

# Effect of Heat Treatment on Microstructure and Mechanical Properties of AZ91 and AZ91 Reinforced Carbon Nanotube

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**Abstract.** In present work the effect of heat treatment on microstructure and mechanical properties of AZ91 and AZ91 reinforced with carbon nanotube (CNT) were tested after undergoes Sintering, T1 at 450 °C, Solution Treatment, T4 at 415°C and Ageing Treatment, T6 at 715°C. Then, all samples will be analyze their microstructure morphology, phase composition, hardness and compression strength by using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Rockwell Hardness machine and Universal Tensile Machine (UTM). CNT were clustered homogeneously into the matrix of AZ91 due to successfully mechanical alloying using planetary mill for 20 hours. Precipitation of  $\beta$ -Phase ( $Mg_{17}Al_{12}$ ) were reveal in XRD pattern usually highest intensity at  $2\theta=30^\circ$  until  $40^\circ$ . Meanwhile, the ageing treatment, T6 nanocomposites found increase in hardness, compare to monolithic has lower value started form 4 hours until 8 hours of ageing.

## 1. Introduction

Powder metallurgy metal matrix composites based on AZ91 alloy matrix reinforced with 0.3 weight percent of multiwall carbon nanotube (MWCNT) were investigated from the point of view of their response to artificial aging as compared to the unreinforced AZ91 matrix alloy [1]. Magnesium alloys are utilized in engineering application for lightweight structural and functional parts in aircrafts, automotive applications, electronics, and other industrial fields, cause of their high specific strength, light automotive applications, electronics, and other industrial fields, due to the corresponding high specific strength, light specific weight, high damping capacity, recyclability, and electromagnetic shocks shielding ability [2]. In contrast, magnesium and its alloy were essentially deforming via its basal slip and twinning at room temperature, which limits their formability. Consequently, thermomechanical frequently carried out at high temperature [3]. It is generally considered that additional slip systems (prismatic and pyramidal) contribute significantly to deformation when the temperature is higher than 300°C, namely, when the associated critical resolved shear stresses are comparable [3].

CNT or multi-walled carbon nanotubes (MWCNT) have become popular for reinforcing metals and even polymers. These nanotubes show extremely high mechanical properties and flexibility as well as a high Young's modulus. Their small size reduces the possibility of thermal mismatch-induced dislocation generation at the matrix/tube interface, which is seen as a further advantage [4]. CNT was to be chosen to enhance magnesium composite properties. Recent researches producing Mg matrix composites reinforced with CNTs has been limited, looking to the problem of agglomeration of CNTs due to Wander wall forces but were largely focused on polymer matrix composites [5]. Therefore, mechanically alloying is one of green technique, where it's easier and cheapest way to overcome this



problem. This technique was also approved as a solution by (Q. Li et al., 2009) through Esawi et al. that tried to disperse carbon nanotubes in aluminium powder by mechanical alloying [6]. Jayakumar et al., (2013) reported that CNT in magnesium improved ductility [5] while Dieringa et al., (2011) addition of CNT increases the hardness and strength of AZ31 [4].

The aim of this research is to synthesize monolithic AZ91 and AZ91 reinforced with 0.3 weight fraction of CNT. To investigate the effect of physical properties of AZ91 with heat treatment is applied.

## 2. Experimental Procedure

Magnesium powder (Mg) supplied by Strem Chemical, 99.8% purity with size of 75-100  $\mu\text{m}$ , Aluminium powder (Al), 95% purity with size in range 50 nm, supplied by Bendosen. Zinc powder (Zn) supplied by Ensure, 95% purity with size < 45  $\mu\text{m}$ . All the powder were used as matrix in composite. The multi-wall carbon nanotube (MWCNT) was supplied by ADV system with specification > 95% carbon purity was used as reinforcement materials. The specification of MWCNT is given in Table 1.

Table 1: Specification of multi-wall carbon nanotube

Materials	MWCNT
Diameter, nm	15-25
Length, $\mu\text{m}$	5-15
Purity	> 95%
Surface Area, $\text{m}^2/\text{g}$	150-210

The nominal composition (wt%) of AZ91 is 9% Al, 1% Zn and others 90% is Mg. The 0.3% of CNT was added to monolithic AZ91 to investigate the influence of CNT toward composite. AZ91 and AZ91 + 0.3 wt% CNT was prepared by milling in planetary mill for 20 hours to ensure that all powder are fully homogeneous without fine the size of all powder.

