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Microstructural study of vapour grown carbon nanofibre/copper composites

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Abstract

Vapour grown carbon nanofibres from different manufacturers have been incorporated into copper in order to obtain metal matrix composites with high volume fraction. The manufacturing route involved copper deposition by the electroless plating technique and further hot-pressing of the composite powders. A material with porosity less than 1 % was obtained. The microstructure was investigated by scanning electron microscopy and transmission electron microscopy. After hot-pressing the carbon nanofibres were seen to be homogeneously dispersed in the matrix and showed a random-planar distribution. Despite the poor wetting between copper and carbon, the Cu/C interface formed was continuous. The matrix was composed of grains in the nanometric range, suggesting that the nanofibres act as grain growth inhibitors.

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1. Introduction

Due to their excellent mechanical and thermophysical properties, vapour grown carbon nanofibres (VGCNFs) are one of the most promising reinforcing materials for metal matrix composites [1,2] in applications such as structural, wear and thermal management. VGCNFs provide an immediate availability and excellent performance-cost ratio [3,4] for the mass production of industrial components, particularly among other reinforcements based on carbon, like carbon nanotubes (CNTs), conventional carbon fibres or diamond. Many papers can be found in the literature regarding properties, manufacturing routes and characterisation of CNTs and their composites (the majority of them with a polymer matrix). However VGCNFs have been much less studied.

VGCNFs consist of an internal hollow core produced by catalytic growth [4] and an external layer composed of the so-call CVD carbon layers. The structure of these layers is turbostratic, and allows the thickening of the fibres in a second step in the manufacturing process [1]. There have been very few studies carried-out to incorporate VGCNFs into metallic matrices [2,5-10]. Those studies that have been carried out have been based on coating technologies such as electroplating [2,5] or electroless plating [6-8]. The dispersion of VGCNFs has been enhanced but the main disadvantage is that these processes can only produce composite powders or thin films. On the other hand, metal infiltration [9,10] has previously been employed to obtain bulk materials. The manufacturing route reported in the present paper involves the use of copper electroless

plating in order to achieve good dispersion of the reinforcement within the matrix, and the subsequent hot-pressing to obtain a material free of porosity.

There are several ways to improve the wetting of carbon nano-reinforcements through the use of ultrasounds [7] and surfactants [2,5], or even by the attachment of some functional groups in order to make the surface more hydrophilic [11]. The so-called “functionalization” offers good dispersion results and is usually done by immersing the reinforcements into strong acids. However, acids can modify the bulk chemistry and structure of the VGCFs, which could in turn reduce the final properties of the composite material. In the present work the dispersion was done by the combination of ultrasounds and the use of a cationic surfactant.

2. Experimental Work

In this study VGCFs from Applied Sciences Inc. (Pyrograf IIItm), Showa Denko Co. Ltd. (SDK heat treated) and Grupo Antolin Ingenieria (GANF1) were used as fillers for metal matrix composites. The basic properties of the VGCFs, taken from the data sheet of the manufacturers are shown in Table 1.

2.1. *Electroless plating process*

VGCFs were coated by copper by the so-called electroless plating technique. This technique was selected due to its simplicity and because it does not need expensive facilities [12].

Electroless plating is based on a chemical reaction leading to the deposition of metallic elements on top of the substrate. Prior to the coating process it was necessary to activate the surface of the

VGCNFs. This was done by immersing the fibres in a catalysing bath composed of hydrochloric acid and tin (sensitizing bath), followed by a bath containing hydrochloric acid and palladium (activation bath). After catalysing, the VGCNFs were soaked in the coating solution, in which the red-ox reaction was carried-out under argon purging in order to prevent oxidation. VGCNFs were kept in the solution until the deposition was complete, which was identified when the bath solution turned transparent. At this point the whole copper from the metallic salt had been converted into metallic copper on the VGCNFs surface. Some extra samples were manufactured without argon purging in order to compare their oxygen amount. Processing conditions are described in Table 2.

The cover thickness, and as a result of it, the amount of the copper matrix in the final composite, were controlled by means of VGCNFs concentration in the plating bath. In this way, different samples containing 20 vol. % and 40 vol. % of reinforcement have been studied. The final volume of filler was determined by weighing the sample after drying. The whole catalysing process was aided by the application of ultrasounds and mechanical stirring. VGCNFs were rinsed and filtered at the end of each step and finally dried under vacuum at 100 °C. Arai et al. [5] have studied how polyacrylic acid (PAA) increases VGCNFs dispersion, in the codeposition with copper by electroplating. According to this procedure, PAA (Aldrich) was added to the plating bath in a concentration of 140 µl/l.

