

# Controlled Surface Treatment of Mild Steel with Carbon Nanotubes at Austenitic Temperature

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**Abstract**— This study reports a novel nanocarburization of mild steel using carbon nanotubes at specified austenitic temperature. Carbon nanotubes synthesized in a horizontal chemical vapour deposition reactor were used to enhance the surface hardness of mild steel at 750°C austenitic temperature for 40 minutes carburization period. Various samples of known composition of mild steel were carburized with as-synthesized carbon nanotubes, purified carbon nanotubes and amorphous carbon. The resultant carburized samples were subjected to surface hardness test, and the results of the analyses indicated improved surface hardness having the highest peak surface hardness value of  $173.842 \pm 4.89$  GPa with the purified carbon nanotubes, followed by as-synthesized carbon nanotubes with  $162.56 \pm 1.55$  GPa; and the least was the amorphous carbon with  $155.74 \pm 4.28$  GPa. These values were still higher than that of the original metal substrate, which was  $145.188 \pm 2.66$  GPa. The enhanced surface microhardness displayed by the carbon nanotubes can be attributed to their nano-sizes which assisted in increased diffusion of these materials at the austenitic temperature under study coupled with higher mechanical properties exhibited by these carbon materials.

**Keywords**—Carburization, mild steel, carbon nanotubes, amorphous carbon, surface hardness

## I. INTRODUCTION

Mild steel is perhaps the most common structural metallic material due to its relatively affordable cost and good mechanical properties which has made it versatile in many technological applications [1]. The properties of this alloy are determined by its chemical composition that usually varies between 0.1–0.29% carbon content. Mild steel is characterized by good ductility but with poor wear resistance, hence as an important structural material mostly used in the development of modern industry which is expected to meet increasing and stringent requirements for mechanical properties, the need for strengthening and modification of this alloy is highly desirable [2].

Several studies have been reported on wear and fatigue defects at surfaces of this material thereby creating failure of its structures [3–5]. These defects have necessitated several

modification processes to improve and increase its strength, surface hardness and its part design to extend its service life time while the chemical composition remains unchanged relative to the core [6–9]. They are designated as carburizing or casehardening steels which depend on the nature of the part; the properties required and preferred processing methods [10]. Hence the need for surface modification with carbon at nanosize which can be referred to as surface nanocarburization is expected to provide a new approach to deepen the research and widen the application of nanomaterials.

Carbon nanotubes (CNTs) synthesis were first reported by Iijima [11] via arc discharge evaporation method [12] and they have received a great deal of attention in many research fields because of their unique properties such as surface property, high tenacity, high electron conductivity which have enabled them to be useful in many selected applications till date [13]. Their exceptional mechanical properties with a well-defined primitive cell, surface, possibility of transport including light mass and ability to improve strength and stiffness [14, 15] make them potential modifying materials for scientific studies as well as a wide range of applications including high strength composites [12, 16]. All of these characteristics make CNTs a good reinforcement as there have been reports of buckling in mild steel due to poor strength retention and possible slenderness, hence the need for an innovative way of increasing its surface hardness without sacrificing other properties [17, 18].

Amorphous carbon on its own has attracted enormous interest in recent years because of the emergence of nanotechnology. It has been extensively used in the last decades for several applications such as field emission display, surface modification and other areas due to its unique properties such as high hardness, low friction coefficient, and chemical inertness [19, 20]. It can be easily deposited at ambient temperature, implying that it could be conveniently deposited on compliant substrates and can be easily combined with other materials. Its compatibility and surface properties makes amorphous carbon a good choice of reinforcement and its chemical inertness also makes it suitable for most surface modification [21–23].

This study investigated and compared the effect of the surface carburization of mild steel with carbon nanotubes to amorphous carbon under an austenitic temperature of 750°C at 40 minutes carburization time. The synthesis, purification and characterization of the CNTs employed were also studied.