The homogeneous blended powders monolithic and reinforced with CNT were compacted into cylinder palette with dimensions of samples is 12 mm D, 5.5 mm thickness. The pressure used is 400 MPa. All samples pass through sintering process at temperature 450°C for 2 hours. After that, the composite undergoes solution treatment, T4 at 415°C for a couple hours and lastly will continue with ageing treatment, T6 at 175°C for 2, 4, 6 and 8 hours.

Specimen for microstructure was examined under SEM Hitachi TM 3000. The changes of phases was studied by using X-ray Diffraction (Bruker, D2 Phaser), using  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406$ ). The XRD scans were acquired from 20° to 80°. Rockwell hardness testing was conducted on samples that were done undergoes T4 and T6 treatment. Force used is 147 N, 1/16 indenter with HrF mode. At least seven tests were carried out in every sample and the mean value was reported. The specimen was polished using 60 ml Ethylene Glycol, 20 ml Acetic Acid, 1 ml Nitric Acid 19 ml distilled water.

## 3. Results and Discussion

### 3.1. Phase analysis Magnesium Composite

Figure 1 illustrates diffraction pattern for solution treatment while figure 2 until 4 illustrate diffraction pattern from the all sample after pass through ageing treatment, T6 at 175°C for 2, 4, 6 and 8 hours of ageing time. The X-ray diffraction is most powerful way to highlight the formation of intermetallic phase or  $\text{Mg}_{17}\text{Al}_{12}$  in magnesium based alloy because it is very sensitive to any disturbance of periodicity of crystal lattice (Nur Hidayah et al., 2016). XRD pattern will show the intensity of  $\alpha$ -Mg and  $\beta$ - $\text{Mg}_{17}\text{Al}_{12}$ . Presence of  $\beta$ -phase is important as hardening effect toward AZ91.

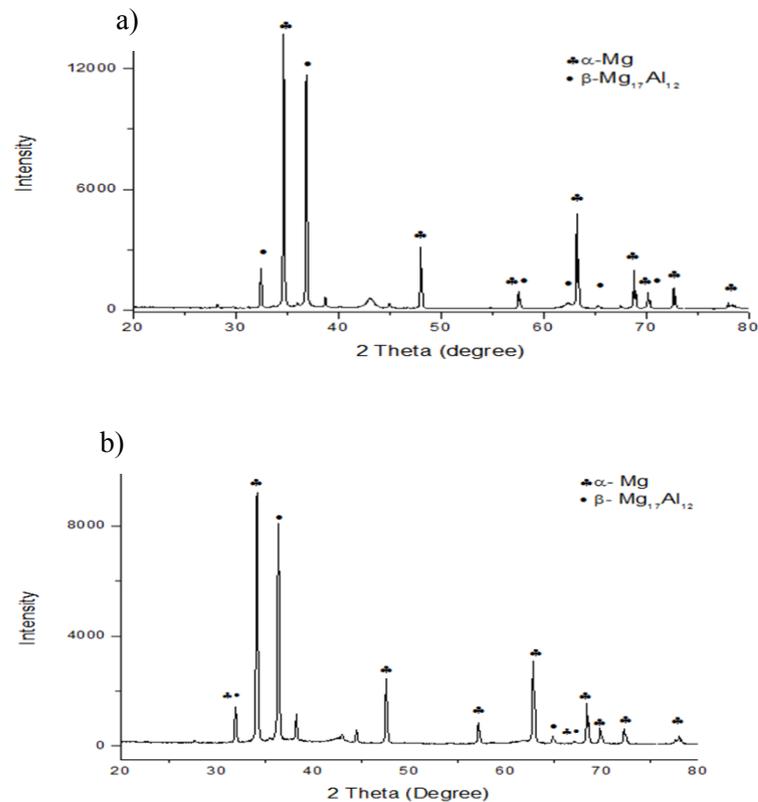
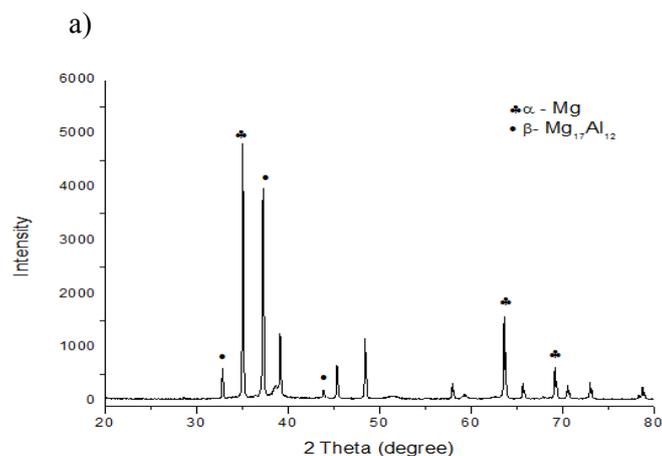


