Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 97 (2014) 1422 – 1433

Procedia Engineering

www.elsevier.com/locate/procedia

12th GLOBAL CONGRESS ON MANUFACTURING AND MANAGEMENT, GCMM 2014

Forming, Characterization and Evaluation of Hardness of Nano Carbon Cast Iron

K. Padmanabhan, K. Sai Sirisha

Centre for Excellence in Nano Composites

School of Mechanical and Building Sciences, VIT University, Vellore-632014, Tamilnadu, India.

Abstract

This investigation deals with forming nano carbon cast iron with the stir casting method, its x-ray and microscopic characterization and measurement of Rockwell C scale hardness before and after heat treatment . Atom Force Microscope and X Ray characterization were carried out on the multi walled carbon nano tube reinforcements as well as the nano carbon cast iron formed by adding the nano carbon with the grey cast iron. As the nano carbon reinforcements tend to agglomerate in the cast iron eutectic melt , prior sonication and coating with copper were done to prevent agglomeration, dissolution and oxidation of nano carbon . Soft and ductile α- ferrite phase was seen to form as a result of the stress relieving heat treatment thereby explaining the lower hardness values obtained compared to the as cast nano cast iron .

Keywords: MWCNT; Nano carbon cast iron; Stir casting, Copper coating; X ray characterization; Atom Force Microscope; Rockwell C Scale Hardness.

---

* Corresponding author. Tel.:+ 91-416-220-2256; fax:+91-416-224-3092.
E-mail address: *padmanabhan.k@vit.ac.in*

Selection and peer-review under responsibility of the Organizing Committee of GCMM 2014
doi:10.1016/j.proeng.2014.12.424

1. Introduction

Great attention has recently been paid to the domain of nano-structured materials. Especially, carbon nanostructures are of considerable marketable importance with curiosity growing more and more rapidly over the decade [1]. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes are made with length-to-diameter ratio of up to 132,000,000:1, knowingly larger than any other material. Cylindrical carbon molecules have uncommon mechanical properties, which are useful; in forming nano composites with superior strength and stiffness. Carbon nanotubes are classified as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). MWCNT are mainly prepared with concentric cylindrical graphitic tubes. They are archetypally 100 times lengthier and outer diameters are typically in the tens of nanometers in dimension. Although it is very easy to produce quantities of MWCNTs than SWCNTs, their structures are lesser understood than SWCNT because of more variety and greater complexity [2].

Cast iron is formed from pig iron , and it usually refers to grey cast iron. It also recognises a large collection of Fe alloys which freeze with a eutectic. Carbon, Manganese and Silicon are the chief alloying elements in a low carbon content iron called as steel. The compositions of most cast irons are around the eutectic point of the Fe-C system, the melting temperatures at about 1,143 °C and a carbon weight percentage of 4.3 % [3]. Cast irons reinforced with nano-sized carbon (MWCNT) tubes are an attractive group of next generation advanced materials, which can be extensively used for high impact applications such as automotive, military, aerospace and machining. Though there are some reports of investigations pertaining to nano carbon steel produced by tailoring the carbon present in the steel in to a nano phase structure [4,5], publications that effectively use the carbon nano tubes to reinforce steel or cast iron are scanty mainly due to processing problems. These nano composites can be designed with improved physical and mechanical properties such as superior strength to weight ratio, good ductility and toughness, high tensile strength, high modulus of elasticity , excellent wear resistance, excellent corrosion resistance, high temperature creep resistance and better fatigue strength.

This investigation deals with the forming MWCNT nano carbon reinforced cast iron with a stir casting method, its x-ray and microscopic characterization and measurement of Rockwell C scale hardness before and after heat treatment (of the Nano Carbon Cast Iron or NCCI) . Atom Force Microscope (AFM) and X- Ray characterization were carried out for the multi walled carbon nano tube reinforcements as well as the nano carbon cast iron formed by adding the nano carbon with the grey cast iron.. As the nano carbon reinforcements tend to agglomerate in the cast iron eutectic melt, prior sonication and coating with copper was done to prevent agglomeration and oxidation of nano carbon . The as cast samples were either cooled naturally or heat treated at 550 ºC and annealed, machined down to size and the Rockwell C scale hardness measured. Stress relieving heat treatment was seen to produce a soft and ductile α-ferrite phase sans graphitization that exhibited lower hardness values compared to the as cast NCCI.

