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THE EFFECT OF POROSITY ON THE YIELD OF CARBON NANOTUBES

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Abstract: *In this work, the porous Magnesium alloy (AZ91) was prepared by Space holder technique to deposit carbon nanotubes, Novalac powder was used as space holding and fugitive materials with different particle size (≥20 μm, ≥500 μm) and amount (50, 52, 54, 56, 58, 60%wt.). Impact of Novalac powder (particle size and additive percent) on density and porosity of porous AZ91 alloy was studied. Fine Novalac powder (≥20 μm) not recommended in the porous AZ91 alloy preparation, concurrently coarse Novalac powder (≥500 μm) was suitable for that purpose. It was found that the density of AZ91 alloy decreased with increasing Novalac concentration. Carbon nanotubes were deposited on the porous AZ91 alloy by catalytic chemical vapor deposition whereas NiSO4.6H2O used as catalyst, acetylene gas as a carbon source and argon gas as a carrier gas with flow rate percent 1:1, at 575°C process temperature for 30 min. Multiwall carbon nanotubes were obtained and characterized by X-ray diffraction and scanning electron microscopy techniques. The average diameter of the multi wall carbon nanotubes was (46 nm). Although the porosity percent of AZ91 alloy was not majorly effect proportionally by the increasing of an additive Novalac percent, the yield (quantity) of Multiwall carbon nanotubes was enhancing due to increase the porous AZ91 alloy surface area..*

Keywords: porous materials, chemical vapor deposition and carbon nanotubes.

1. INTRODUCTION

Multiwall carbon nanotubes (mwnts) was discovered by iijima [1]. carbon nanotubes (CNTs) had interested more and more research concerns, because of their extraordinary properties and different potential applications [2, 3]. carbon nanotubes had matchless properties (mechanical, thermal, electrical and optical etc.) that made them potentially practical in a wide diversity of applications [4, 5].

Carbon nanotubes were prepared with three main methods, arc discharge, laser ablation and chemical vapor deposition [6]. chemical vapor deposition cvd used like simplicity and up scalability, which preferred in commercial production [7]. many factors like carrier gas, carbon source, catalyst type, substrate, process temperature and surface area influenced on the synthesis of cnts (length, diameter, type and yield etc.) in chemical vapor deposition cvd method [8].

There are many methods to manufacture porous metallic materials, and these different methods could be arranged based on the state of the metal as an example:

To form powdered solid metal from liquid metal, through a metal vapor or gaseous metallic substances and also from a metal ion solution, the solid metal in the powdered form process could be acquired porous materials by using filler materials (space-holding) and metal powders. the mass of space-holding material is mixed with tiny metal powder as shown in Figure 1. suitable solvent [9] or even an organic binder [10] perhaps used for mixing the space holders and the metal powders [11].

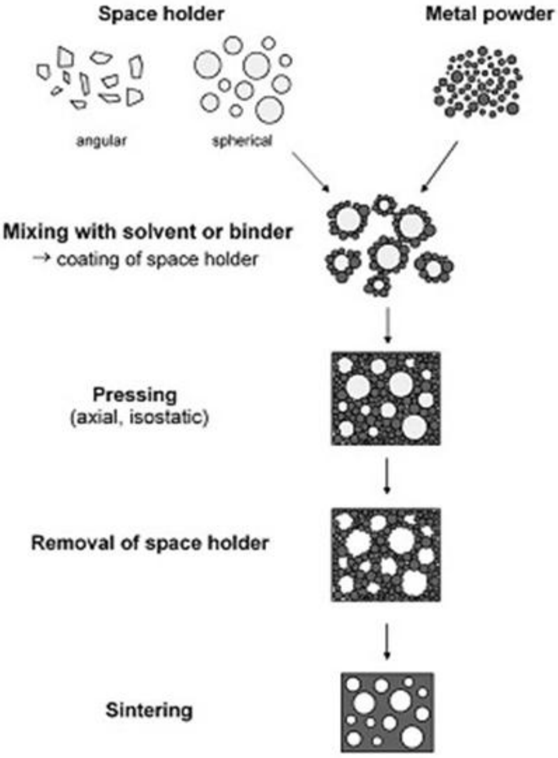

Figure 1: for preparation of porous materials by space holder technique.