Figure 1: a) XRD pattern of solution treatment of AZ91 at 415°C for 2 hours b) XRD pattern of solution treatment of AZ91+0.3% CNT at 415°C for 2 hours.

On figure 1 a and b show the x-ray diffraction pattern for AZ91 and AZ91 + 0.3% CNT for solution treatment process at 415 °C temperature. AZ91 shows the decreasing number of  $\alpha$ -phase compared to AZ91+0.3% CNT. At this process for AZ91, its shown six peak formation of  $\beta$ - phase where's 2 peaks sharing high intensity  $\alpha$  and  $\beta$  phase on peak 57° and 70°.  $\beta$ -phase were form at 33°, 37°, 63°, and 65°. While the formation of  $\beta$ -phase on AZ91 + 0.3% CNT decrease in this process where it is formed at 37° and 65°. Two peak was shown formation of  $\alpha$  and  $\beta$ -phase on 33° and 67°. This analysis can be conclude that solution treatment give positive effect on hardening of AZ91 not to AZ91+0.3% CNT.



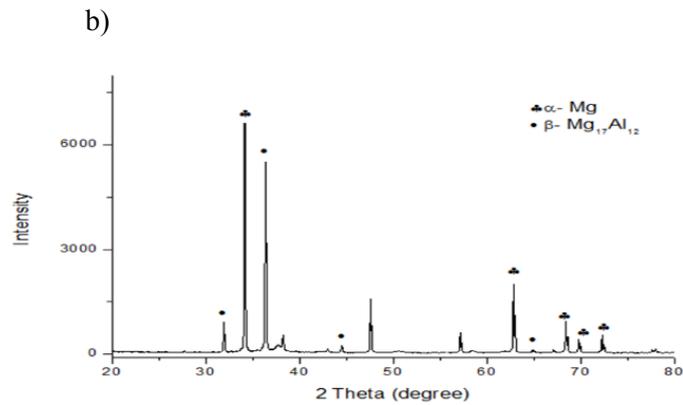


Figure 2: a) XRD of AZ91 after 2 hours ageing at 175°C b) XRD of AZ91+0.3% CNT after 2 hours ageing at 175°C.