2. Experimental Procedure

2.1 Characterization of MWCNT

The MWCNT processed through CVD, obtained from Quantum Materials Corporation, Bangalore, with a bulk density of 0.2 to 2.2 g/cu.cm and an average density of about 1.5 g/cu.cm were X rayed and observed under the AFM (Atom Force Microscope) to determine their structure further, prior to their use as a reinforcement in the grey cast iron. The specifications of the X Ray equipment [6] were as follows;

Make	:	BRUKER, Germany.
Model	:	D8 Advanced.
Source	:	2.2KW Cu anode, Ceramic x-ray tube.
Detector	:	lynx Eye detector (silicon strip detector).
Beta Filter	:	Ni Filter.
Sample Holder	:	Zero background and PMMA sample holder.

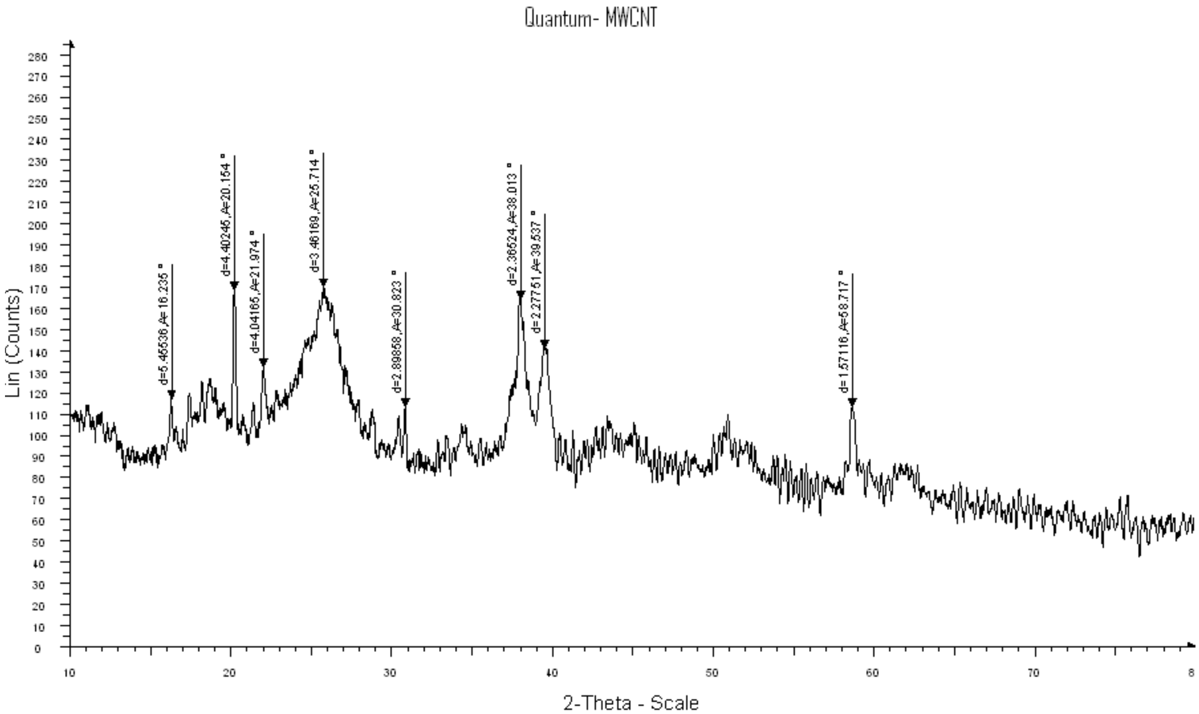

Figure 1. X Ray diffraction pattern of MWCNT showing impurities.

From the X Ray diffraction pattern in Figure 1 , it was inferred that the procured MWCNT had certain impurities like SiO_2 and Fe. The (020) and (022) facets of the as deposited MWCNT were prominently detected.

The Atom Force Microscope (AFM) was used to find the surface topography of the MWCNT clusters in the contact tapping mode. In the static force operating mode, the bend of the cantilever, due to the force acting on its tip, was measured using a laser beam deflection system. An image of the surface is made by recording the sample height as the tip is scanned over the sample surface in the X and Y directions. From the AFM observations seen in Figures 2 and 3, it was inferred that the MWCNT had dimensions between ~ 50-100 nm in diameter and ~ 30 µm in length. The clusters of hundreds of such MWCNT s which were larger, could be observed through an optical microscope. Hence the need for sonication and copper coating prior to incorporation in the cast iron matrix.