Ceramic particles or cavity spheres, polymer grains or cavity polymer spheres, salts, or even metals could be used as space holders. then, the filled mass either simply compacted at room temperature[12], or pressed at elevated temperatures to improve compaction so, it became sintering processes among the metal powder particles if the space holders were heat resistant [13].

In both states, a compound became acquired, and consisted of a metal matrix with inserted small grains filler. if the metal content was low enough, it would remove the space holder material almost entirely in an additional process step because the network formed by the filled material was interconnected. this could be performed by thermal treatment, leaching, or by using of an aqueous solvent. a final sintering step could be implemented to more density of porous metallic network [14, 15].

The aim of this study was to prepare porous alloy with high porosity percent, also to study the impact of a porosity percent in az91 alloy on yield (quantity) of carbon nanotubes, which prepared by chemical vapor deposition process in order to increase the production of carbon nanotubes. also, it aims to the possibility of controlling the deposited carbon nanotubes quantities through dominating on the percentage of the porous az91 alloy.

2. EXPERIMENTAL WORK

This part is divided into two stages:

Preparation of porous material.

Preparation of Carbon Nanotubes (CNTs).

2.1. PREPARATION OF POROUS MATERIAL

Magnesium alloy (AZ91 Mg-9 wt%Al-0.7%Zn) was prepared by powder metallurgy as porous material. The specification of materials used is shown in Table 1.

Table 1: The particle size of materials used.

No.	Material	Particle size µm	
1	Mg powder	≥75 µm	Fluka Co. Germany
2	Al powder	≥53 µm	Fluka Co. Germany
3	Zn powder	≥75 µm	Fluka Co. Germany
4	Mn powder	≥75 µm	Fluka Co. Germany
5	Novalak powder	≥20 µm	Trade India
6	Novalak powder	≥500 µm	Trade India

The metal powders were mixed in a mortar for 5 minutes, followed by mixing in a ball mill for 30 minutes at rotation speed 750 RPM and this is AZ91 powder. The powder metals and Novalac powder (used as holding material with different particle size (≥20 µm, ≥500 µm) were mixed in a mortar. The AZ91 alloy powders was mixed with different wt% (50, 52, 54, 56, 58, 60%wt.) of Novalac powder. The powders were compacted by using a tool steel die of 15mm diameter with compacting pressure 174 MPa. Four samples were prepared for each mix.

Several sintering attempts were tried. First the sample were heated under argon at 250˚C , holding at this temperature for 30 minutes ,and then the sample were furnace cooled to room temperature. It was found that in this sintering cycle, the temperature wasn't sufficient to remove all the Novalac from the compacting, therefore another attempt was utilized.

The proper sintering process was done under argon by heating the green samples to 250˚C and hold at this temperature for 30 minutes. The temperature was then raised to 500˚C and hold at this temperature for another 30 minutes. The samples were then furnace cooled to room temperature. The second attempt had given good samples, and then all of them were sintered by using that heating cycle.

The samples were cleaned in acetone followed by ultrasonic cleaning for 10 minutes, and then oven dried at 100˚C for 30 minutes. The porous AZ91 alloy became ready to make density and porosity tests.

2.2. PREPARATION OF CARBON NANOTUBE

2.2.1. CATALYST PREPARATION

The catalyst solution was prepared by dissolving 1 gm of $NiSO_4.6H_2O$ in 100ml of distilled water. The solution was then mixed ultrasonically for 20 minutes. The AZ91 sintered sampled were dipped in $NiSO_4.6H_2O$ catalyst solution for 30 min. Each sample was then dried in an oven at 150˚C for 30 minutes in atmospheric air. The weight of each sample was taken using 4 digits' electrical balance. These AZ91 sintered and dipping coated samples are ready to be used in chemical vapor deposition (CVD) process.