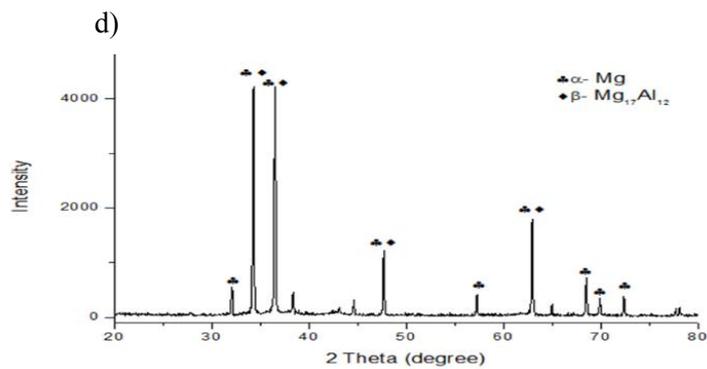
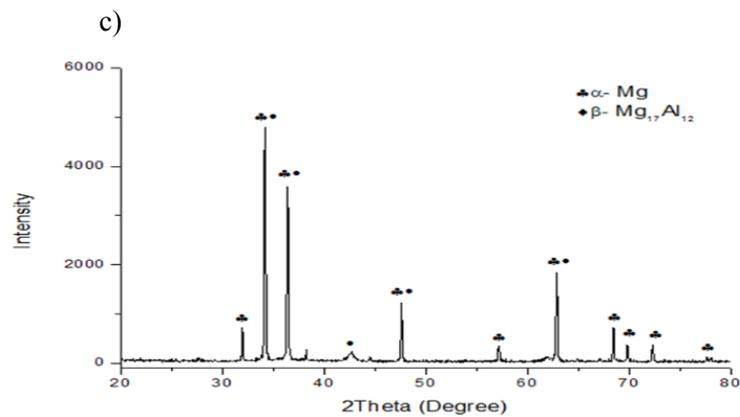


Figure 3: c) XRD of AZ91 after 4 hours ageing at 175°C d) XRD of AZ91+0.3% CNT after 4 hours ageing at 175°C.

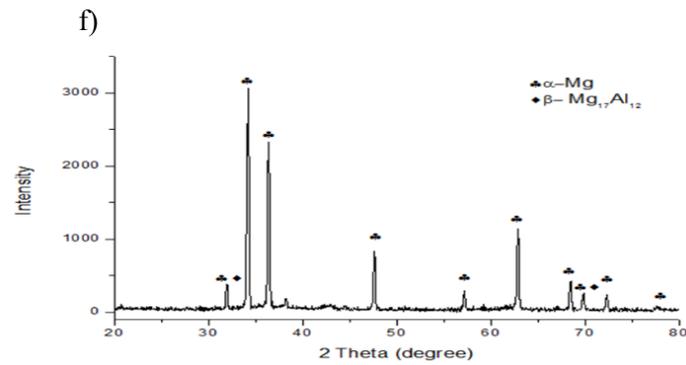
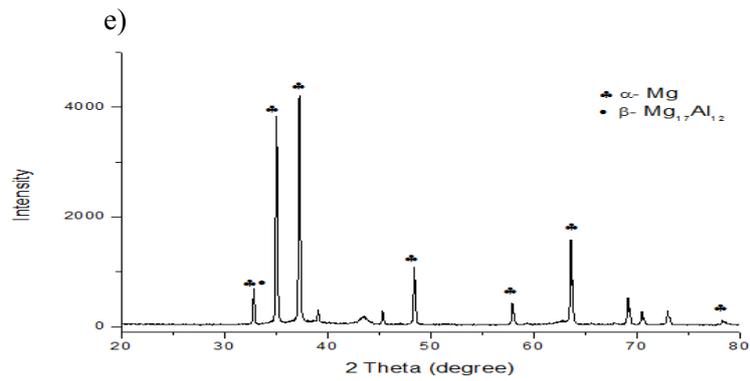
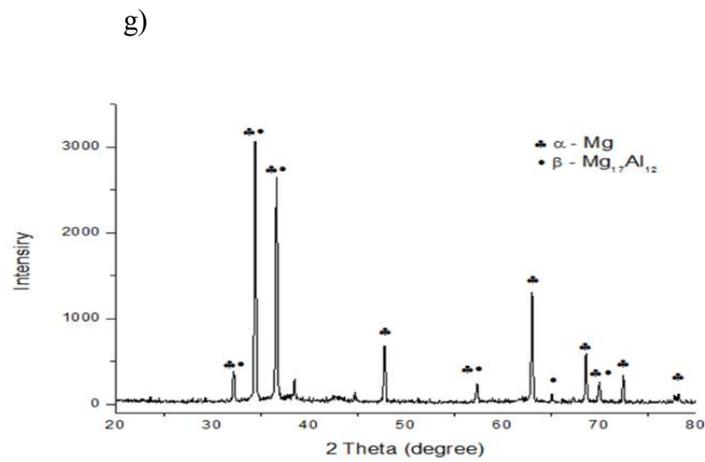