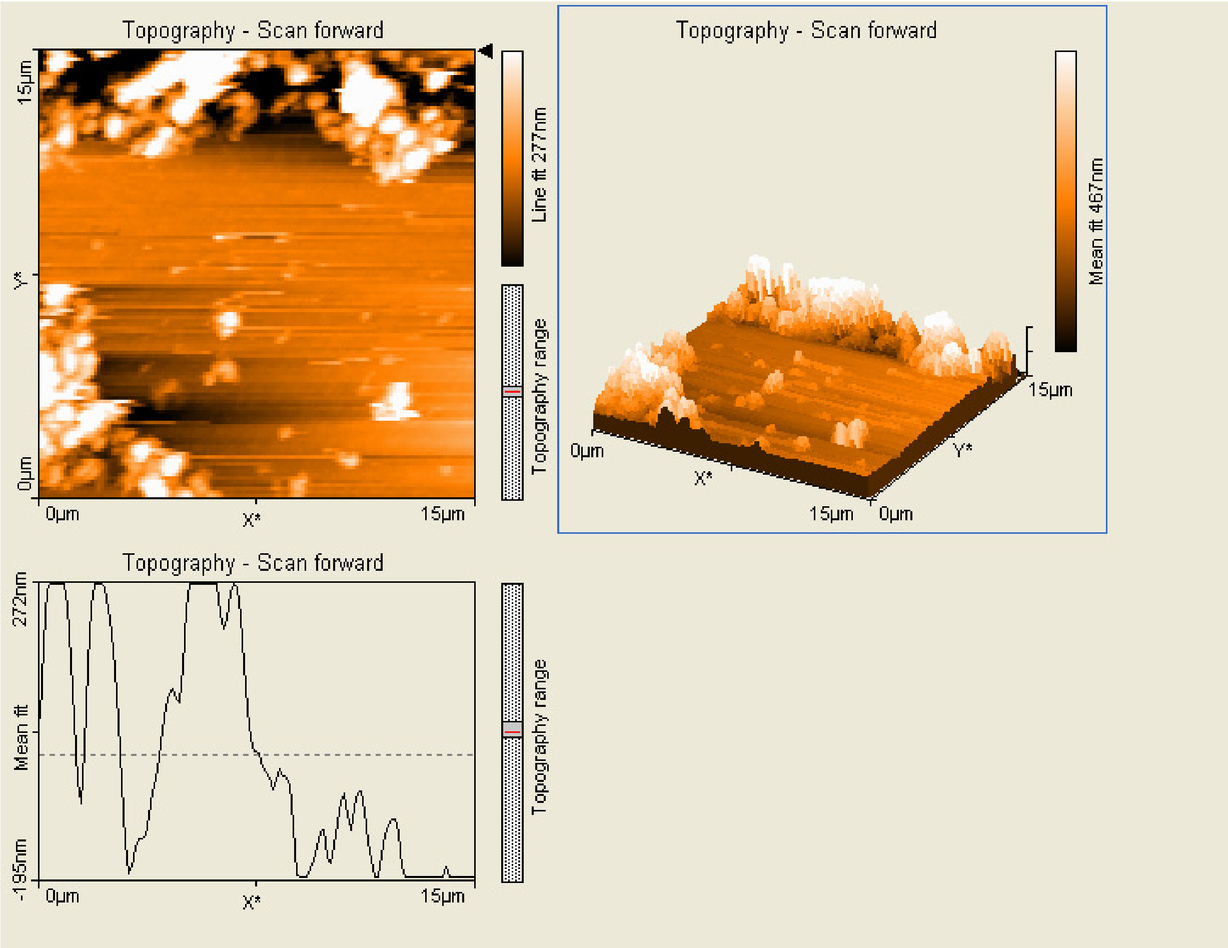

Figure 2 : The AFM surface morphology and topography plot of MWCNT samples.