## II. MATERIALS AND METHODS

Carbon nanotubes were prepared in a horizontal chemical vapour deposition (CVD) reactor using bimetallic Fe–Co metal catalyst prepared on calcium carbonate support. The preparation of the bimetallic catalyst and detailed

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description of the CVD reactor have been described elsewhere [24 – 26]. In order to synthesize the CNTs, a specified quantity of the prepared catalyst was carefully spread in a quartz tube to form a thin layer, placed in the centre of the quartz tube and inserted into the reactor. The reactor was placed in tubular furnace which was heated from room temperature to 700°C at 10 °C/ min under the flow of nitrogen gas at 180 ml/min in order to purge and heat up the reactor. At the set temperature of 700°C, acetylene gas was introduced at a constant flow rate of 90 ml/min to begin the catalytic decomposition of the gas at the reaction temperature. The flow of the acetylene was stopped after 60 minutes reaction time and the furnace was left to cool to room temperature under the continuous flow of nitrogen. The boat was then removed from the reactor and the carbon deposit produced was collected, weighed and recorded.

The as-synthesized CNTs were purified using a single step acid treatment [27, 28] by soaking measured quantity (about 0.5 g) of the raw CNTs in 100 ml of 55% HNO<sub>3</sub> (Merck Chemicals, SA). The CNTs and acid mixture was stirred vigorously for 4 hours at room temperature in order to remove the amorphous carbon, traces of catalysts and their support. The resulting mixture was soaked in 200 ml of water for 12 hours and later thoroughly washed with distilled water until a pH neutrality was achieved. The purified CNT sample was dried in an oven at a temperature of 110°C overnight and characterized together with the as-synthesized samples using the SEM and TGA. Mild carbon steel samples with chemical composition C=0.14–0.2; Mn 0.6–0.9; P<0.04; S<0.05; Fe balance, were prepared into sizes of 10 × 10 × 6 mm and polished with a surface grinder to obtain even and uniform surfaces. The mild steel samples were carburized at 750°C for 40 minutes with carbon nanotubes and amorphous carbon obtained by pulverizing coal in a laboratory muffle furnace, similar to the process employed by some authors [29, 30]. The carburizing process consisted of heating up to this temperature (750°C) at a speed of 10 °C/minute, at varying periods of time to effect a defined number of boost and diffusion processes at this temperature and cooling to room temperature under the same condition. The cross-sections of the as-received and carburized mild steel samples were carefully polished after hot mounting in struers polyfast resins while grinding was carried out to achieve a flat surface and to remove scratches using struers 320, 600 and 1200 grit, silicon carbide paper. The samples were then polished for 10 minutes using struers MD Largo with 9 and 6 μm and MD Dac with 3 μm diamond paste and 1 μm with oxide polishing suspension (OPS) then rinsed in ethanol and dried. The samples were etched with natal 2% solution of ethanol and nitric acid solution to reveal the microstructures. The as-received and carburized surfaces of the metal samples were observed with the Olympus SC50 optical microscope and the hardness distribution of the carburized layer was inspected with a Vickers FM 700 micro-hardness tester.

### III. RESULTS AND DISCUSSION

#### A. Scanning electron microscopy (SEM)

The SEM images of the as-synthesized and purified CNT samples are shown in Fig. 1. The images show the CNTs with a spaghetti-like orientation with several millimeters long and the diameters of the CNTs are

distributed in the range of 42-52 nm which is similar to the images obtained by Wanga et al, [31].