Figure 4: e) XRD of AZ91 after 6 hours ageing at 175°C f) XRD of AZ91+0.3% CNT after 6 hours ageing at 175°C.



h)

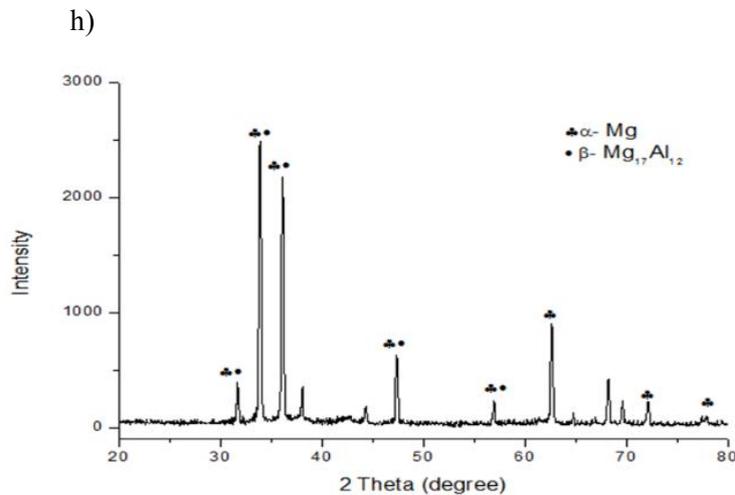


Figure 5: g) XRD of AZ91 after 8 hours ageing at 175°C h) XRD of AZ91+0.3% CNT after 8 hours ageing at 175°C.

Figure 2 a) shows X-ray diffraction for AZ91 while b) X-ray diffraction for AZ91+0.3% CNT for 2 hours of Ageing, T6 treatment. Figure shown that's, there are more  $\beta$ -phase of  $Mg_{17}Al_{12}$  were form at peak 33°, 37°, and 44° while  $\alpha$ -phase of Mg on peak 35° and 64°. Although there are many of  $\beta$ -phase formation for AZ91 but it cannot compete with formation of  $\beta$ -phase of AZ91+0.3% CNT where's this phase have four peak on this samples at 32°, 36°, 44° and 65°. Others is  $\alpha$ -phase of Mg. This result shown that 2 hours of Ageing give positive hardening effect toward AZ91+0.3% CNT compared to AZ91.

Figure 3 c) shows X-ray diffraction for AZ91 while d) X-ray diffraction for AZ91+0.3% CNT for 4 hours of Ageing, T6 treatment. As shown in figure, it shows there are many sharing peak between  $\alpha$  and  $\beta$ -phase for both samples. For AZ91 formation of both sample at peak 34°, 36°, 47° and 64° while on AZ91+0.3% CNT at peak 34°, 36°, 47° and 63°. Only on peak 43° stand formation of  $\beta$ -phase,  $Mg_{17}Al_{12}$  alone. This result shown positive hardening effect toward AZ91+0.3% CNT with have four peak of  $\beta$ -phase compared to AZ91 with have only three  $\beta$ -phase peaks.

Figure 4 e) shows X-ray diffraction for AZ91 while f) X-ray diffraction for AZ91+0.3% CNT for 6 hours of Ageing, T6 treatment. On this hours of ageing shown decreasing number formation of  $\beta$ -phase of  $Mg_{17}Al_{12}$ . AZ91 as shown in figure 4e)  $\beta$ -phase form on peak 33° only while on AZ91+0.3% CNT this phase form at 33° and 70° as shown in figure 4f). Others peak have full with formation of  $\alpha$ -phase. This result shown that's, AZ91+0.3% CNT have good hardening effect compared with AZ91.

Figure 5 g) shows X-ray diffraction for AZ91 while h) X-ray diffraction for AZ91+0.3% CNT for 8 hours of Ageing, T6 treatment., there are more  $\alpha$ -phase of Mg and  $\beta$ -phase of  $Mg_{17}Al_{12}$  sharing their peak on 33°, 34°, 37°, 57° and 70° while only single  $\beta$ -phase on peak 65°. But, for AZ91+0.3% CNT as shown in figure# h) shown that's  $\alpha$ -phase and  $\beta$ -phase sharing their peak together at 33°, 34°, 36°, 47° and 63°. There are no single  $\beta$ -phase stand alone. This result shown that 8 hours of Ageing give positive hardening effect toward AZ91 compared to AZ91+0.3% CNT.