2.2. Consolidation by hot-pressing

Copper coated VGCNFs were consolidated into dense samples by hot pressing (HP). The consolidation was performed in the solid state (the melting temperature of copper is 1083 °C). Thus, composite powders were inserted in a high strength graphite die (25 mm inner diameter)

and hot-pressed under high vacuum with different pressure and temperature parameters: 25 and 35 MPa; 700, 900 and 1000 °C for 2 hours.

2.3. Characterization (Materials and methods)

A complete material microstructural assessment has been carried out. This microstructural study has been performed on both loose composite powders and consolidated bulk material by low vacuum pressure scanning electron microscope (SEM), model JEOL JSM 5910LV. Coated VGCFs samples were fixed on an adhesive tape and subsequently gold sputtered in order to build a conductive thin layer of about 5 nm. Consolidated samples were also cut and embedded into epoxy resin holders. Once cured, the samples were progressively polished using a silicon carbide grid, and finally polished with diamond paste to a mirror finish. These samples were etched with a $\text{FeCl}_3\text{:HCl:H}_2\text{O}$ (1:1:1) solution for 7 seconds. Energy dispersive spectroscopy (EDS microprobe, model OXFORD-INCA-300, attached to the SEM) was employed in order to check the composition and assess the contamination.

Further detailed observations were carried-out by transmission electron microscopy (TEM) at CMC-UCM facilities (Spain). For this examination a JEOL model 3000F transmission electron microscope with 300 KV acceleration voltage was used. The microscope was equipped with a double-tilt simple holder (up to max $\pm 20^\circ$) with ± 0.1 mm z-axis displacement and 0.17 nm point to point resolution. The microscope was fitted with an Oxford model X-ray energy spectrometer giving resolution of 136 eV at 5.39KeV. Coated VGCFs samples were embedded in Spurr resin. Ultrathin sections were cut with a diamond knife in a Reichert Ultracut E ultramicrotome and collected on uncoated copper grids. Consolidated samples were observed by preparing TEM thin

foils by ion milling (Gatan model 691), at 5 kV and 1 mA, keeping the temperature at 20° C and using an Ar beam with an incidence angle of $8\pm$. Specimens had first been mechanically polished and dimpled.

Total porosity was obtained by direct calculation, while open porosity was measured by Helium pycnometry (Accupyc 1330). The presence of oxides was analyzed by X-ray diffraction (Siemens diffractometer with Kristalloflex K710H generator and goniometer model D-500). The hardness of pure copper and the composites was measured by a micro-Vickers' hardness tester (Fischerscope H100V, load 0,1g, standard ISO 6507.1). The amount of oxygen was measured in a LECO TC-436 analyzer.

3. Results and discussion

3.1. Coated samples by electroless plating

The different morphologies of the as-received carbon nanofibres are shown in Fig. 1. Their typical diameters vary between manufacturers, and range from 20 to 200 nm. In some cases traces of the catalyst (employed for their manufacturing) can be observed (Fig. 1a). Table 3 shows the samples manufactured by the electroless plating technique.

The SEM images corresponding to the coated samples are shown in Fig. 2. Fig. 2a corresponds to a coated sample with 20 vol. % of Pyrograf III nanofibres. It can be observed that some fibres remain uncoated. This absence of coating has also been reported in work by Kim and Lee [7]. The causes of this shortage are still unknown, but it was probably due to random morphology of

the as supplied nanofibres which determined their coating behaviour. In Fig. 2b SDK coated fibres (40 vol. %) are observed. Fig. 2c shows this sample at higher magnification. It is clear that a higher volume of VGCFs means finer copper thickness, but when this volume is increased a less homogeneous coating is obtained. One explanation is based on the fundamentals of the electroless coating process. This coating growth is initiated on the catalytic centres (Pd particles) and then grows laterally and vertically to form a continuous layer [13]. Therefore, with 40 vol. % of reinforcement the amount of available copper is not enough to completely cover the surface of the fibres. Nevertheless in the majority of the samples it is possible to find well coated nanofibres (Fig. 2c). Similar observations have been recently reported by Kim and Lee [7] while coating VGCFs from Showa Denko, presumably at low vol. %. They observed uniform and densely copper coated plates. Finally, 20 vol. % coated GANF1 are shown in Fig. 2d. Only slight differences can be seen with respect to the other nanofibres, mainly due to the different aspect ratios and morphologies. Furthermore, some coated samples were observed by TEM in order to explore their microstructure in detail, as well as their copper/carbon interface.