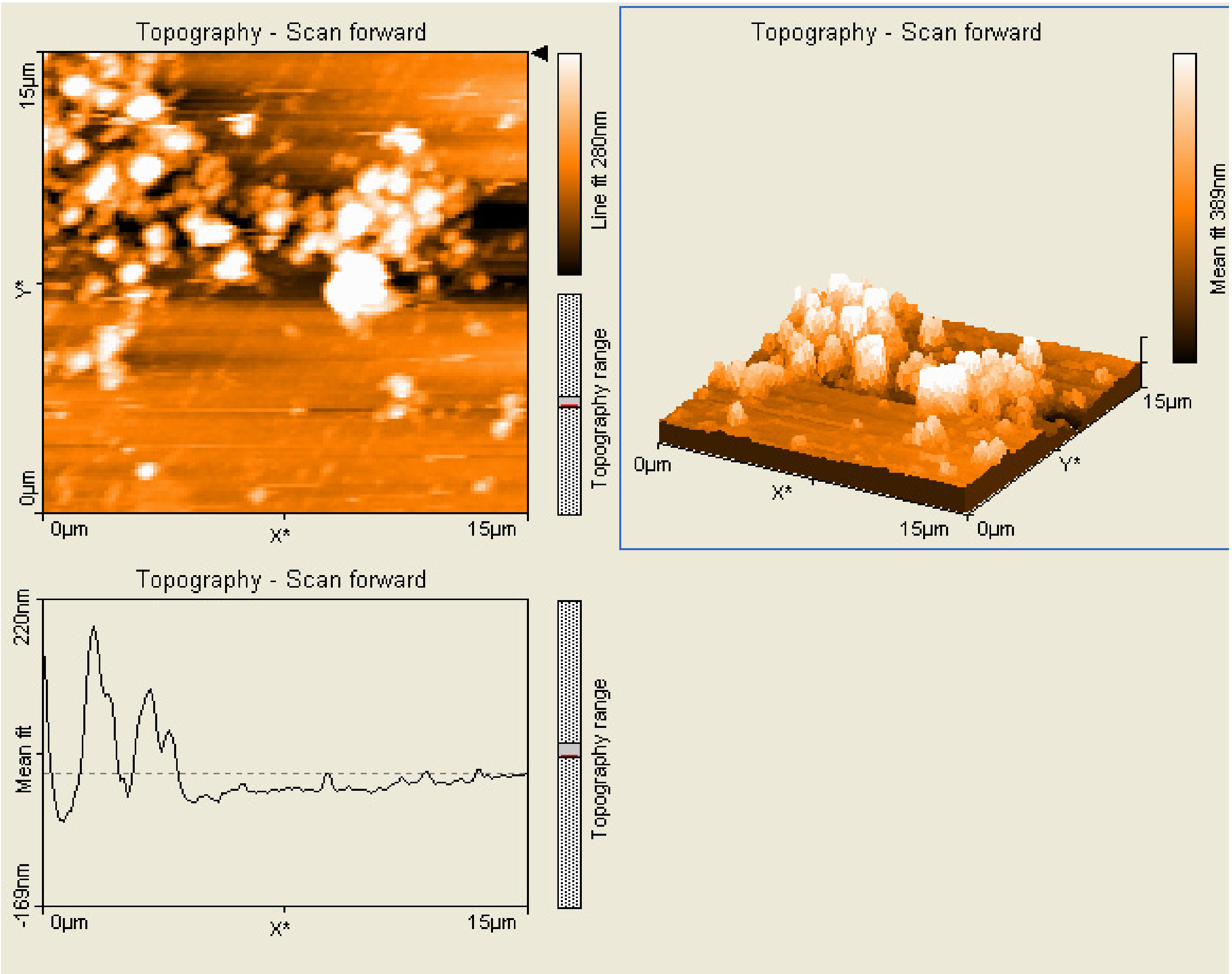

Figure 3 : Another AFM surface morphology and topography plot of a MWCNT cluster.

2.2. Forming and Characterization of Nano Carbon Cast Iron.

The MWCNT tubes normally tend to agglomerate if used as a filler in cast irons. To prevent this and increase the chances of good distribution, the MWCNT reinforcements were sonicated using an ultrasonic sonicator for a few minutes. Further, as the nano tubes had to be mixed thoroughly using the stir casting method, in the grey cast iron eutectic melt at approximately above 1143 ºC , they had to be coated with copper before stir casting. The reasons were two fold. Firstly, to prevent the MWCNT from dissolving in cast iron and secondly to allow MWCNT to retain its form and structure and reinforce cast iron for strength and toughness. Copper coating was done to prevent clustering up of multi walled carbon nano tubes and as copper is good for corrosion resistance, it prevents dissolution and reactivity between the carbon and Fe in the cast iron. The sonicated MWCNT were immersed in melted copper and immediately removed from the pit furnace. As the melting point of copper was almost equal to that of grey cast iron, it prevented MWCNT from dissolving or reacting with the cast iron melt during addition.

