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The Effect of CNT Content and Sintering Temperature on Some Properties of CNT-reinforced MgAl Composites

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Abstract:

Magnesium and its alloys are considered as an important material for modern light structures at the present time and therefore they have a wide area of usage especially in electronics, aircraft, and automotive industries. Its popularity increases further as a result of its production as a composite material. In this study, carbon nanotube (CNT) reinforced MgAl matrix composite materials were produced by using the hot pressing method. While 0.25 wt%, 0.50 wt%, 0.75 wt%, and 1.00 wt% CNT were added, 450°C, 500°C, and 550°C was selected as sintering temperatures. The effect of sintering temperature and amount of CNT on some properties of the composites was examined. Microstructure and phase composition of the materials were examined by using optical microscopy (OM), scanning electron microscope (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS). The hardness of the composites was measured in Brinell. Relative densities of the materials were determined in accordance with Archimedes' principle. A dense and slightly porous structure was obtained based on both SEM images and density measurements. XRD analyses showed that there were Mg, Mg₁₇Al₁₂, and MgO phases in the composites. The reason for the absence of Al in graphics was that Al formed the solid solution by being dissolved in Mg. Also, the C peak could not be determined for CNT. The hardness of the composites increased with the increasing sintering temperature and CNT addition. The highest hardness value was measured as 88.45 HB10 with the addition of 1.00 wt% CNT at 550°C. Free distribution of CNT in the matrix caused this hardness increase.

Keywords: MgAl alloys; CNT; Composites; Hot press sintering.

1. Introduction

Magnesium alloys have a specific importance in the defense industry and transportation sector due to their properties of lightness and high specific strength (strength/density) [1-3]. Its unalloyed form has low strength and toughness values; therefore, it is used as alloyed.

Magnesium also has high thermal conductivity, high dimensional stability, good electromagnetic protection, high damping, high workability, and easy recycling properties [4,

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5].

These properties make Mg alloys valuable in numerous industries such as automotive, computer, aviation, mobile phones, and sports materials. Mg is also used as an implant material due to low weight and compatibility to metabolism [6, 7]. In addition, the number of studies conducted on using energy resources more efficiently has increased in recent years. In this context, studies have been conducted on making vehicles lighter in order to reduce fuel consumption in automotive industry [8].

The use of magnesium alloys may substantially decrease weights of structures without compensating their structural properties. Among alloy elements, Al, Zn, and Mn increase strength, toughness, and corrosion resistance, respectively. However, the increase in the amount of Zn causes to red shortness. As alloy elements; rare earth elements are added for reducing microporosity, Zr for grain refining, Ag or Cu for improving high-temperature properties, and Th for improving friction properties at the present time [9, 10].

Recently, metal matrix composites (MMCs) are commonly researched and produced due to their excellent advanced technological properties. Magnesium matrix composites among these MMCs are interesting materials because of low density, high strength and high wear resistance [11, 12]. In composite materials, on the other hand, the reinforcing member is desired to have small grain size, low density especially for light structures, and high hardness for strength. Carbon nanotubes (CNT) are new generation materials to be used for this purpose. Due to their strength/density ratios, CNTs are one of the ideal reinforcing elements for composite materials. In recent years, they are also used as reinforcing element in Al, Mg, Ti, and their alloys [13-15].

Magnesium alloys and composites can be produced by using different methods. These methods are mainly casting and powder metallurgy methods. In the casting method, which is an expensive and detailed method, it is difficult to control the formation of intermetallic brittle phases. This brings the powder metallurgy method into the forefront in the production of these materials. In addition, in the casting method, it is a problem to homogenous mix reinforcing element, especially in composites. However, a homogenous mixture can be obtained by using powder metallurgy method [16].

In this study, MgAl alloys were produced by the powder metallurgy method adding carbon nanotubes. In this way, strengths of MgAl alloys were increased with both formation of phases and external addition of particles. Thus, the effect of production parameters and material addition on some properties of composites was experimentally examined.

2. Experimental procedures

2.1. Materials and fabrication

In this study, carbon nanotube reinforced (CNT) MgAl matrix composite materials were produced. An alloy of the mixture (95% Mg + 5% Al) containing magnesium (Alfa Aesar) with 99.8% purity and -325 mesh grain size and also aluminum powder (Alfa Aesar) with 99.5% purity and -325 mesh grain size was used as matrix material in all experiments. The multi-walled CNT was chosen as 9.5 nm in diameter and 1 micron in size (Sigma-Aldrich). 0.25 wt%, 0.50 wt%, 0.75 wt%, and 1.00 wt% CNT were added into the matrix in order to determine its effect on properties.

It is required to mix the chosen powders well and to ensure their homogeneous distribution in the matrix in order for them to yield the required performance in the matrix in composite production. For this purpose, powder mixers operating based on triaxial rotation principle were used. Firstly, 5 wt.% Aluminum was added into magnesium powder which was supplied as ready. This mixture was stirred at 20 rpm for 30 minutes and then at 20 rpm for 120 minutes in the powder mixer by adding CNT at different ratios. 1 wt% PEG (polyethylene glycol) was added into composite powder mixture to maintain distribution, to

prevent taking off matrix powders from graphite molds, and to minimize frictions between mold and powder. After the mixing process was completed, the mixture was kept in storage tubes in order to prevent contact with air and oxidation. The powder mixtures stirred in the mixer, was operating according to triaxial rotation principle, were pressed in the hydraulic cold pressing machine. The goal of cold pressing is to easily place powder mixtures in graphite molds before hot pressing and to use molds with a smaller volume. Then, composites placed in graphite molds were transformed into bulks in sizes of 10 x 10 x 40 mm by using a PLC controlled vacuum hot press machine (Zhengzhou Golden Highway, SMVB 80, China), which was operating according to principle of direct resistance heating, at 450°C, 500°C, and 550°C for 4 minutes and under 35 MPa.