Fig. 3 shows TEM images, in which dendritic growth of the coating can be observed (Fig. 3a). Moreover coating of the inner holes of the nanofibres can also be observed. There is one example in Fig. 3b. Fig. 3c shows GANF1 coated fibres (20 vol. %). In this sample the coating shape is quite smooth and homogeneous, with minimal deviation from a perfect cylinder. Nevertheless some dendritic growth is observed. Fig. 3d shows the copper/carbon interface. The carbon appears as a clear phase. The carbon walls and the CVD external layer are clearly identified. The copper layer, which appears as the darker phase is composed of several rectangular grains in the nano-metric range: < 5 nm. Despite the absence of wetting between

copper and carbon [14,15], the observed interface is quite continuous and no gaps or voids have been observed.

3.2. Composite consolidation

Table 4 summarizes the consolidation results obtained by hot-pressing. In terms of the porosity values it can be seen that the best results are obtained with SDK nanofibres and a combination of 900 °C and 35 MPa. In the case of 20 vol. % reinforcement, no open porosity is obtained. This means near perfect material. On the other hand with 40 vol. % of reinforcement both open and close porosity values are below 5 vol. %, which is still acceptable.

SEM micrographs of consolidated samples are shown in Fig. 4. Composites with 40 vol. % of Pyrograf III nanofibres are shown on Fig 4a and b. These pictures correspond respectively to sections in planes parallel and normal to the pressing direction. After consolidation, a reorientation is produced as a consequence of the uniaxial pressing. Most of the fibres are oriented in planes normal to the pressing direction. This “random planar” configuration has been observed in other works studying the consolidation of conventional micron sized fibres [16]. The effect in the case of VGCNFs is reported here for the first time. This configuration points out that 2D composites are obtained and thus the properties will be highly anisotropic. VGCNFs appear to be well dispersed into the copper matrix in all inspected areas. Comparatively, as suggested by the work by Jang and Kim [9], while studying the liquid infiltration of copper into VGCNFs from Showa Denko, there is no uniform distribution but rather areas of densely distributed VGCNFs. In addition, their manufacturing process also results in local unidirectional alignment of the VGCNFs.

Some VGCFs are in contact with others, as an effect of the high volume of reinforcement. This suggests that the percolation threshold (PT) could be reached, which is beneficial for the electrical and thermal conductivity properties. Measurement of these properties is now on-going. The samples containing 40 vol. % of VGCFs show the same degree of contact between the VGCFs, regardless of the grade/type of nanofibre. Fig 4c and Fig. 4d show samples with 20 vol. % of reinforcement and still some degree of contact is observed. This suggests that the percolation threshold is less than 20 vol. %. Furthermore, it can be seen that the etching occurred preferentially on the copper/carbon interface, as seen in Fig. 4d.

TEM images show that even though the consolidation is performed at temperatures as high as 1000 °C, the copper/carbon interface is still quite continuous (Fig. 5a). VGCFs are still well embedded into the copper matrix. Vickers's hardness was measured in samples reinforced by SDK nanofibres (ref. C4 and C5 in table 4), and in a pure copper target manufactured at the same conditions (ref. C0), in both sections parallel and normal to the pressing direction. The results are shown in Fig. 6. A considerable increase in hardness is achieved by the incorporation of VGCFs. Hardness increases with the volume fraction. The maximum increase is 34 % for 40 vol. % of VGCFs. The hardness of the composite is higher in the parallel direction, thereby indicating the anisotropy of the material. Jang and Kim [9] previously reported a good mechanical contact at the Cu/VGCFs interface, which resulted in 476 MPa tensile strength at 13 vol. % of VGCFs. Additional mechanical testing at 20 and 40 vol. % of VGCFs is also underway and will provide supplementary data to the previous work.