Three grams of copper coated MWCNT were added to six hundred grams of grey cast iron melt thereby making the addition as 0.5 wt % . Stir casting was adopted to prepare the specimens and it involved the following procedure:

1. Melt preparation was the first step involved in the casting process. The grey cast iron matrix was melted in a pit furnace and the copper coated MWCNT reinforcement added to the liquid matrix just before pouring the melt in to the moulds. The mixture was continuously stirred in order to distribute the reinforcement evenly in the matrix.
2. The melt was then poured carefully into the sand moulds at a constant slow rate to avoid blow holes.
3. The moulds were then left undistributed for some time allowing the castings to cool to atmospheric temperature.
4. The as cast specimens thus formed were then withdrawn from the moulds, as shown in Figure 4.
5. After solidification of the specimens , the heat treatment process was applied to a few NCCI specimens (Nano Carbon Cast Iron) and followed by annealing because of non uniform cooling of casting, to stress relieve and improve machinability. The temperature of heat treatment was 550^0C. This is described in the next section.
6. After the heat treatment process, both the heat treated and as cast nano carbon cast iron specimens were machined down by using turning operation with carbide tips on lathe as per the standard specimen size requirements.

Figure 4 : As cast specimens of NCCI (Nano Carbon Cast Iron).

2.3. Heat treatment and Machining

Six specimens were cast in all using sand moulds. Three of them were set aside for heat treatment at 550 ºC. The specimens were heat treated in a muffle furnace to the required temperature at a heating rate of about 500 ºC per hour and held there for 2 hrs. The furnace was then shut off and the specimens annealed in side the closed furnace for two days. This was done to stress relieve, improve the machinability and promote the growth of graphite from carbon that is already present in the cast iron that would increase stiffness and provide good wear resistance [7]. Further, it was hoped that the porosity, blow holes and cracking of this nano composite would reduce with the conduct of heat treatment and annealing. The heat treated and the as cast specimens were turned in a lathe using carbide tipped tools. The final machined shape and the appearance of one such a specimen is shown in Figure 5 .

Figure 5: A machined test specimen of NCCI.

2.4. Hardness Testing Procedure

Rockwell hardness C test (HRC) [8], is used to calculate the hardness number of a ferrous material. It consists of indenting the test material with a diamond cone or hardened steel ball indenter. The diamond indenter used here is forced into the test material under a preliminary minor load of usually 10 kgf. When equilibrium was reached , an indicating device which follows the movements of the indenter and responds to changes in depth of penetration of the indenter was set to a datum position. While the preliminary minor load was still applied an additional major load was applied with resulting increase in penetration . When equilibrium was again reached, the additional major load was removed but the preliminary minor load was still maintained. Removal of the additional major load allowed a partial recovery, so reducing the depth of penetration. The permanent increase in depth of penetration, resulting from the application and removal of the additional major load was used to calculate the Rockwell hardness number in C Scale. All the six specimens, heat treated and as cast, were hardness tested and the hardness values were recorded..

3. Results and Discussion

The X Ray diffraction pattern of an as cast nano carbon cast iron revealed impurities that normally exist in the cast iron, like manganese, silicon, and trace amounts of other additions like iron oxides. Further, the copper impurities due to coating and the impurities present in the as supplied MWCNT were replicated. In addition, Fe_2O_3, Fe_3O_4, FeO, Mn and Si impurities were also detected. This is shown in Figure 6 which also reveals that the 1.57116, 2.27751 and the 2.89858 d spacing MWCNT peaks were seen in the as cast nano cast iron. However, a very minor shift was also recorded in these peaks which could be attributed to the copper coating on the MWCNTs prior to stir casting and the mild solubility of the same in cast iron. It is clear from the x-ray of the as cast nano iron that the MWCNT d spacing peaks appear at 1.58433, 2.26832 and 2.87563 values among the other peaks that are typically representative of a grey cast iron. The 2.26832 peak is common to both the Quantum MWCNT and a conventional unfilled grey cast iron as it is most likely that it is Fe_5C_2 phase [9] which is present as an impurity in both. So, compared to the other two peaks which confirm the presence of MWCNT as a separate undissolved phase in the cast nano iron, one cannot be certain in this respect as it is either due to the MWCNT or the grey cast iron or both after casting . Figure 7 shows the X Ray diffraction pattern of a heat treated and annealed nano carbon cast iron specimen. It was seen that the intensity vs 2θ curve showed a pronounced change in the structure of the annealed NCCI . Small amounts of impurities present seem to dissolve in the NCCI due to heat treating thereby suppressing the impurity peaks. However, the two α-ferrite peaks at a 2θ value of 44.981 º and 65 º in Figure 7 show that the phase evolved is a (110) ferrite [10]. Heat treatment at 550 º C appears to improve , solid solubility. Copper found in trace amounts (because of coating the MWCNT) naturally leads to better corrosion resistance and strength in the NCCI in addition to protecting the MWCNT in the as cast NCCI. However, solid solubility of copper and MWCNT in the NCCI appear to take place as a result of heat treatment which is evident from Figure 7. This ferritizing anneal reduces the hardness of the NCCI as seen later.

