

# IN-SITU SYNTHESIS OF CARBON NANOTUBES ON FUNCTIONAL SUBSTRATES AND APPLICATIONS IN NANO-COMPOSITE

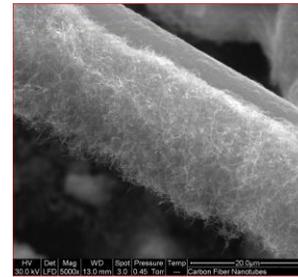
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## Introduction

Carbon in its form as nanotubes has outstanding mechanical, electrical and thermal properties [1-4]. This has made carbon nanotubes (CNTs) an excellent candidate material for applications as reinforcement in advanced high performance composites. It has been shown that the remarkable properties of these nano constituents can be transferred to macro-level behavior of materials such as polymers, metals and ceramics [5] by incorporating the nanotubes as reinforcement in their composites. The properties of the products, however, are largely influenced by the quality of the CNTs, the choice of the matrix material and the nature and properties of the CNT/matrix interface [6]. Limitations in achieving the fullest benefits from the incorporation of CNTs in composites also arise due to the difficulties in dispersing the nanotubes uniformly into the matrix and clustering of the CNTs into bundles. Proper dispersion and alignment of the CNTs along a preferred orientation will help in achieving superior properties in the direction of orientation of the tubes [7]. Considerable research and development efforts have focused on each of these problems and innovative solutions have been proposed [8]. A novel method of incorporating MWCNTs into polymer matrix composites, consisting of in-situ synthesis of CNTs directly on the surface of long carbon fiber and using these fibers with a nanocoating of CNTs in composites, was developed by our group and employed for fabricating polymer matrix composites. Due to the presence of CNTs on the fiber surface significant improvements in properties were achieved in relation to plain carbon fiber reinforced composites [9, 10]. Individual fibers in a tow or a woven fabric showed a uniform nanocoating of CNTs. Short lengths of CNTs oriented perpendicular to the fiber surface formed initially and as growth continued these developed into a network of CNTs around individual fibers in the form of a sheath [Fig.1].

In the first part of the present work CNTs have been synthesized on carbon fibers and these fibers are used as reinforcement after chopping into short lengths. Aluminum metal has been used as the matrix material and composite samples have been produced using powder metallurgy route. In the second part of the work CNTs are synthesized directly on aluminium powder particles. The CNT coated Al particles are then mixed with plain aluminum powder into which the Al/CNT master powder is dispersed. Composite samples have been prepared and tested to assess the effectiveness of this approach in achieving uniform dispersion of CNTs as reinforcement in the matrix.



**Fig. 1** Morphology of carbon nanotubes grown directly on the surface of carbon fibers.

## Experimental

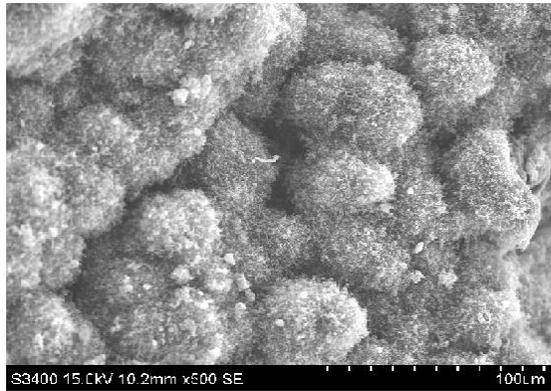
Each of the two parts of the present work involved two steps. The first step was in-situ synthesis of the CNTs followed by the second step consisting of preparation of composite samples by powder metallurgy route. In-situ synthesis of CNTs was carried out on carbon fibers by chemical vapor deposition process using acetylene as precursor and nickel nanoparticles as catalysts. Process details for the CNT synthesis on carbon fibers are described in ref [10]. The sizing on the carbon fibers was first removed using concentrated nitric acid. Fibers were cleaned in distilled water, and soaked in a 0.25 N Nickel chloride salt solution for an hour, dried, and placed in a tubular furnace. Reduction of the salt particles was carried out at 500<sup>0</sup> C in hydrogen atmosphere giving rise to the formation of catalyst nanoparticles. CNT synthesis was then carried out at 750<sup>0</sup> C for one hour by using acetylene as precursor and argon as a carrier gas. The carbon fibers coated with carbon nanotubes were chopped into short lengths and the fiber dust thus obtained was used as reinforcement. Commercially available aluminum powder was used as matrix for preparing the composite samples.