Additional observations at higher magnifications reveal that the matrix is still composed of copper nanograins (< 5 nm), as seen before hot-pressing (Fig. 3d). This nanocrystalline size has also

been calculated through the Scherrer formula [17], $D = k\lambda / B \cos \theta$, i.e. from a XRD profile performed on a sample with 40 vol. % of SDK nanofibres (ref. C5 in Table 4), where D is the calculated grain size, k is a constant of shape factor (0.9 value), λ is the wavelength of X-ray (1,54051 Å), θ is the angle of diffraction (21.7255 °) and B is the full width at half maximum peak of the copper (FWHM, 0.280). The grain size is thus estimated as 1.30 nm which is in accordance with the TEM observations. From this result it is possible to state that VGCFs would act as grain growth inhibitors into metallic matrices, avoiding the growth and coarsening of the grains during the heating, when the consolidation is carried-out. Similarly some grain growth inhibition has also observed by Huang and Gao while studying the sintering of BaTiO₃/Multiwall nanotube composites [18].

3.4. Oxygen content of the samples

The oxygen amount after the hot-pressing was measured in a LECO analyzer. The average amount of oxygen in the samples is 0.35 wt. %. Further coating performed without bubbling argon shows an average content of 1.34 wt. %. Heat treatments in reductive atmosphere such as hydrogen, lead to an instability of the copper coating and finally to an aggregation of the copper into particles [11]. Therefore, coating under inert atmosphere would be more suitable for reducing the amount of oxygen. Finally, a XRD profile performed on on a sample with 40 vol. % of SDK nanofibres (ref. C5 in Table 4) revealed some oxide formations, which were composed of both cuprous and cupric oxide, with the former being found in higher quantities.

3. Conclusions

Novel copper metal matrix composites reinforced by high volume fractions of VGCFs have been manufactured by electroless plating followed by hot-pressing. The copper coating is quite smooth and homogenous for thin coatings, but on the other hand was seen to grow dendritically for thicker coatings. Copper deposition has also been observed on the inner walls of the VGCFs. After consolidation the VGCFs are homogeneously distributed within the copper matrix. Highest densification with a residual porosity of only 1% has been achieved with coated 20 % Showa Denko nanofibres at 35 MPa and 900 °C. Despite the lack of wetting between copper and carbon, the interface is continuous in both the composite powders and the consolidated material. It has also been seen that the matrix is composed of nanometric grains (< 5 nm), even after consolidation by hot-pressing, suggesting that VGCFs act as grain growth inhibitors. Finally it has been seen that only a minimal amount of oxidation is present in the final composite, being primarily cuprous oxide. Characterisation of mechanical and transport properties is currently under way.

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Figure Captions

Fig. 1. Electron microscope images of the uncoated VGCFs. (a) SEM image of Pyrograf III, (b) SEM image of SDK nanofibres., (c) TEM image of SDK nanofibres and (d) SEM image of GANF1

Fig. 2. SEM images of coated VGCFs. (a) Pyrograf III 20 vol. % composite (ref. E1), (b) SDK 40 vol. % composite (ref. E4), (c) SDK 40 vol. % composite at higher magnification and (d) GANF1 40 vol. % composite (ref. E6)

Fig. 3. TEM images of coated VGCFs. (a) Pyrograf III 20 vol. % composite (ref. E1), (b) Coating of the inner cavity of Pyrograf III 40 vol. % composite (ref. E2) (c) Coating of GANF1 20 vol. % composite (ref. E5) (d) Copper/Carbon Interface on Pyrograf III 40 vol. % composite (ref. E2)

Fig. 4. SEM images of consolidated samples. (a) Pyrograf III 40 vol. % composite (1000 ° C and 25 Mpa, ref. C2) in parallel direction to the pressing, (b) Pyrograf III 40 vol. % composite (1000 ° C and 25 Mpa, ref. C2) in normal direction, (c) SDK 20 vol. % composite (900 ° C and 35 Mpa, ref. C4) in parallel direction, (d) SDK 20 vol. % composite (1000 ° C and 25 Mpa, ref. C4) at higher magnification

Fig. 5. TEM images of consolidated samples. (a) Pyrograf III 20 vol. % composite (1000 ° C and 25 Mpa, ref. C1), (b) Magnification of the matrix phase in Pyrograf III 40 vol. % composite (1000 ° C and 25 Mpa, ref. C1).

Fig. 6. Influence of the volume fraction of reinforcement on the Vickers hardness of composites reinforced with SDK nanofibers.

Tables

Table 1
Properties of VGCNFs

Reference	Diameter (nm)	Length (μm)	Surface Area (m^2/g)
Pyrograf III	60-150	30-100	50-60
SDK.	150	100-200	13
GANF1	20-200	> 30	150-200

Table 2.
Characteristics of Catalysing and Plating baths.