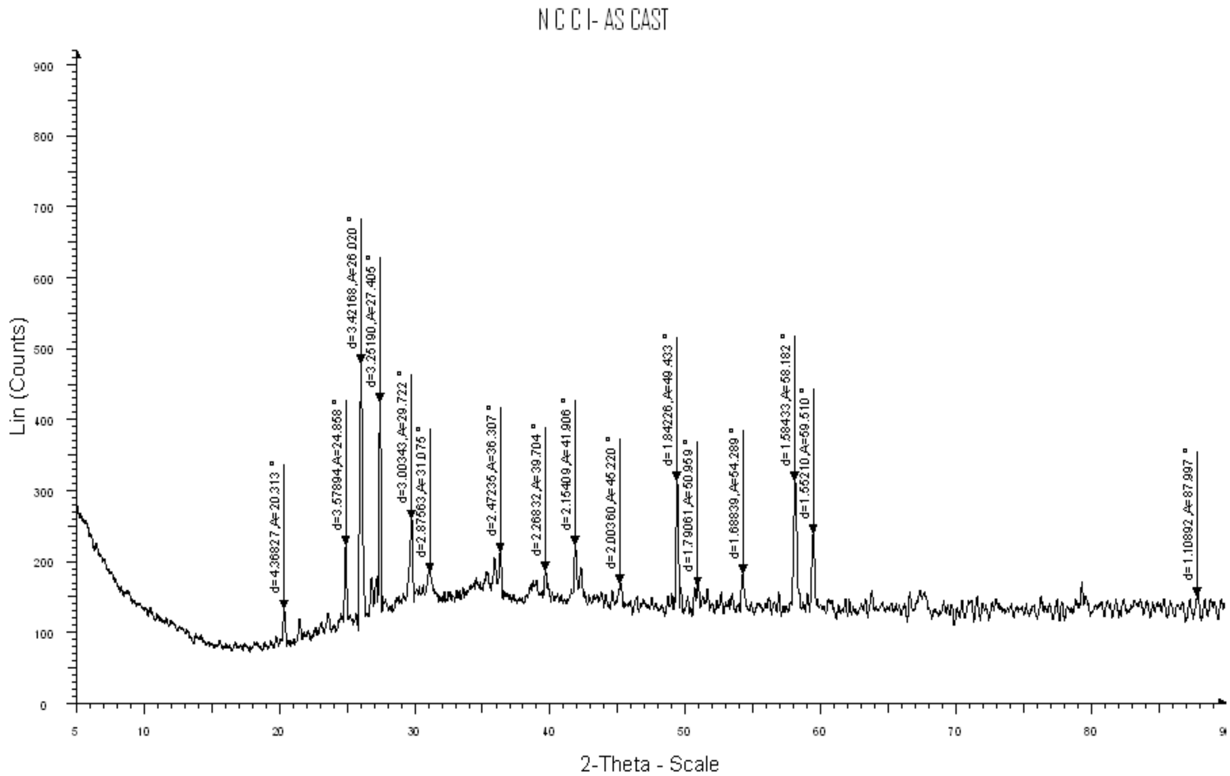

Figure 6: X Ray diffraction pattern of as cast NCCI showing undissolved impurities.

