeneous distribution of MWCNTs in Cu matrix and low friction coefficient of exposed MWCNTs on the worn surface. Cu/CMWCNTs nanocomposites has the best wear resistance up to 2 wt%. Thus, the number of CMWCNTs on the surface increases and this lead to increasing lubricant effect. In Cu/CMWCNTs nanocomposites the dispersion and adhesion of CMWCNTs with the matrix is good up to 2 wt%. Beyond 2 wt% CMWCNTs the dispersion becomes poor which leads to degrading in wear resistant. The decrease in the wear rate of Cu/MWCNTs composites and Cu/FMWCNTs composites up to 0.5 wt% and 0.1 wt% respectively can be explained by the effect of dispersion.

CONCLUSIONS

1. Coating of MWCNTs with copper metal remarkably enhances the dispersion ability and adhesion with the copper matrix in Cu/MWCNTs nanocomposites materials.
2. The hardness and wear resistance of fabricated Cu/MWCNTs nanocomposite are significantly increased with increasing the wt% of MWCNTs up to a certain wt%.
3. The mechanical properties of Cu/CMWCNTs nanocomposites are higher than these of Cu/ MWCNTs and Cu/FMWCNTs.

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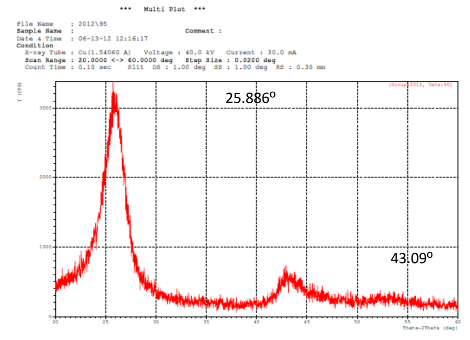
Table (1) Bath composition and operation condition for copper electroless plating [10].

Composition	Quantity
$CuSO_4.5H_2O$	25 g/L
$KNaC_4H_4O_6.4H_2O$	40 g/L
$NiCl_2.6H_2O$	2 g/L
Polyethylene glycol 6000	40mg/L
HCHO (added later)	12 ml/L
pH(adjusted by NaOH)	11.5
Temperature	25 °C



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***   Multi Plot   ***

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Date & Time   : 06-13-12 12:16:17
Condition
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  Scan Range : 20.0000 <-> 60.0000 deg   Step Size : 0.0200 deg
  Count Time : 0.10 sec    Slit  DS : 1.00 deg  SS : 1.00 deg  RS : 0.30 mm
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Figure (1). XRD for purchased MWCNTs.

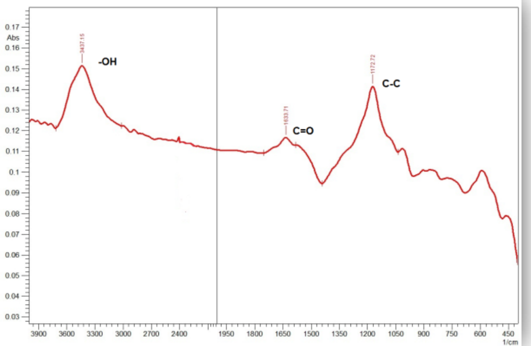

Figure (2). FTIR spectrum of functionalized MWCNTs.

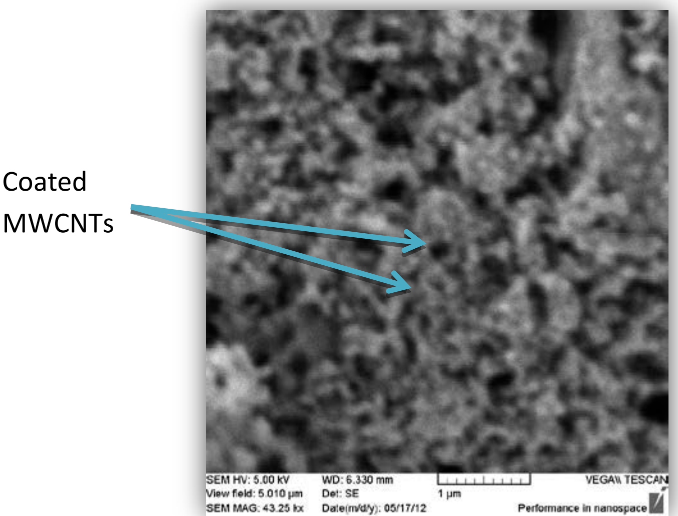

Figure (3). SEM image for coating CNTs.

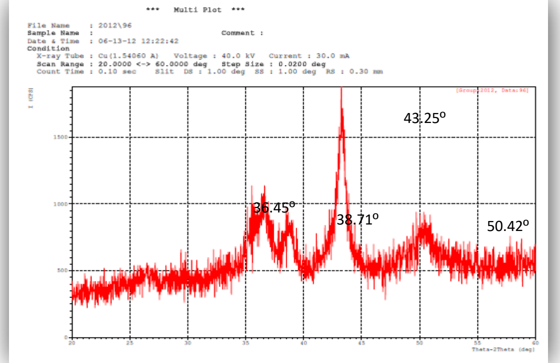

Figure (4). XRD for copper coated MWCNTs.