Step	Composition	Concentration	Time
Sensitization	HCl	40 ml/l	30 Min
	SnCl ₂	10 g/l	
Activation	HCl	0.5 ml/l	30 Min
	PdCl ₂	0.25 g/l	
Plating	CuSO ₄	10 g/l	Up to end of reaction
	NaK(COO) ₂ (CHOH) ₂ 4H ₂ O	50 g/l	
	NaOH	10 g/l	
	HCHO	15 ml/l	
	PAA	140 $\mu\text{l/l}$	

Table 3
Coated samples

Reference	Nanofibre Type	Vol. % Filler
E1	Pyrograf III tm	20.81
E2	Pyrograf III tm	39.36
E3	SDK	19.21
E4	SDK	38.57
E5	GANF1	21.54
E6	GANF1	39.00

Table 4
Consolidated samples

Ref.	Nanofibre Type	Vol. % of filler	Temperature (°C)	Pressure (MPa)	Density (g/cm^3)	Porosity %	Open Porosity %
C0	-	0	900	35	8.85	0.22	0.00
C1	Pyrograf III tm	20	1000	25	7.22	3.23	1.74
C2	Pyrograf III tm	40	1000	25	5.54	7.12	6.40
C3	SDK	20	700	35	7.15	2.27	1.68
C4	SDK	20	900	35	7.31	1.14	0.00
C5	SDK	40	900	35	6.11	2.15	1.87

Figure 1

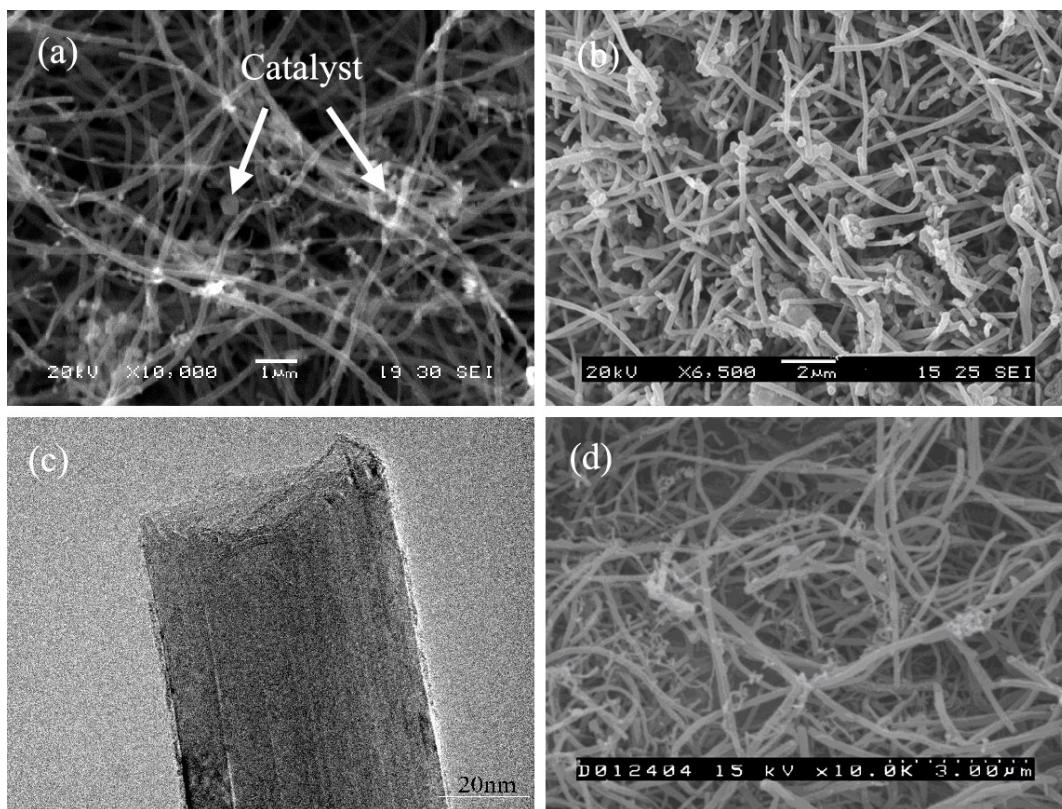
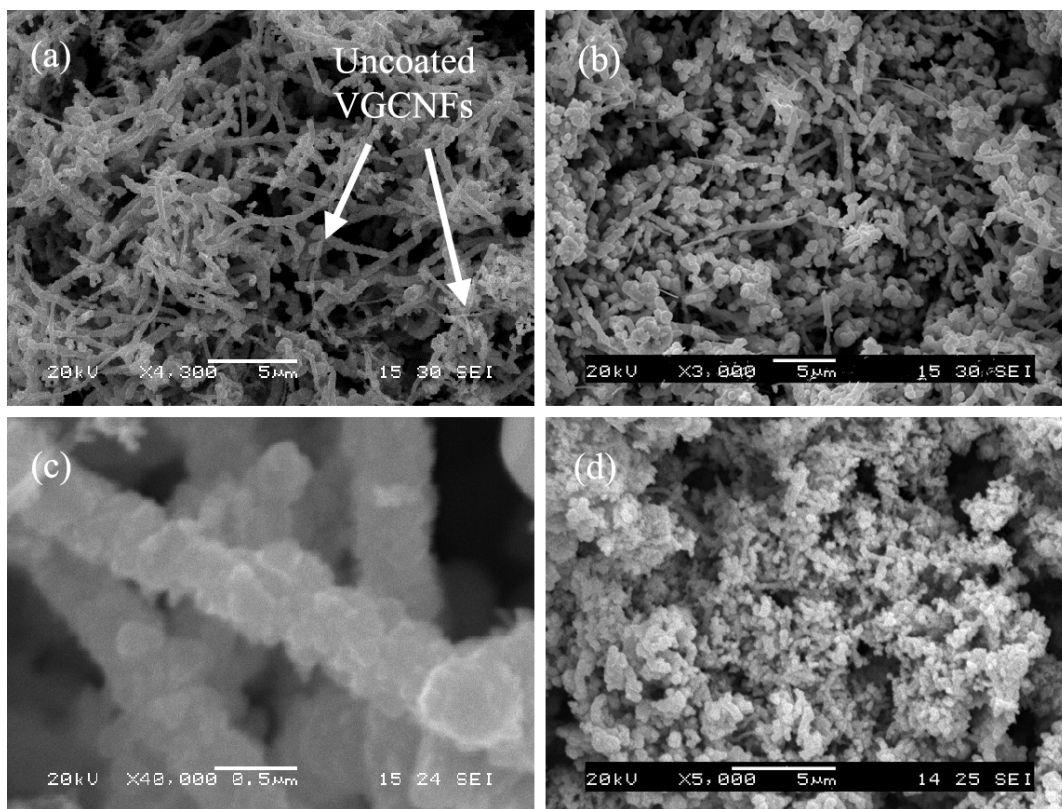