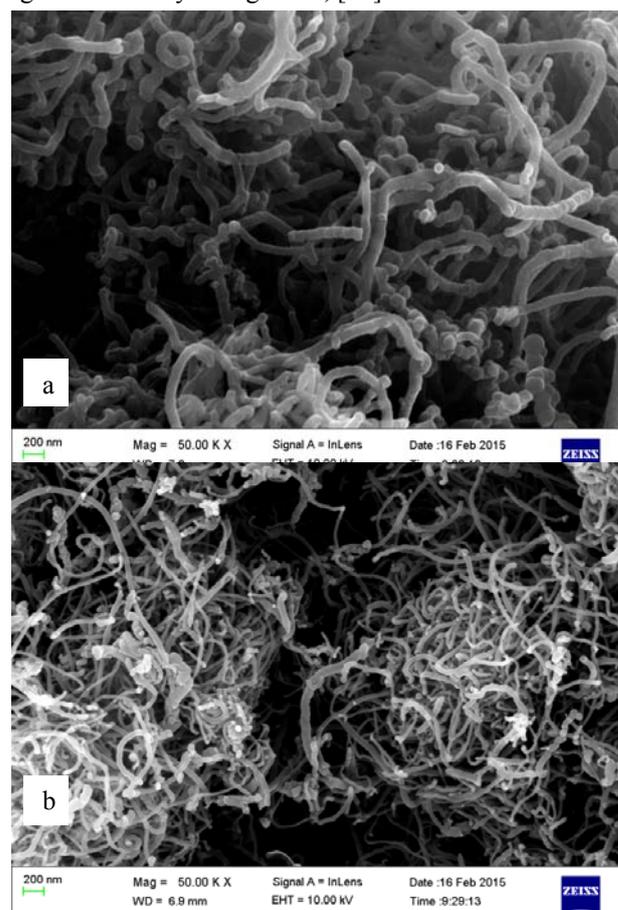


Fig. 1. SEM images of (a) as-synthesized and (b) purified CNT samples

Fig 1a shows a dense network of carbon material with a vast amount of CNTs that are tightly bonded and entangling each other with a diameter of 52.99 nm. Fig 1b reveals the spaghetti strand-like structure with a node-like close end and the other end is capped with the catalyst particles (with varying lengths and a spongy appearance). It can be observed that the purified CNT sample shows a lower degree of entanglement as compared to the raw CNT (Fig. 1a) and this can be attributed to the purification processes the former have undergone which assisted in separation of their strands.

#### B. Thermogravimetric analysis (TGA)

Fig. 2 shows the plotted TGA data for the as-synthesized and purified CNT samples. The TGA was conducted under oxidizing environment using oxygen gas. The as-synthesized CNT sample shows that the sample was thermally stable to 503°C where decomposition started to take place with a mass loss of 78%. This can be attributed to the presence of impurities possibly from the support and catalyst used in the sample [32]. The purified sample shows a significant mass loss of 85% at a thermally stable temperature of 550°C before decomposition commenced at temperatures higher and this was maintained till 600°C. The percentage of the residue left showed that CNTs are relatively pure after the acid treatment which reduced the remaining residue to about 15% and that treatment of CNT in acid for 4 hours was enough to remove most catalyst and support residues as well as any other impurities. The

initiation and decomposition temperatures of the purified CNTs are higher than those of the as-synthesized CNTs and this is ascribed to the reduction of catalyst particles and amorphous carbon impurities [33].

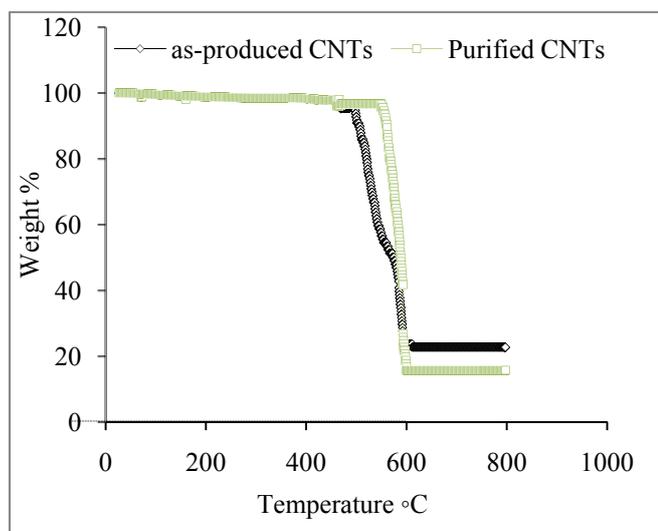


Fig. 2. TGA of as-synthesized and purified CNT samples

The rate at which the sample decomposed increased from the temperature of 593°C of the as-produced CNTs to 598°C in the purified CNTs shows that the structure of carbon was not damaged by the acids used which in turn improved the thermal stability of the carbon nanotubes [34].