2.2.2. FURNACE DESCRIPTION

Two furnaces were used as primary and secondary heating furnace. Each furnace with quartz tube length (600mm) and (47mm) inside diameter with maximum temperature (1100oC). Another long inner quartz tube (reaction chamber) was inserted inside the two furnaces. This quartz tube reaction chamber is 600mm long with inside diameter 28mm and 30 mm outside diameter. The first half of the reaction chamber is called secondary chamber used to preheat the reaction gases. The second half of the reaction chamber is called primary chamber and contain AZ91 sintered coated samples. These AZ91 were put at distance 15 cm from the outlet end. The acetylene and argon gases are fed through the secondary chamber which was used for preheating of acetylene and argon gases. These gases were discharge from primary chamber as shown in Figure 2.

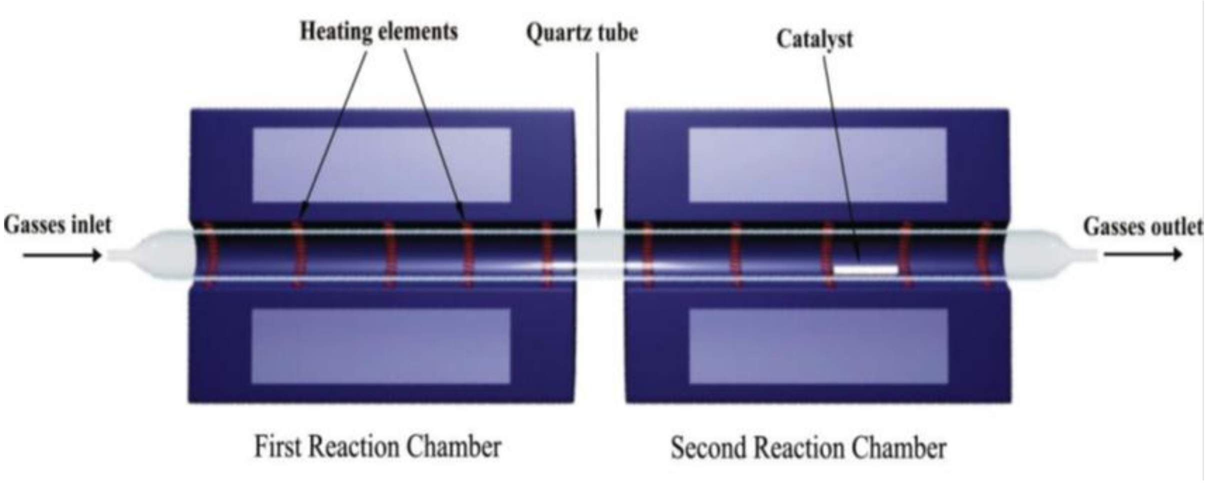

Figure 2: Illustration of the CVD furnace system.

The heat distribution of the primary reaction chamber is shown in Figure 3. The reaction chamber was charged with argon gas first to avoid any oxidation until the temperature of the secondary furnace and the primary furnace reach 300 and 575 °C respectively. Then, acetylene (as Carbon source) and argon gases were charged together into the reaction chamber. The flow rates of the two gases (1:1 SLPM) for 30 minutes. Then the sample was allowed to cool under argon into room temperature. The weight of each sample was recorded (4 samples for each run) before and after CVD process to find the weight of CNTs deposited.