### 3.2. Microstructure analysis

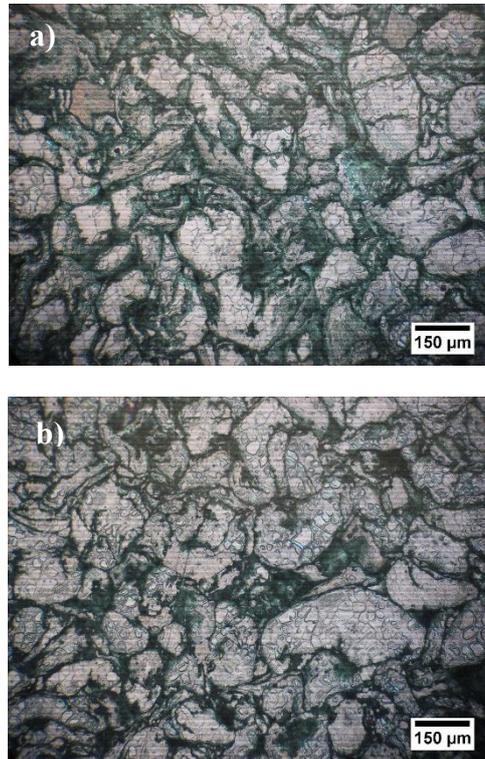


Figure 6: Optical microscope images solution treat sample at 120 minutes a) AZ91 b) AZ91+0.3% CNT.

Solution treatment of composite samples at 415 °C for 2 hours ensures that all the  $Mg_{17}Al_{12}$  can be redissolved in to matrix. No massive  $Mg_{17}Al_{12}$  has been seen with the solution treated samples. Figure 4 shows the microstructure of AZ91 and CNT added composite samples are solution treated for 120 min. The significant microstructural difference between these samples is the amount of discontinuous precipitates at the grain boundary. The black appearance at the grain boundary indicates the initiation of discontinuous precipitates. CNT added structure shows fewer amounts of discontinuous precipitates compared to the AZ91 composite [7].

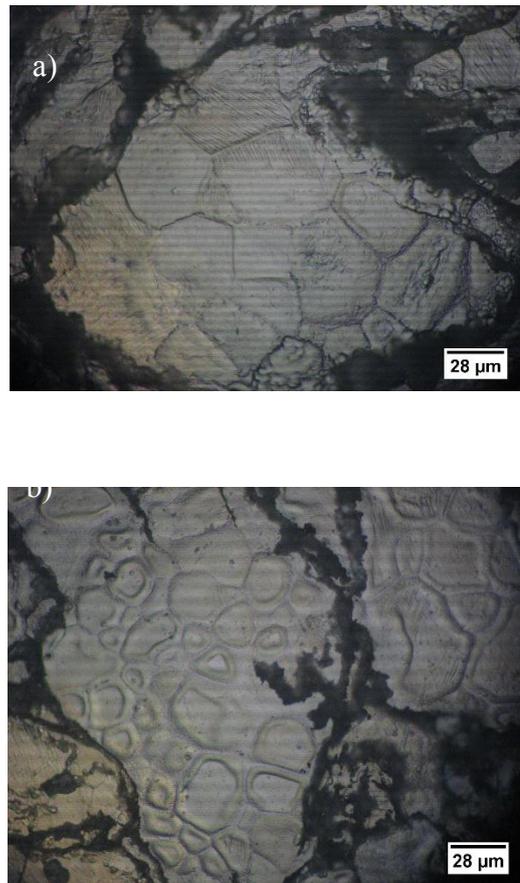


Figure 7: Optical microscope images ageing sample at 4 hours a) AZ91 b) AZ91+0.3% CNT.