Fig. 3a shows the starting microstructures of the mild steel sample, which consists of coarse-grained ferrite-pearlite microstructures, with the light coloured region representing the ferrite while the dark region represents the pearlite (a mixture of ferrite and iron carbide). The images in Fig. 3b-d show the dissolution of the pearlite into the austenite phase, which forms at the pearlite boundary. The layer closest to the carburized surface shows a nucleation of the pearlite transforming into austenite with varying grain sizes that are slightly bigger in the micrographs carburized with amorphous carbon (Fig. 3b). This can be attributed to the different sizes of the carbon powders used as amorphous carbon is in micrometre while the CNTs are in nanometre.

The grain boundaries in the images as can be seen are all clearly visible which can be attributed to the slow furnace cooling from the austenitic temperature of 750°C to room temperature. The formation of the austenite from the dissolution of the pearlite at the surface is controlled by the diffusion rate of the carbon atoms showing some pearlitic regions, which are not totally dissolved. Hence, leading to formation of high ferrite hardness as the carbon atoms move from areas of dissolving pearlite to regions around the ferrite grains with some inclusions and decrease in pearlite.

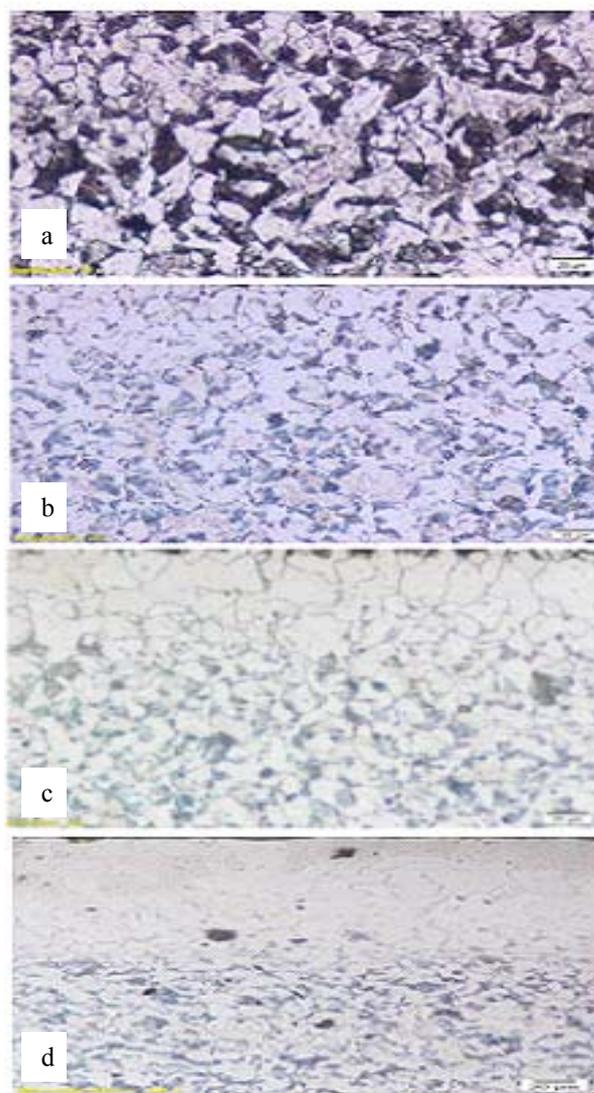


Fig. 3: Optical images of (a) as-received mild steel (b) amorphous (c) raw CNTs and (d) purified CNTs carburized mild steel at 750°C. (Mag = 20 μm)

The heat treated samples have ferritic matrices with irregular grain sizes which could be due to the distribution of the austenite from a carbon enriched zone of the ferrite from the dissolution of the pearlite grains. However, it can be observed that a more defined austenite grain structure is obtained especially in those samples carburized with CNTs (Fig. 3c-d). This may be attributed to the increased number of sites, which are suitable for the nucleation of ferrite and also the recrystallization of carbon with the initial austenite structure and also present in the grains formed are inclusions which might be as a result of the precipitating carbon atoms.