In the second set of experiments nanotubes were synthesized directly on aluminum powder surface [Fig.2]. The powder was first cleaned to remove the oxide layer and then anodized again using sulfuric acid to develop a porous film of aluminum oxide on the surface of the particles. Nickel was used as catalyst. Growth was carried out at 650 degree Celsius for 30 minutes using the same equipment as was used for the synthesis of CNTs on carbon fibers.

## Preparation of the composite samples

Composite samples were prepared with varying additions of SCF/CNT (short carbon fiber-carbon nanotube complex) or Al/CNT (aluminum powder coated with a nanocoating of CNTs) powder concentrations. The aluminum powder to be used as matrix was mechanically milled in argon atmosphere.

Green compacts of 17 mm diameter were prepared by placing the powder mix in a closed die by uniaxial loading in a hydraulic press. The green compacts were sintered in nitrogen atmosphere at 500<sup>0</sup> C for four hours. Hardness and compression tests were carried out.



**Fig. 2** Aluminum powder particles after coating with carbon nanotubes.

Samples without any addition of CNTs were also prepared under identical conditions and tested. Samples thus tested were annealed for one hour at progressively increasing temperatures and hardness was measured after each exposure to these different temperatures.

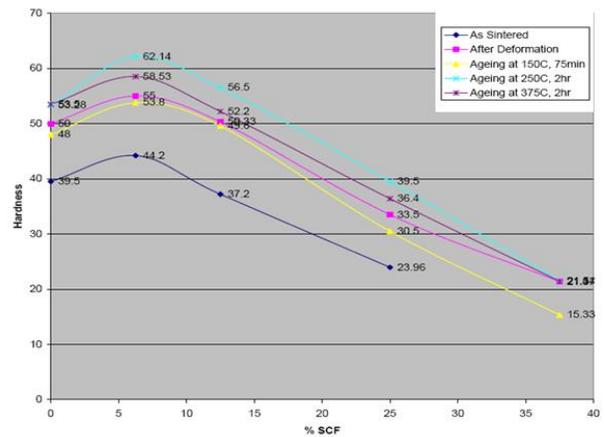
### Results and Discussion

It is seen that the hardness increased initially up to about 5wt percent addition of the reinforcement but thereafter a continuous drop in the hardness of the samples occurred. The drop in hardness is attributed to the formation of clusters of SCF/CNT particles. Dispersion of the nanotubes is not effectively achieved at microscopic level during the sample preparation for higher concentrations of CNT additions. Samples were found to get work hardened during deformation. Low temperature annealing after deformation resulted in slight but consistent decrease in hardness in samples at all concentration levels of the CNTs. Annealing at higher temperatures, however, increased the hardness levels at intermediate temperatures and then decreased at the higher temperature used in the present work. Other than the catalyst particles which remained embedded into the CNTs after their growth, there were no additions of any constituent which could give rise to ageing processes involving precipitation hardening and over ageing in the composite samples. The increase in hardness after ageing treatment may be attributed to this. Additions of CNTs with aluminum powder as carrier showed similar trend.

### Conclusions

The process used for in-situ synthesis of CNTs has given satisfactory quality of nanotubes which remain attached to the surface of the substrate. The substrates used in the present work can thus be used as carriers of the CNTs. The nanotubes are multiwall type with diameters varying between 20 and 150 nms and lengths up to few microns. Clustering of the nanotube carriers has been observed in the matrix, both, in the case of SCF/CNT and Al/CNT additions at higher levels of their contents.

Hardness values and compressive strength of the composites increased with the addition of the SCSF/CNTs and Al/CNT as reinforcements at low concentrations. The properties deteriorated at higher levels of the reinforcement



**Fig. 3** Hardness values measured on composite samples as a function of CNT contents and annealing temperatures.

additions. The clustering of particles appears to impose limitations on the uniformity of the distribution of CNTs at microscopic level. This also seems to lead to the formation of pores which can act as stress raisers and also interfere with the process of sintering. The full strength levels cannot be achieved and the reinforcement cannot make an effective contribution of to the strengthening of the matrix material.

The observations indicate that there is scope for further improvements in the process developed for using carriers with in situ synthesized CNTs and their uniform incorporation in metal matrix composites at microscopic level.

### References

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