Figure 2



ACCEPTED

Figure 3

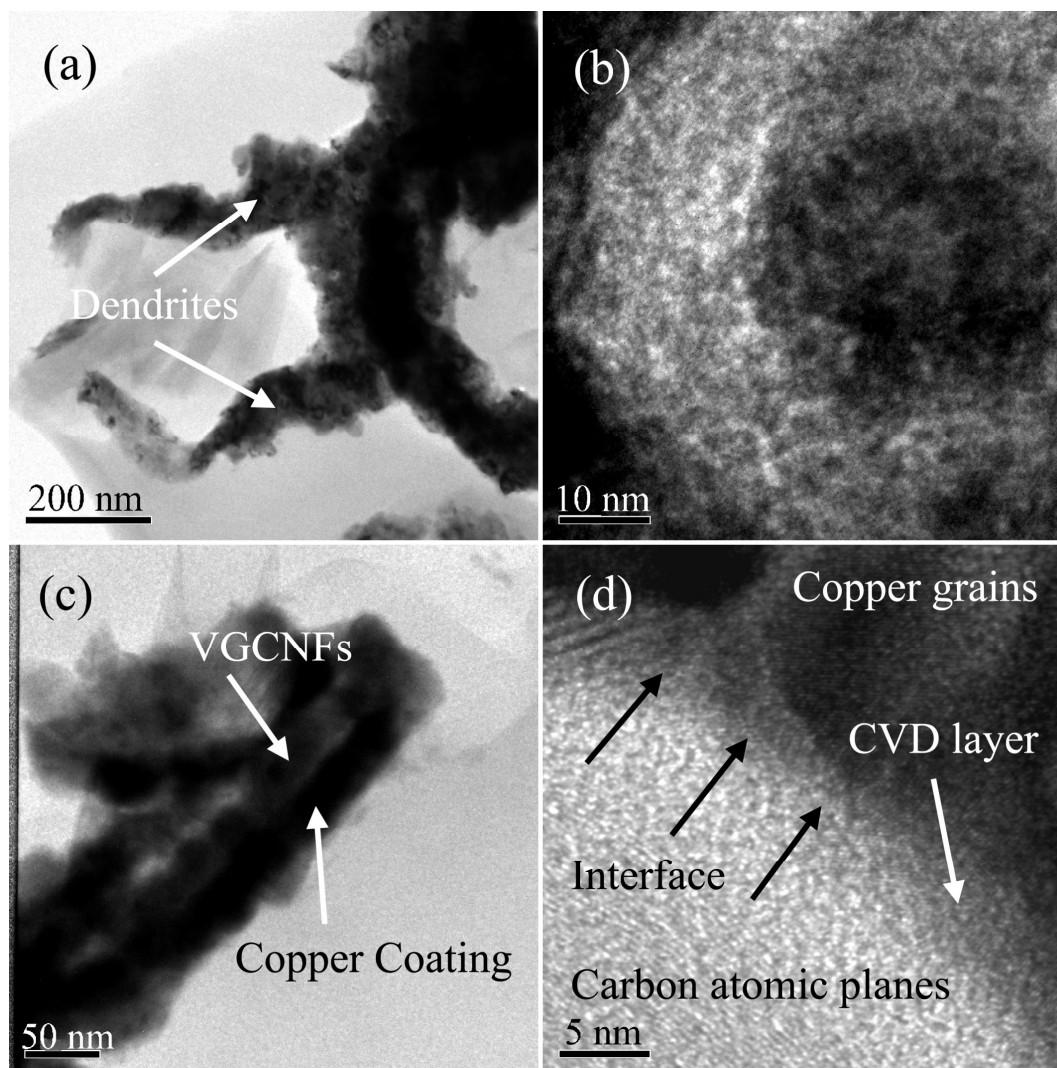


Figure 4

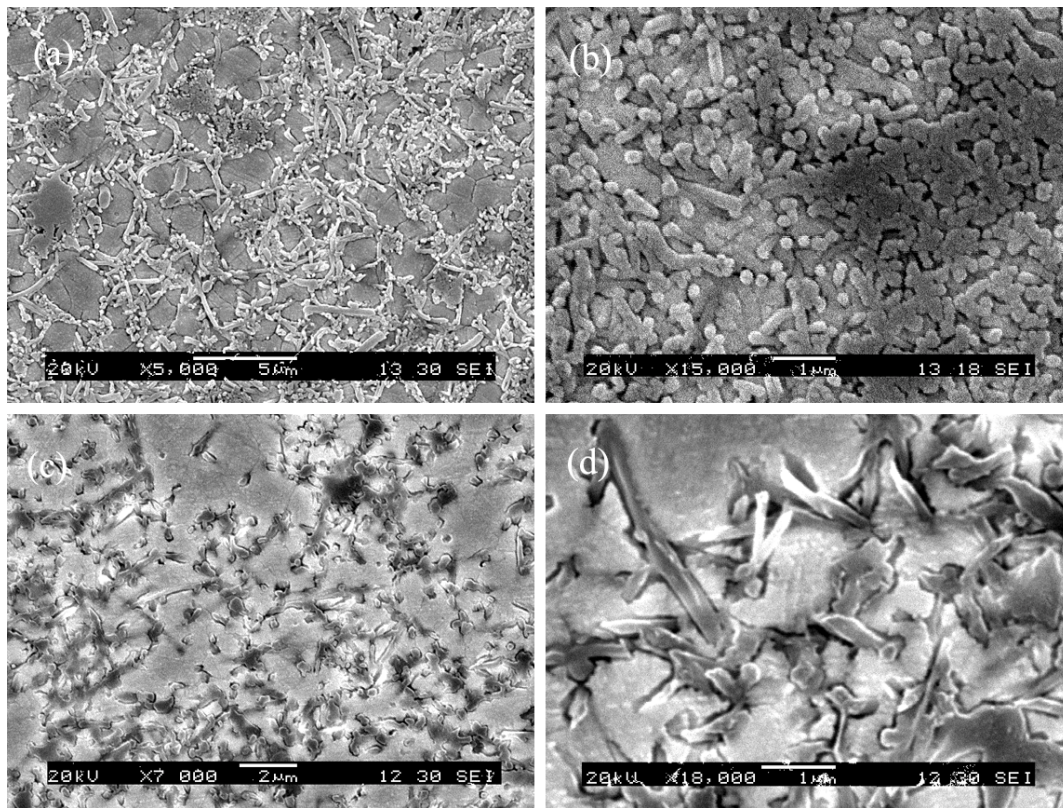
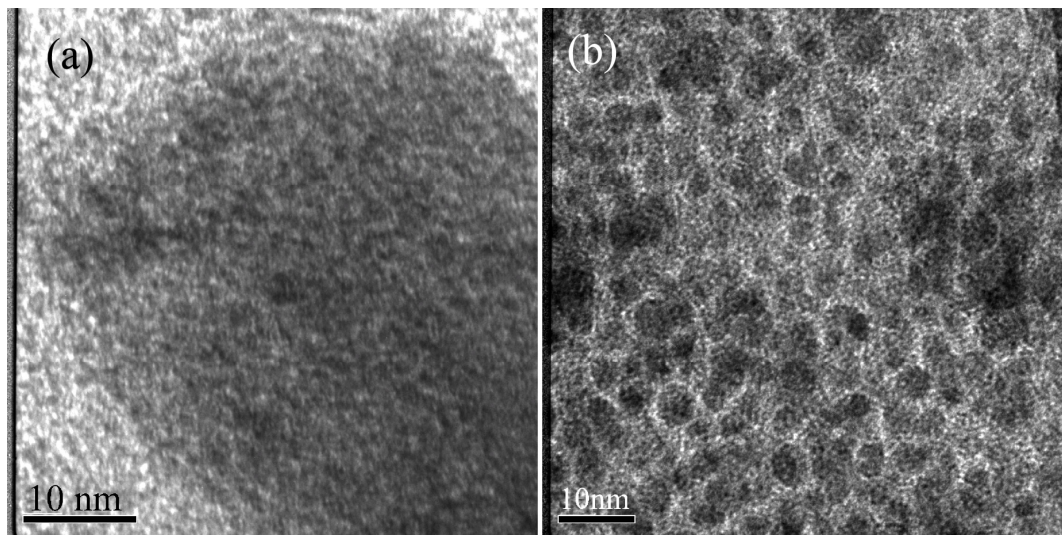