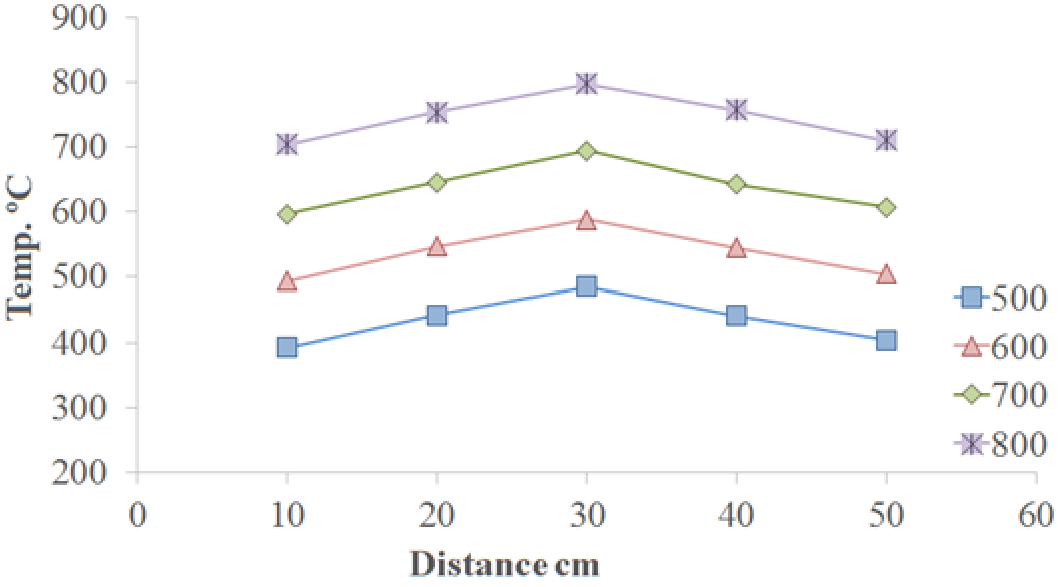

Figure (3): Temperature distribution in side tube furnace.

2.2.3. CNTS PURIFICATION

The produced CNTs were purified by heating 0.5 g of MWCNTs inside furnace at 450˚C for 2hrs under atmospheric air to oxidize the amorphous carbon. Then the CNTs were soaked in 250 ml of acidic solution consisted of sulfuric acid and nitric acid with a ratio (3:1) respectively [15] and stirred for 1 hour at 90˚C using magnetic stirrer hot plate. The CNTs solution was then centrifuged using a centrifuge (Unimedica 800 centrifuge, China) at 3000 RPM for 10 minutes. The remaining CNTs would be washed with deionized water and then centrifuged for another 10 minutes at 3000 RPM. This process was repeated 3-4 times until the pH of the solution is 7. CNTs were then dried in an oven at 90˚C for 2 hours [16]. The purified CNTs were characterized by XRD.

3. TESTS

In this part there were some tests which done on pours AZ91 alloy samples and the other would be performed on Carbon Nanotubes.

3.1. DENSITY AND POROSITY TEST

ASTM D 792 standard reference was used in density and porosity measurements, which were based on Archimedes principle. The Density of the material and the porosity were calculated using equation 1 and 2 respectively. Four measurement were done and the average value was taken [16].

$$Sp.Gr = \left[\frac{Wd}{Wd - Wi}\right] * acetone\ S.G. \qquad (1)$$

Where Sp.Gr = Specific gravity of material, Wd= weight of material in air (gm), Wi= weight of material suspended in acetone (gm) [4].

$$P = \left[\frac{Ws-Wd}{Ws-Wi}\right] * acetone\ S.G. \qquad (2)$$

Where P= Porosity of material Ws = Weight of Wet material, i.e. weight of soaked material in air.

3.2. SCANNING ELECTRON MICROSCOPY

Carbon Nanotubes samples were characterized using HITACHI S-4160 Scanning Electron Microscope (SEM), Scanning Electron Microscope Lab. /Tehran University.

3.3. X-RAY DIFFRACTION (XRD) TEST

The X-Ray Diffraction test was done for Carbon Nanotubes samples at Specialist Institute for Mechanical Industry, Baghdad, Republic of Iraq.

4. RESULTS AND DISCUSSION

4.1. DENSITY AND POROSITY TEST

In this work, pours AZ91 alloy sample was prepared by using Novalac as space holding material with particle size (20< particle size< 500 µm) and (≥500 µm). In this work, it was found that all the samples were failed when Novalac powder particle size (20< particle size< 500 µm) as shown in Figure 4. This is due to the small particle size of Novalac powder particle size. This very fine powder is situated interstitially into particles of metal powders. During sintering process, when Novalac evaporated, the gases entrapped between metal particles causing cracks of the samples as shown in Figure 4.

