Effect on Mechanical Properties of Fe/MWCNT Nanocomposites after Vary the Weight present of MWCNTs prepared by High Energy Ball Milling

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Abstract: The Fe/MWCNT nanocomposites has been prepared by high energy ball milling (HEBM) of powder milling. The morphology and X-ray diffraction studies on the milled powder revealed that carbon nanotubes (CNTs) has been uniformly distributed in the Fe(iron)matrix. The hardness of the samples were carried out using Vickers hardness testing machine. The results revealed that hardness of the prepared Fe/MWCNTs nanocomposites depends upon the weight fraction of filler. It was also analyzed that the delineates partial destruction of Fe-C bonds in Fe/MWCNTnanocomposites was due to the spark plasma sintering (SPS).

Keywords: High Energy Ball Milling, Nanocomposite, Multi Wall Carbon Nanotube, Vickers Hardness

1. Introduction
Carbon nanotubes are unique reinforce materials with high mechanical, thermal and electrical properties. These features of MWCNTs inspired in the development of nanocomposites with remarkable properties [1]. Many research groups reported the use of multiwall carbon nanotubes (MWCNT) as a reinforcing material in the matrix of aluminum [2-5]. The problem of production of metal matrix composites arises from the weak interfacial bonding between metal matrix and MWCNTs. The transition metals are highly preferred for the interaction with MWCNTs because of the unoccupied d orbital which can lead to hybridization with the p orbital of the MWCTs[6]. Controlling the sintering condition produce Fe- C interstitial phase around the dispersed carbon particle, which has the structural advantage of a nearly coherent interface with lattice distortion involving anisotropic energy [6].Sintering temperature plays a very important role in the enhancement of the mechanical property of Fe-MWCNTs.

In this study Fe and MWCNTs are mechanically alloyed as a function of MWCNTs using a planetary ball mill. The spark plasma sintering route was used to produce Fe/MWCNTs nanocomposites. The mechanical property of the prepared Fe/MWCNTs nanocomposites as a function of MWCNTs were investigated in detail.

2. Experimental Procedure
2.1 Materials
The primary materials used in the present study are Fe powder and multiwall carbon nanotube (MWCNT) of determined sizes and shapes.

![SEM image of iron powder](image-url)
Iron powder (Sigma Aldrich) of purity ≥99%, size 325 mesh, and irregular shape is used to represent the matrix, although MWCNT the fabricated by chemical vapor deposition (CVD) method with purity >98wt% and having 1-2nm outer diameter with 3–8 length have been used for the investigation. Fig 1 shows the FE-SEM and Fig 2 (a-b) show the TEM micrographs of the as-received CNTs in use for the present experimentation.

The ball mill method was carried out at room temperature using tungsten carbide vial (jar) and balls in high energy ball milling (Fritsch Pulversitte-6Gramny) planetary mill. The Fe-CNT complex absorbents were obtained by consistently mixing the Fe powder with various weight fractions MWCNTs (0.5wt%, 0.7wt%, 1wt%). The Fe-CNT powder was placed in 250 ml tungsten carbide jar, and one weight percent stearic acid added as a process control agent (PCA) to prevent the excessive sticking and agglomeration of Fe powders. The tungsten carbide jar filled with inert gas. The ball to powder ratio 5:1 and the rotation speed were maintained as 200 rpm correspondingly. The samples with 0.5wt% CNTs to 1wt% CNTs were milled only for 3hrs. The Samples were taken out from the vial at the end of the milling process and were subjected to the characterization techniques. X-ray diffractometer (XRD, Philips X’Pert with Cu Kα radiation) was utilized to analyze the constituent phases in the nanocomposite powder (Fe+CNT). The X-ray measurements were obtained using a step size of 0.002° in the 2θ range 20–80° and an integration time of 30s at each step. Morphology powder sample and polished samples after SPS finds out by optical microscopy and field emission scanning electron microscope (FESEM). Transmission electron microscope (TecnaiF-20) was used for the detailed structural and interface study of Fe- MWCNTs.