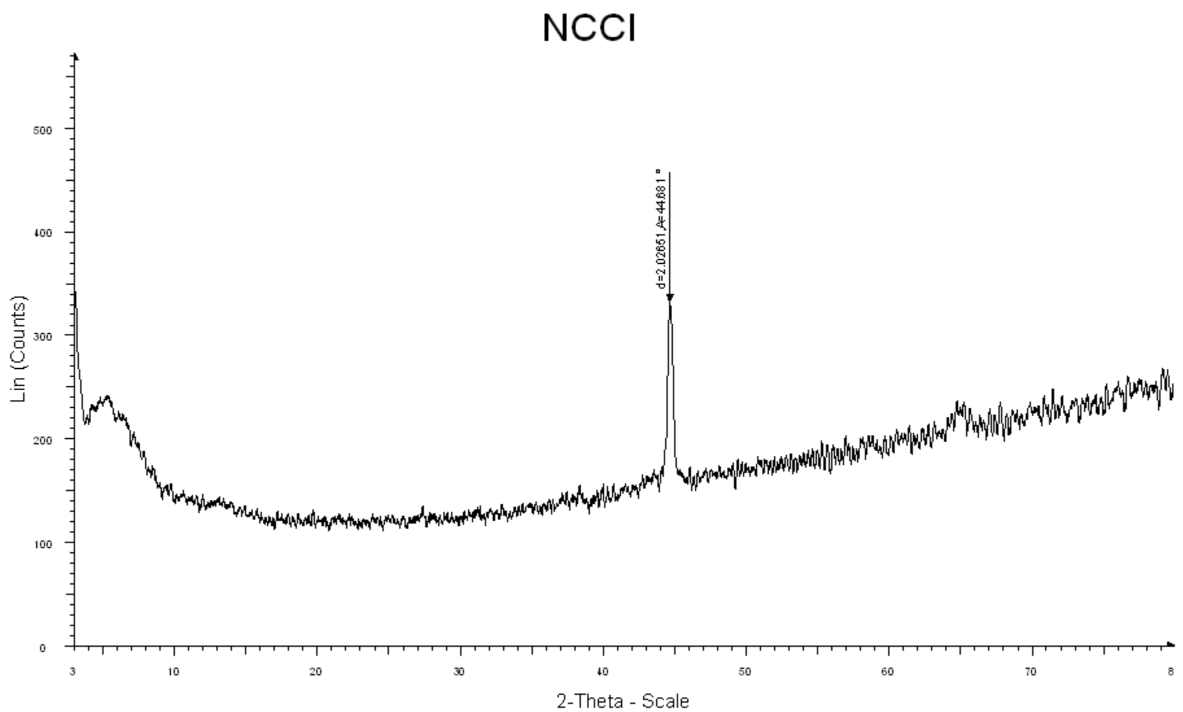

Figure 7: X Ray diffraction pattern of heat treated and annealed NCCI Samples.

The optical microstructures of heat treated and as cast cast iron revealed information about the MWCNT distribution, porosity, distribution of inherent carbon present and the grain structure of the as cast and heat treated cast iron phase. Though nano-scale reinforcements were added, their clusters could well be observed through an optical microscope and hence the effort. Figure 8 shows the microstructure of the grey cast iron showing graphite flakes in an iron matrix. An idea of the grain sizes that prevailed before stir casting could also be obtained from the micrograph.

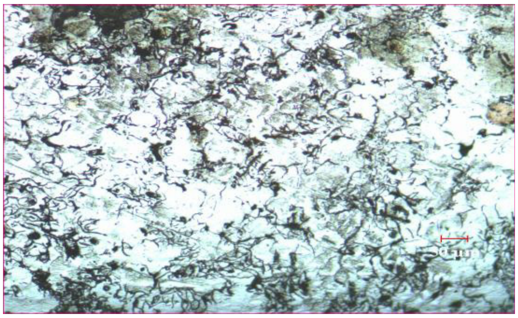

Figure 8: The optical microstructure of grey cast iron before the addition of MWCNT.

Figure 9: Micrograph of as cast NCCI showing fair distribution of the MWCNT cluster.

Figure 9 reveals the microstructure of an as cast NCCI sample showing the even distribution of the copper coated nano carbon phase. Some amount of porosity was also observed in the representative micrograph. Figures 10 and 11 reveal the details of the microstructure of an annealed NCCI sample. The grain size shows an increase and the porosity inherent to as cast samples appears to be lesser in this case. There is no appreciable difference in the distribution of the copper coated MWCNT clusters due to heat treatment and annealing though the cluster nodules appeared larger in size indicating the possibility of softening to occur. The reinforcement structure is barely intact. As the material tends to get softer due to annealing as is seen later, polishing scratches could not be avoided in the annealed samples.

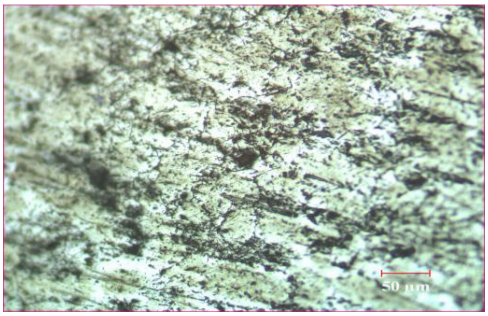

Figure 10: Micrograph of a region in a heat treated and annealed NCCI.

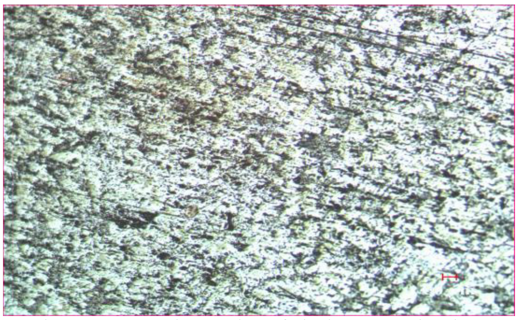

Figure 11 : Another region of the heat treated and and annealed NCCI.