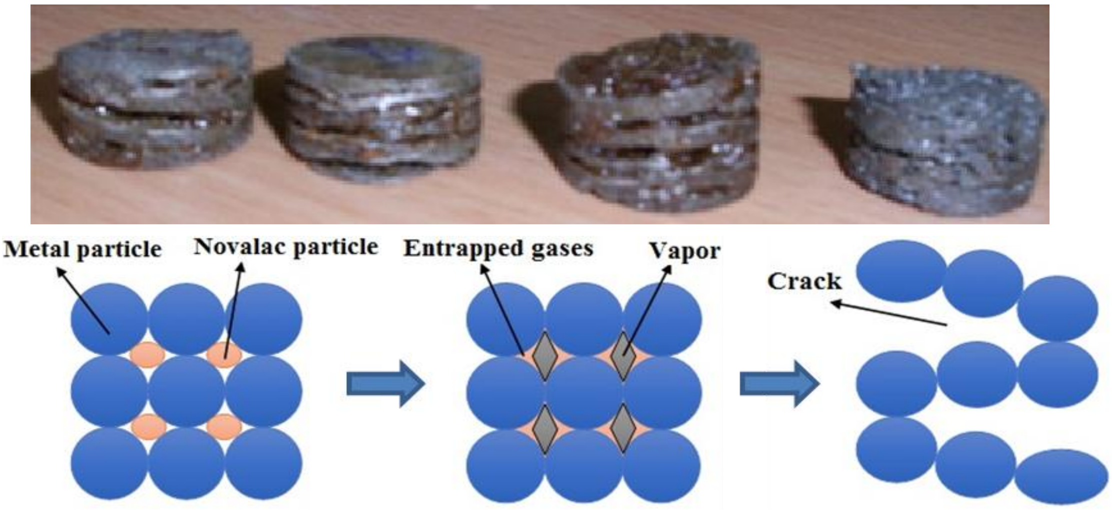

Figure (4): Show failed samples.

When the Novalac powder with a particle size (≥500 µm) was used, no cracks in the sintered samples were observed and these sample are good as shown in Figure 5.In sintering process, when coarse Novalac powder evaporated there was enough space for the gases to escape and no entrapment as shown in Figure 5. Therefore, the powder particles size of the metal powder should be smaller than the average powder particles size of the space holder [17].