Raman spectroscopy was carried out at room temperature in AIRIX STR 500 CONFOCAL MICRO Raman Spectrometer. Raman spectra of nanocomposites milled for various times were recorded under Argon Ion laser excitation at 514 nm at a very low power (< 1mW) to avoid excessive heating. Vickers' hardness was measured on fine-polished specimens with an indenter load of 300gf. The composite powder was sintered using a Dr. Sinter 515 S apparatus (SPS, Syntex Inc., Japan) at a temperature of 700 °C with heating rate 100°C/min under high vacuum (10⁻³ Pa) respectively. The diameter and height of the final products of Fe-CNT nanocomposite around 20mm and 5mm were polished with Sic paper to remove surface contamination from the graphite die and foil before conducting structural and property characterization.

3. Results and Discussion

3.1 Morphological analysis

The SEM images of Fe/CNT nanocomposite as a function of CNT contents (0.5, 0.7, and 1wt %) depicted in after high energy ball milling fig. 3. The success of the milling process or collision energy between balls decreases with increasing PCA content [7–9]. The ball milling includes two important processes cold welding
and fracturing which leads to increasing particle size and particle refinement, respectively [10]. Fig 3a shows the agglomeration and cold welding is less because of the concentration of MWCNT in the matrix is lower. The distorted particle decreased because of the agglomeration content increased with increasing the CNT content.

![Image](image_url)

**Fig 3** The SEM of Fe-CNT composite powder at the end of 3h of milling. (a) 0.5 wt% (b) At higher magnification show the CNT on the Fe matrix uniformly distributed, (c) 1 wt% (d) at higher magnification shows that agglomerated CNT and uniformly distributed CNT.

Agglomeration content is closely related to distribution density of reinforcement particles on the matrix powders shown in Fig. 3 C.

4. Optical Analysis.
The optical images of the sintered Fe/MWCNT nanocomposites as a function of CNT filler (0.5, 0.7 and 1 wt %) are shown in Fig. 4. The sintered microstructures of the Fe/CNT nanocomposites shows the CNT particles circulated to the grains boundaries (Fig. 4). The effect of volume diffusion during the sintering process. The Fe/CNT nanocomposite reinforced with lower CNT particle content (0.5, 0.7 and 1 wt %) exhibit lower agglomeration. Fig 4 shows that after spark plasma sintering, grain size are reduced because of the MWCNTs work as lubrication.
4.1 XRD Analysis
XRD patterns of the three hours milling of Fe as a function of different wt% of MWCNT are shown in fig 5(a). The XRD results of Fe/MWCNT nanocomposites consists only Fe-phase after 3 hours of milling. After 30 minutes of milling, MWCNT peak disappears completely, and Fe peak broadens due to the continuous reduction in particle size and growth of lattice strain with increasing milling time. The disappearance of MWCNTs peak in the XRD pattern for the following reasons: (i) the carbon atoms take up interstitial side in Fe lattice and interstitial Fe–C solid solution is produced, (ii) carbon atoms go through into the inter-grain boundaries of the Fe grain, and (iii) amorphization of MWCNT layers[11]. Fig 5(b) shows that the peak (110) shifting lower angle side due to the dissolution of MWCNT in the Fe matrix [12].

4.2 Raman Analysis.
Raman spectroscopy revealed information about the MWCNT after high energy ball milling and find out the effect on G band and D band in the MWCNTs shown in Fig. 6. In Raman spectroscopy D band show defect in MWCNT and G and G' give the information about the crystalline and amorphization. The intensity of D band G' is increased and intensity of the G band is decrease after high energy ball milling because more defect is created in MWCNT during the high energy milling. The change in the band intensities quantified with the ratio $I_D/I_G$ calculate in Table 1. By comparison from the $I_D/I_G$ ratios of theses spectra in fig. 6. It found that the
ratio varies primarily in the mixed CNT. The amount of defect it seems that increased in the CNT after mixing due to the mechanical alloying [6].