Table 1 depicts the Rockwell C scale hardness values of three as cast specimens of NCCI. The NCCI is soft and ductile as per the values exhibited. Table 2 shows their hardness values after heat treatment and annealing. There is a marked difference in the hardness values and the annealed NCCI is clearly the softer of the two. Annealing clearly forms a softer ferrite phase and dissolves the MWCNT reinforcement partially. The micrographs also reveal that the MWCNT cluster nodules get larger after heat treatment and annealing. These effects are reflected in the hardness values of the as cast and annealed NCCI. As the heat treatment temperature of 550 º C is lower than the transformation temperature of 727 º C required for austenite formation, ferrite forms instead and annealing makes it soft and ductile. A clear α-ferrite formation as indicated by the XRD pattern is seen to occur even at a low heat treatment temperature of 550 º C which is otherwise used for stress relieving. This is noteworthy in the present case. No appreciable graphitization was seen to occur though the heat treatment and annealing were an equilibrium process. More studies are on to find the tensile properties and toughness of the NCCI samples and correlate the same with the structure of the NCCI.

Table I : HRC of as cast NCCI

Sp No	Hardness Number
1	25
2	21
3	22

Table II : HRC of Annealed NCCI

Sp No	Hardness Number
1	17
2	19
3	17

4. Conclusions:

Forming of MWCNT nano carbon reinforced cast iron with the stir casting method was carried out. The x-ray diffraction, microscopic characterization and measurement of Rockwell C scale hardness before and after heat treatment (of the Nano Carbon Cast Iron or NCCI) were also conducted. X- Ray and Atom Force Microscope (AFM) characterization were carried out for the multi walled carbon nano tube reinforcements as well as the nano carbon cast iron formed by adding the nano carbon with the grey cast iron.. As the nano carbon reinforcements tend to agglomerate in the cast iron eutectic melt, prior sonication and coating with copper were done to prevent agglomeration, dissolution and oxidation of nano carbon . The as cast samples were either cooled naturally or heat treated at 550 ºC and annealed, machined down to size and the Rockwell C scale hardness measured. The annealed samples show reduced hardness values compared to as cast samples due to the formation of α-ferrite. They also exhibited less porosity and a low tendency for graphitization.

Acknowledgements

The authors thank the Dean, School of Mechanical and Building Sciences, VIT-University, Vellore, and the VIT management for all the support and facilities extended. The XRD facility at SAS and the AFM facility at VIT-University-Vellore are dutifully acknowledged for the test services.

References

[1] PM Ajayan and S Iijima, Smallest carbon nanotube, Nature, 358(6381), (1992) pp23-23 .

[2] TW Ebbesen and PM Ajayan, Large scale synthesis of carbon nanotubes, Nature, 358(6383), (1992) pp 220-222, .

[3] Sidney H Avner, Inroduction to Physical Metallurgy, Second Edition, Tata McGraw-Hill Edition, (1997) p231 .

[4] F.Foroozmehra, A.Najafizadehb and A. Shafyeib, Effects of carbon content on the formation of nano/ultrafine grained low-carbon steel treated by martensite process, Materials science and engineering A, 528, (2011) pp 5754-5758.

[5] N.Tsuji, R.Ueji, Y.Minamino and Y.Saito, A new and simple process to obtain nano-structured bulk low-carbon steel with superior mechanical property , Scripta Materialia, 46 (4), (2002) pp305-310

[6] X Ray Diffractometer, Model D8 Advanced, Manual, Bruker, Germany, 2006.

[7] ASM International, Heat treater's guide : practices and procedures for irons and steels, ASM International handbook, Metals Park, Ohio, (2007) .

[8] SR Williams, Hardness and Hardness Measurement- A Report, American Society for Metals, Metals Park, Ohio, (1942).

[9] Tasgin Y, Kaplan M, Yaz M, Investigation of effects of boron additives and heat treatment on carbides and phase transition of highly alloyed duplex cast iron, Materials and Design (2008), doi: 10.1016/j.matdes.2008.11.015

[10] CA Bixler, KL Hayrynen, J Keough, G Pfaffmann and S Gledhill, Locally Austempered Ductile Iron, SAE International Journal of Materials and Manufacturing, Vol:3, No:1, August (2010) pp380-390.