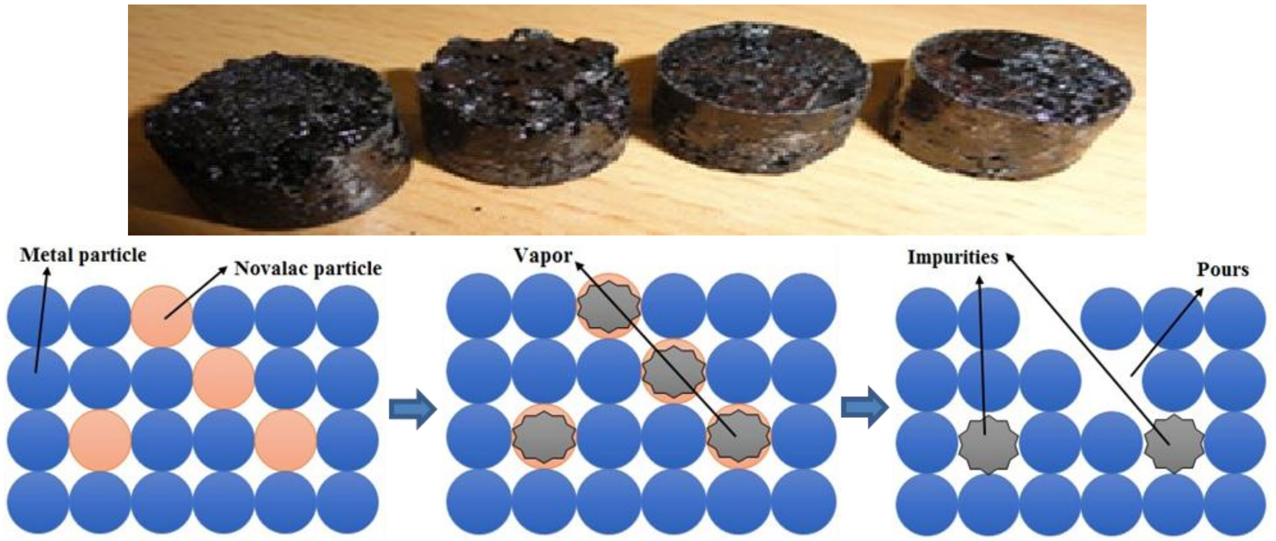

Figure (5): Show open pores and close pores in good samples.

From Figure 6, the density of the sintered AZ91 decreases with Novalac percent due the open pores and the impurities left after Novalac evaporation, where a general difficulty of this method is the removal of large quantities of the space holder materials from the compacted mix, this result agrees with previous study [18].

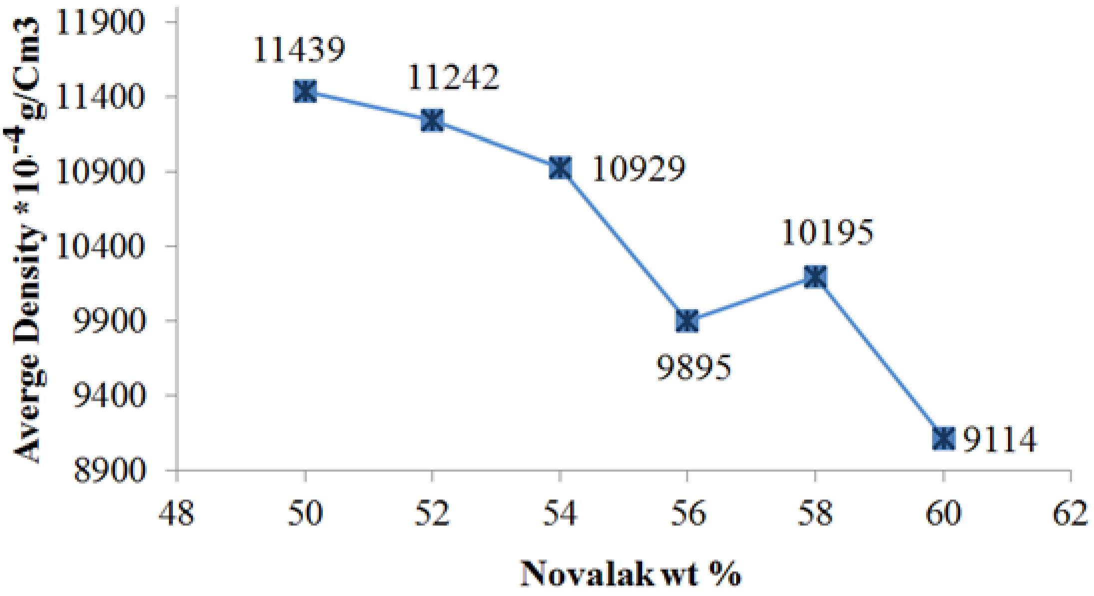

Figure (6): Effect the Novalac additive percent on the AZ91 alloy density.

The porosity of the AZ91 sintered samples vs. Novalac wt% is shown in Figure 7. The change in the porosity does not proportional to the changes in the density. This is may be due to the closed pores which contained impurities caused by Novalac evaporation and the Segregation of Novalac particle during mixing the metal powder with the often much larger space holders material, where Segregation minimize Novalac activity in increasing AZ91 sintered porosity, this result agrees with previous study [19].