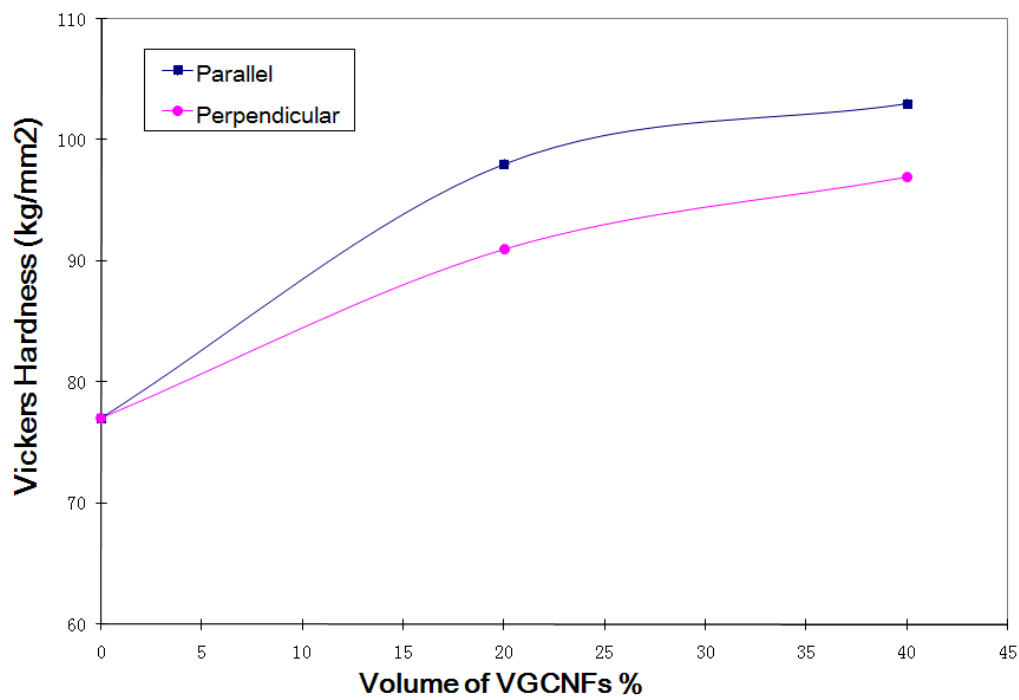


Figure 5



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Figure 6



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