### C. Analysis of microhardness

The detailed hardness distribution in the carburization layer of the mild steel as a function of time and temperature is illustrated in Fig. 4. Each hardness value represents a mean of five indentations and the average hardness was calculated.

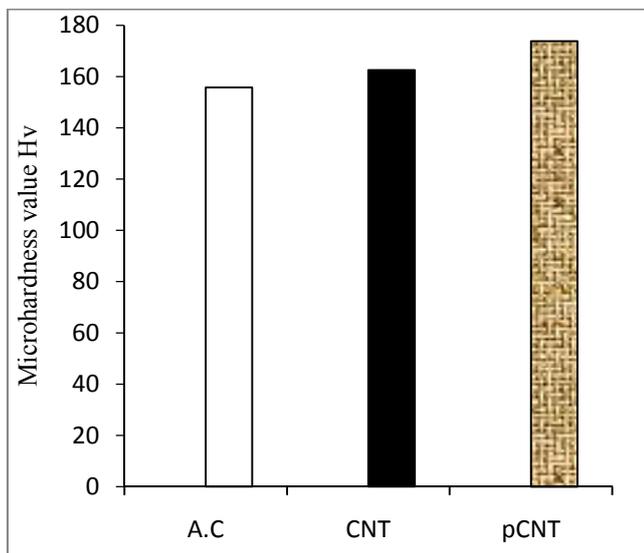


Fig. 4. Comparison between the Vickers microhardness obtained for amorphous carbon, CNT and pCNT

Fig. 4 illustrates the Vickers Hardness (HV) of the mild steel samples with the various reinforcements used in carburizing at a constant temperature of 750°C as a function of time. A Vickers microhardness of 155.74 ± 4.28 GPa with a load of 0.5 kg was obtained for amorphous carbon. The CNT showed a steady increase in its microhardness over the amorphous carbon with a value 162.56 ± 1.55 GPa while the purified CNT has the highest hardness value of 173.842 ± 4.89 GPa and this can attributed to the effect of purification treatment on the structural properties of CNTs which resulted in more available surface area and less concentration of residual catalyst inside the grown materials. The microhardness values, as compared amongst the reinforcements, showed that carburization with the purified CNT displayed the higher value when compared with those of the as-synthesized CNT sample and the amorphous sample. In addition, carburization with the amorphous carbon has the least hardness value. The hardness values of the mild steel samples reinforced with different forms of carbon show an improved surface hardness as compared to the original mild steel substrate of 145.188 ± 2.66 GPa.

#### IV. CONCLUSIONS

A novel method termed “nano-carburization” was adopted in this study to improve the surface hardness of mild steel at austenitic temperature using both raw and purified carbon nanotubes. The microhardness and microstructural analyses of the resultant carburized mild steel samples were investigated and compared with the conventionally employed amorphous carbon and the following conclusions were drawn from the study.

- The as-synthesized CNT sample showed purity percentage of 78% while that of the purified sample showed 85% with no damage to the CNTs with diameter ranging from 42-52 nm.
- The growth process of the CNTs carburized mild steel samples has variations in the microstructures indicating rapid growth of austenite as a result of the rapid diffusion of carbon at high temperature.
- The microhardness values obtained from the reinforcements used showed increase in hardness value from 155.74 ± 4.28 GPa obtained for amorphous carbon

CNT with 162.56 ± 1.55 GPa and the purified CNT has the highest hardness value of 173.842 ± 4.89 GPa while the original substrate mild steel sample has a surface hardness of 145.188 ± 2.66 GPa.

- The reinforcements used in this study are promising enough in increasing the mild steel surface hardness as a little amount has resulted in improved surface hardness with purified CNT as the best overall reinforcement as it has the highest surface microhardness in this study.
- The mechanism CNTs surface hardness enhancement is due to more rapid diffusion rate compared to the amorphous carbon which was attributed to its nanosize and their high capability to alter and improve most materials even with addition at very small fractions and specifically, their superior strength, and high surface area to volume ratio which was also observed in their grain sizes.

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