The microstructural changes during the ageing treatment at 175 °C have been observed in all composite samples using optical microscopy. Figure 7 shows the microstructure of AZ91 and CNT added alloy samples aged for 4 hours. The black appearance at the grain boundary indicates the initiation of discontinuous precipitates. CNT added structure shows fewer amounts of discontinuous precipitates compared to the AZ91 composite. In fact, discontinuous precipitates are rarely seen with CNT added composite, which indicates that CNT effectively suppresses the nucleation of discontinuous precipitation. As the ageing time increased, the number of nucleation sites for discontinuous phase increases and the already formed discontinuous phases grow into the adjacent grains as evident from the microstructures of 6 hours aged samples (see Figure 8).

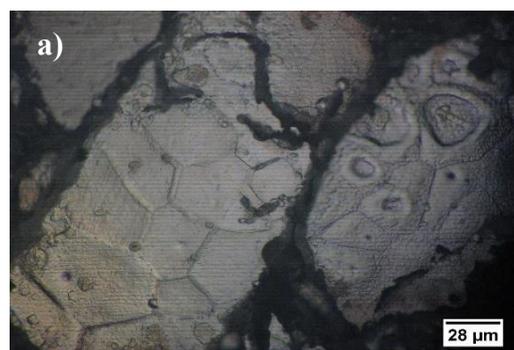




Figure 8: Optical microscope images ageing sample at 6 hours a) AZ91 b) AZ91+0.3% CNT.

### 3.3. Heat Treatment Behavior

The heat treatment behavior of hardness for AZ91 with and without CNT addition is shown in Figure 9.

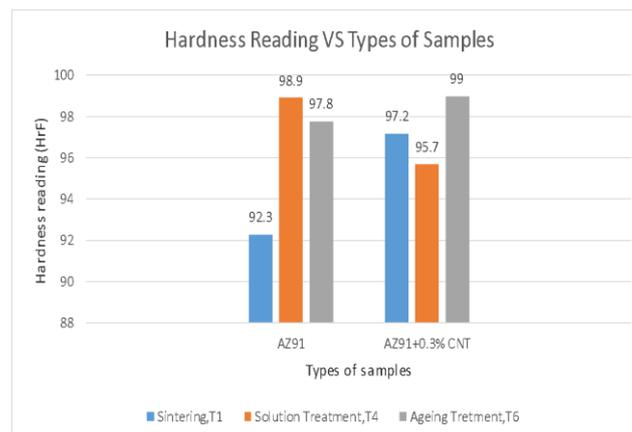


Figure 9: Rockwell Hardness (HrF) versus Type of Samples after pass through various type of heat treatment.

Rockwell hardness versus types of heat treatment was done by AZ91 composite is shown in figure 9. According to figure 9 the AZ91 reinforced CNT is highest hardness in sintering process compare to monolithic composite. But, after past through solution treatment, T4 it's shown that AZ91 increase drastically in hardness reading compared to AZ91 reinforced CNT drop into 95.7 N. Finally, AZ91 reinforced CNT slightly increase in hardness reading, 99.0 N after treated in T6 for 4 hours compared to AZ91 shown drop in hardness, 97.8 N after T4. This is contrast with result that be reported by Nur Hidayah et al.,(2015) the hardness for AZ91 + 0.3% CNT is lower than AZ91 [1]. In this research find that, 4 hours of ageing of AZ91 reinforced CNT give accelerate in hardness compared without CNT AZ91. But, same result was report by Nur Hidayah et al., state that hardness drop constantly until at 24 hours ageing. In this research, hardness reading of AZ91 reinforced CNT was drop when hours of ageing increase to 6 hours and 8 hours.