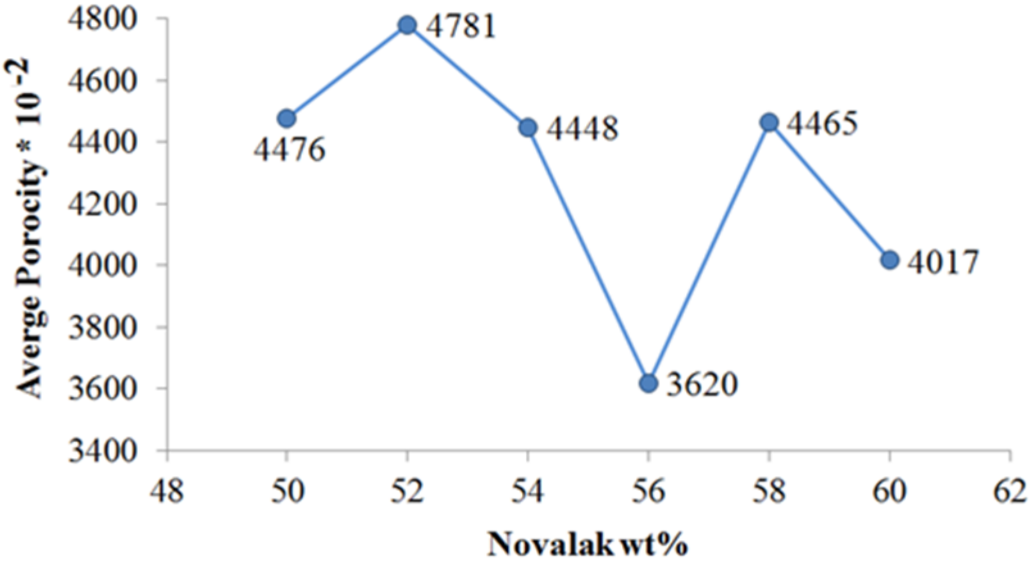

Figure (7): Effect Novalac additive percent on the AZ91 alloy porosity.

4.2. SCANNING ELECTRON MICROSCOPE (SEM) AND XRD

The CNTs were examined by SEM and the average diameter was (46.66 nm), as shown in Figure 8.

This indicates that the produced CNTs by CVD method are MWCNTs. XRD of Multiwall Carbon Nanotubes (MWCNTs) shows the peak at 26.6 based on the (0 0 2) diffracting plane as shown in Figure 9. The (0 0 2) peak was shifted from 26.6 to 26 due to the high curvature and high strain energy of MWCNTs [20].

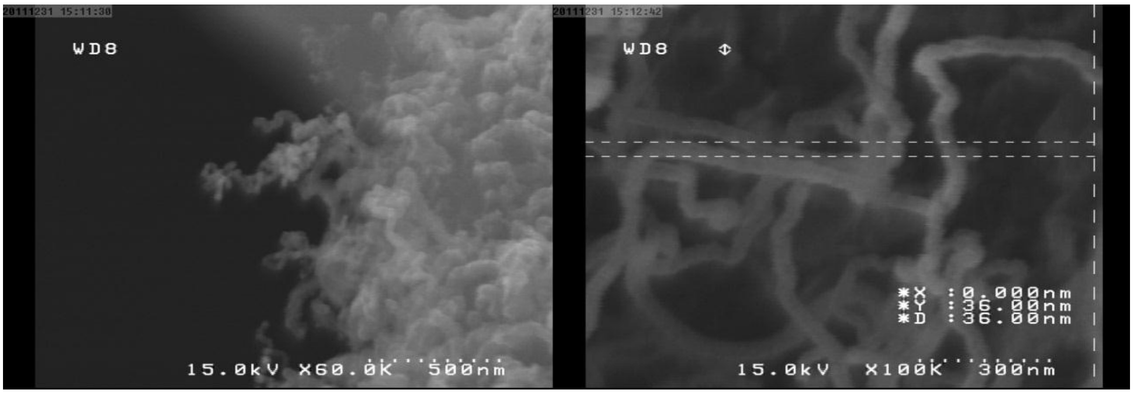

Figure (8): Show the SEM image for carbon nanotubes.