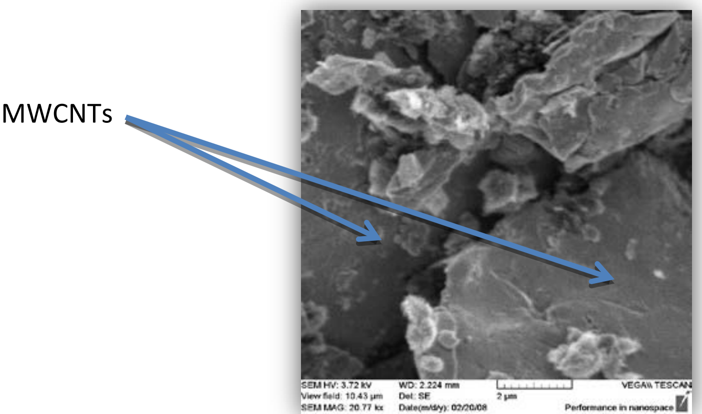

Figure (5). SEM image of Cu/ 0.5 MWCNTs powder.

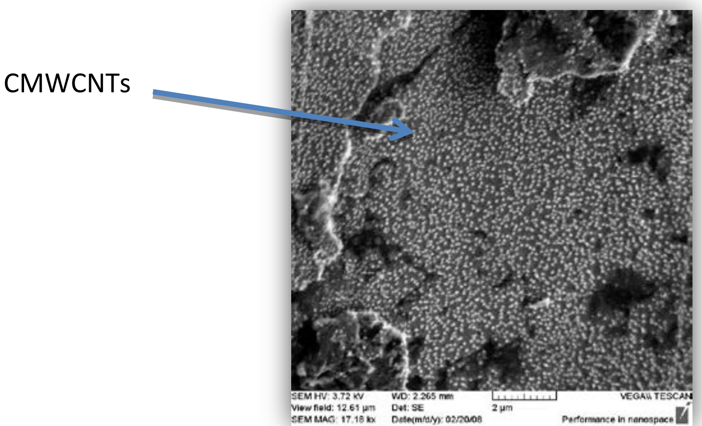

Figure (6). SEM image of Cu/2 wt% CMWCNTs powder.