![Raman spectra after different wt% of CNT in Fe after mixing by high energy ball milling.](image)

**Table1.** Raman spectra of Fe-MWCNTs nanocomposites after HEBM.

<table>
<thead>
<tr>
<th>Wt% CNT</th>
<th>Peak Position(cm$^{-1}$)</th>
<th>Ratio I_D/I_G</th>
</tr>
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<tbody>
<tr>
<td>0.5Wt% (Fe+MWCNT)</td>
<td>1348 I_D, 1573 I_G</td>
<td>1.03</td>
</tr>
<tr>
<td>0.7Wt%(Fe+MWCNT)</td>
<td>1347 I_D, 1577 I_G</td>
<td>1.04</td>
</tr>
<tr>
<td>1Wt%(Fe+,WCNT)</td>
<td>1339 I_D, 1587 I_G</td>
<td>1.08</td>
</tr>
</tbody>
</table>

### 4.3 TEM Analysis

The evolution of structure of MWCNT during the way of high energy balling of Fe/ MWCNT (1wt %) composite has been studied by Transmission electron Microscopy shown in fig 7. The studied only Fe/MWCNT (1wt %) sample because of the more change during ball milling and after spark plasma sintering. It is observed that Multiwall CNTs have maintained structural identity with increase in milling time and after SPS. Mixing of metal particles with CNT and its consequent embedding on iron particles is also observed after three hours of milling shown in Fig.7b. The electron diffraction pattern of Fig.7a reveals the concurrent presence of CNT and iron. After three hours milling, the interfacial bonding seems to have been quite good with concurrent damage of MWCNT. Fig 7 Show that cementite phase not present in TEM study.

![TEM image of Fe/CNT(1 wt%) nanocomposites](image)

**Fig7.** TEM image of Fe/CNT(1 wt%) nanocomposites (a) SADE pattern of Fe+1 wt% MWCNTs and (b) HRTEM image of Fe/MWCNTs( 1wt%)
4.4 Hardness

The Fe/MWCNTs with different weight fraction of MWCNTs nanocomposites sintered at 600°C by spark plasma sintering. The graph plotted between wt% of CNT and hardness shown in Fig 8. The variation of the hardness values with increasing wt% of MWCNTs shown in fig 8. The temperature is directly related to change of the Fe–C phase according to the diffusion of carbon particles in Fe. The hardness increases with the formation of Fe–C interstitial alloyed phase, and then it decreases with the formation of the cementite (Fe₃C) phase with increasing sintering temperatures. The result again proof that not cementite phase is present in TEM and XRD analysis. So Vickers hardness is increased. Most of the researcher finds out the hardness of pure iron around 98HV. In the study hardness is increase 111 HV after adding the 1 wt% of MWCNTs in Fe. The change in the Vickers hardness after vary the wt% of MWCNT in Fe are calculate in Table 1.

![Fig 8 Vickers hardness values of the Fe/MWCNTs nanocomposites with different wt% of MWCNTs in matrix Fe.](image)

<table>
<thead>
<tr>
<th>Table 2 Vickers hardness value with different wt% of MWCNT in Fe.</th>
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<tr>
<td><strong>Samples</strong></td>
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<tr>
<td>Fe+0.5 wt% MWCNT</td>
</tr>
<tr>
<td>Fe+0.7 wt% MWCNT</td>
</tr>
<tr>
<td>Fe+1 wt% MWCNT</td>
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5. Conclusion.

In this study investigate the Fe/MWCNTs composites containing Fe–C interstitial alloyed phases. MWCNTs make strong bonds with Fe atoms after spark plasma sintering, and it leads to transfer the load to MWCNTs. In the Fe/MWCNTs nanocomposites hardness increased after varying wt% of MWCNTS.

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References