### 3.4. Compression Test Magnesium Composite

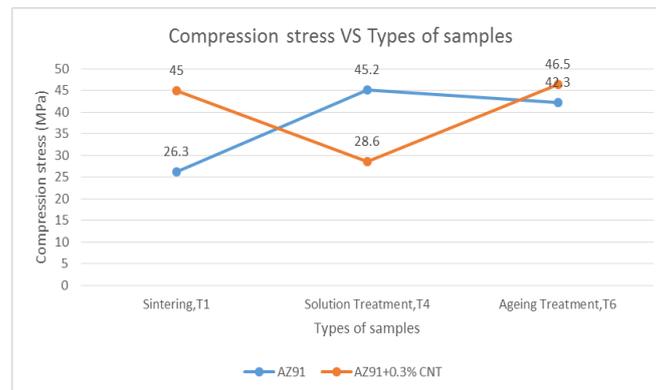
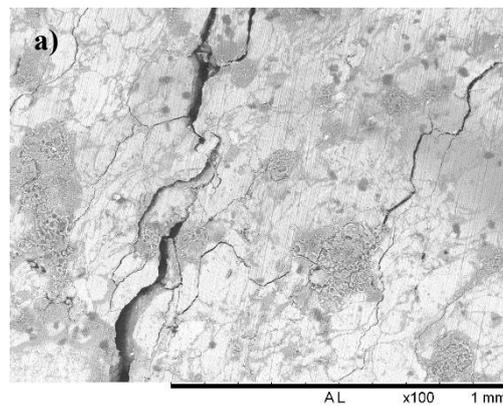


Figure 10: Compression test (MPa) versus Type of Samples after pass through various type of heat treatment.

Compression test was conducted for investigation of crack behavior in samples according to standard ASTM E9 at room temperature with L/D: 1.5 and strain rate of  $1 \times 10^{-4} \text{ s}^{-1}$ . The tests were continued till two points: 1- ultimate reduction of stress which was assumed as fracture point and 2- the point in which 8% strain was occurred. Figure 10 shown that sintering of AZ91 give low hardening. But, it was obviously slightly increased from T1 to T4 go through 45.2 MPa. This result shown that AZ91 give good hardening at Solution Treatment process compared to AZ91+0.3% CNT that show drastic slope of lowering in reading off compression stress on T4, 28.6 MPa. But, after undergoes T4, AZ91 are little drop in reading, 42.3 MPa compared to AZ91+0.3% CNT it was shown drastic positive slope of increasing in strength at Ageing treatment, T6. The reading is 46.5 MPa increase from 28.6 MPa on T4.

### 3.5. Fracture Analysis under SEM



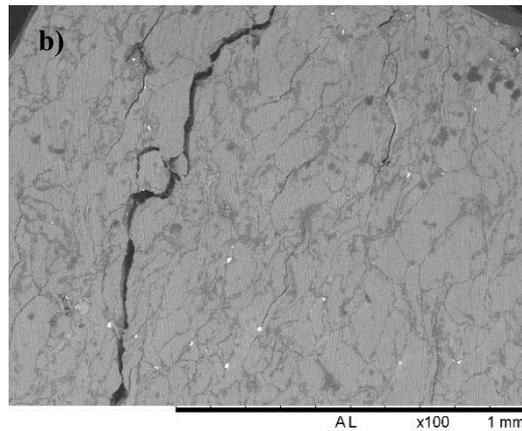


Figure 11: SEM image of crack propagation for AZ91+0.3% CNT a) Ageing for 2 hours b) Ageing for 8 hours.

The fracture surface shows on figure 11 elongated dimples indicating that significant plastic deformation takes place during compressive deformation [8]. Figure 11a) crack propagation aged sample of AZ91 + 0.3% CNT for 2 hours. It's shows that transgranular fracture. The fracture follows the edges of lattices in a granular material, ignoring the grains in the individual lattices. This results in a fairly smooth looking fracture with less sharp edges than one that follows the changing grains while in figure 11b) shown that intergranular fracture. The fracture that grows along the grain boundaries of the material.

#### 4. Conclusion

AZ91 and AZ91 reinforced carbon nanotube were successfully fabricated using powder metallurgy method. The way to avoid clustering of CNT is by using mechanically alloying because its can dispersed CNT homogeneously into the matrix of AZ91. The current investigates effect of solution treatment, T4 and ageing treatment, T6 toward magnesium composite. T4 give positive hardening effect to AZ91 while T6 give positive hardening effect to AZ91 with addition of CNT. The CNT reinforced react as softening mechanism during initial ageing which was attributed to dislocation recovery before the formation of coherent precipitates which are responsible for strengthening the material in the early of ageing. Composite AZ91 + 0.3% CNT shows accelerated aging and achieve peak aged hardness at 4 hours of ageing time. The positive effect of hardening is expected due to the precipitation of  $Mg_{17}Al_{12}$ .

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