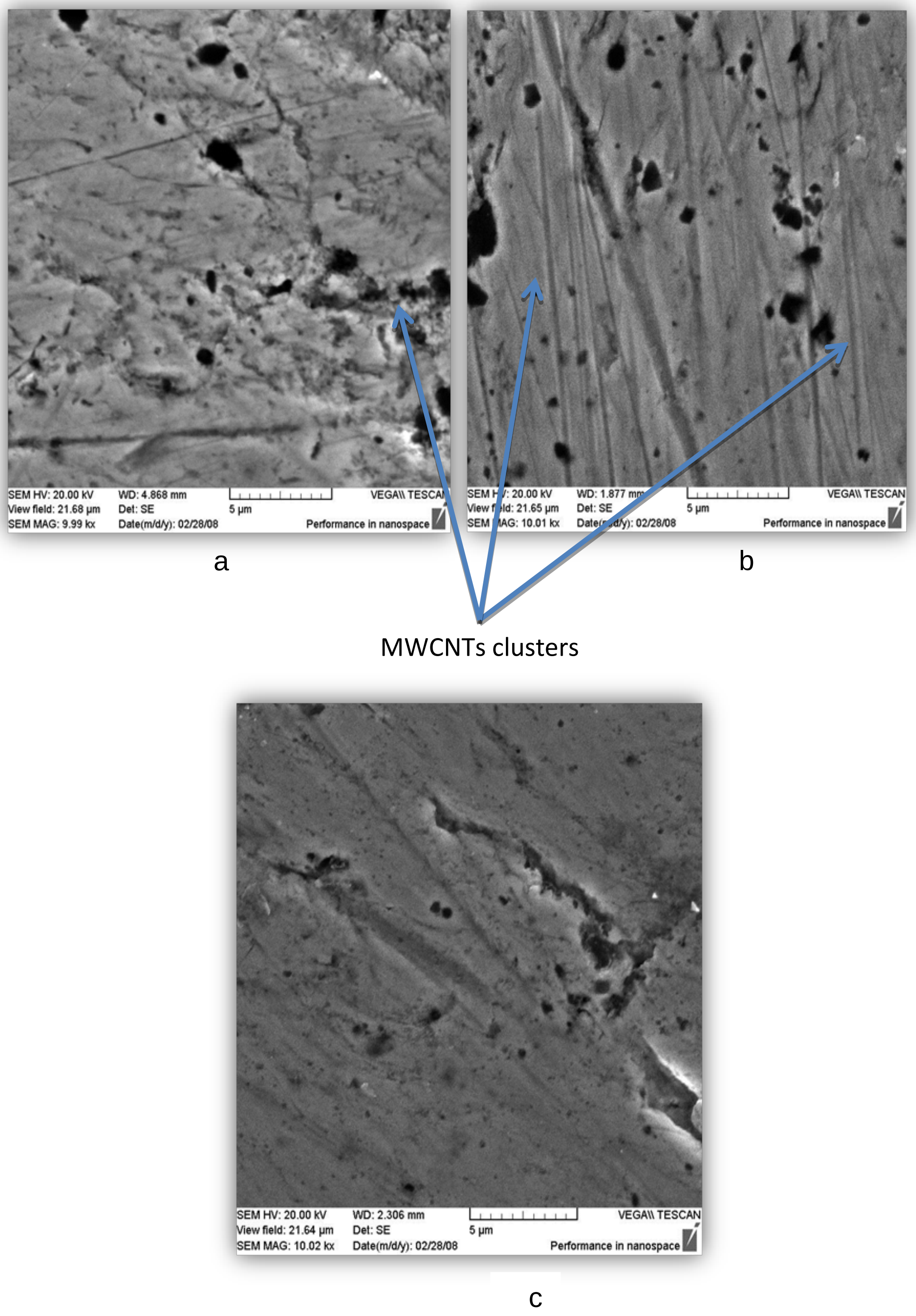

Figure (7). SEM images for (a) Cu/1wt% MWCNTs (b) Cu/1 wt% FMWCNTs (c) Cu/1wt% CMWCNTs.

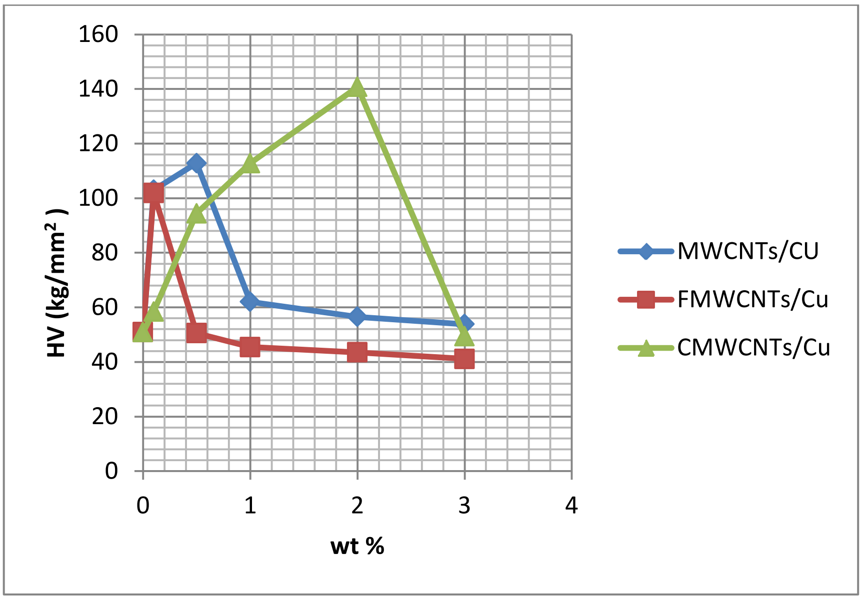

Figure (8). Vickers hardness measurements of Cu/ CNTs composites.

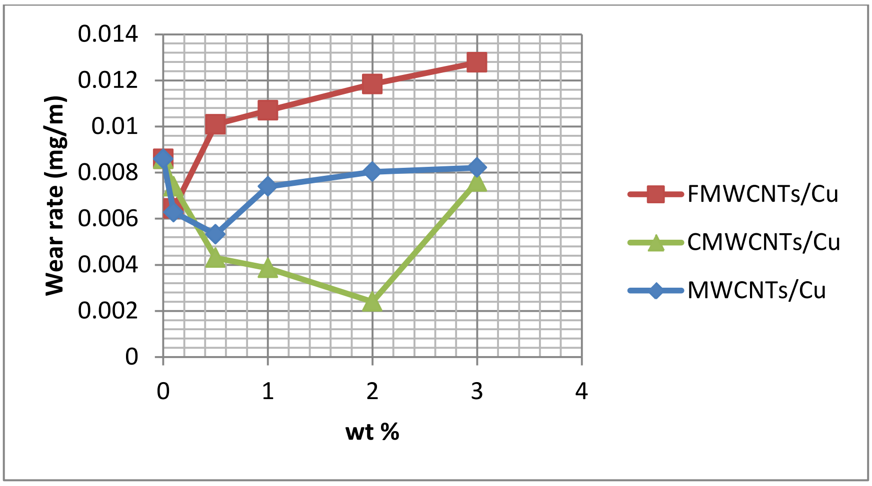

Figure (9). The wear rate of Cu/ MWCNTs, Cu/ FMWCNTs and Cu/ CMWCNTs composites.