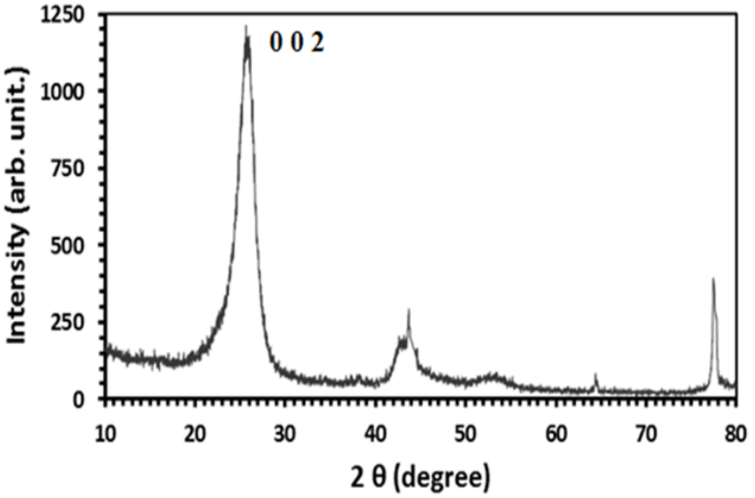

Figure (9): XRD of MWCNTs.

The quantity of MWCNTs yield produced by CVD using AZ91 as porous substrate as a function of Novalac wt. % is shown in Figure 10. The quantity of MWCNTs (yield) is Influenced by AZ91 open pores surfaces and the lumpy surface which left by segregated Novalac Contributing to increase AZ91 surface area, from Figure 10 can be noted the fluctuating in The yield of CNTs with a clear increase along increasing in Novalac wt.%, to discuss that , from Figure 7 it could note the porosity at 54 and 58 Novalac wt.% are approximately equal but, in Figure 10 The quantity of MWCNTs yield at 58 Novalac wt.% is a doubled of The quantity at 54 Novalac wt.% ,this improve that the porosity is not The only influential on The quantity of MWCNTs yield but there is another influential, which is the lumpy surface which left by segregated Novalac on AZ91 surface, the last factor might be the main factor in increasing carbon nanotubes quantity.

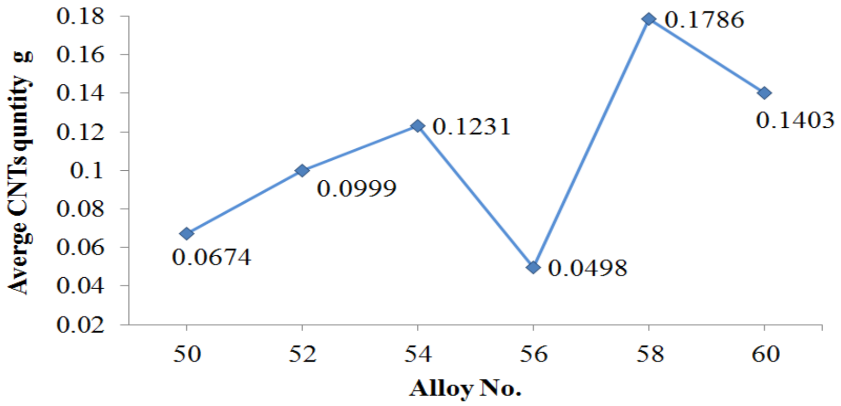

Figure (10): effect the Novalac additive percent on the CNTs quantity.

5. CONCLUSIONS

Particle size of the space holder (Novalac powder) should be appropriated to particle size of metal powders to stop samples cracks. The closed pores had negative affecting on the activated porosity (surface area). It is not recommend using Novalac powder in the preparation of porous metallic materials due to the segregation which occurred to the Novalac powder.

Although the increasing of which occurred in deposited carbon nanotube in compatible with the raising of porosity, where it is not controlled on it, due to the difficulty of controlling on porosity percentage of AZ91 alloy.

The carbon nanotubes quantity would be increased with Novalac powder percent increase.

6. ACKNOWLEDGEMENTS

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