2.2. Characterization of the composites

In order to determine densities of the composites, densities of all samples were measured by using a scale (AND GR-200) with 10^{-4} precision according to Archimedes' principle. According to this method, dry weights of the samples in the air were first measured and then they were placed into a tared metal basket and immersed into a measuring cup full of distilled water, the temperature of which was measured. After the samples were weighed again in the water, their density values were calculated according to the equation (1) below:

$$d = \frac{(A)x(d_s)}{A - B} \quad (1)$$

In this equation; d is the density of sample (g/cm^3), A - weight of the sample in air (gr), B - weight of the sample in the water (gr), and d_s - density of water at the temperature measured (g/cm^3). Relative densities of samples were calculated according to the following formula (2) by considering theoretical densities and experimental densities of the composites:

$$\rho_b = \frac{\rho}{\rho_k} \times 100 \quad (2)$$

Where, ρ_b - relative density (%), ρ - experimentally measured density (g/cm^3) and ρ_k - theoretical density calculated based on powder mixture ratios (g/cm^3).

The hardness of the samples obtained by using hot pressing method was measured in Brinell by using a 2.5 mm diameter ball with a 62.5 kg load in the brinell hardness testing machine. In order to determine hardness exactly, hardness values were measured from the middle, end, intermediate, and rear parts of the samples and a total of 6 hardness values were taken from each sample. Mean hardness values of the samples were calculated by taking an average of remaining hardness values after ignoring the highest and the lowest values.

For metallographic examinations, the samples were molded by using cold molding technique and ground by rough and fine grinding stages, respectively. Ground samples were polished by using 3 and 1 micron diamond solutions, respectively and etched by using HNO_3 (40 pct.) + $\text{C}_2\text{H}_5\text{OH}$ (60 pct.) solution. Olympus GX4 inverted metallurgical microscope and Stream image analysis system was used for optical examinations. FEI QUANTA 250 FEG SEM device was used to carry out SEM analyses. EDS analyses were also carried out along with SEM in order to determine the chemical composition of the microstructure. X-ray analysis was performed in order to determine the phases in the microstructure. X-ray analyses were performed by using Bruker D8 Advance device.

3. Results and discussion

Fig. 1 and Fig. 2 shows optical images of the composites. It was clearly seen from the images that Mg and Al powders were mixed homogeneously. However, carbon nanotube particles were observed to have a partially homogeneous distribution. They were observed to coagulate in clusters at some points. CNTs were generally located at points where powder particles joined. It was also seen from images that the structure became tighter as sintering temperature increased.

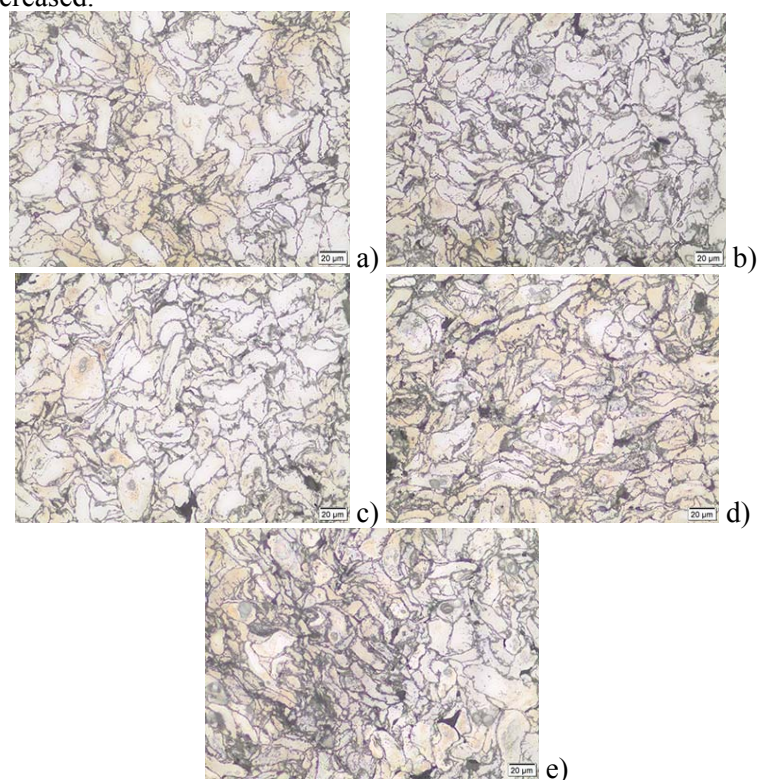


Fig. 1. Optical images: (a) MgAl, (b) MgAl- 0.25% CNT, (c) MgAl- 0.50% CNT, (d) MgAl- 0.75% CNT and (e) MgAl- 1.00% CNT.

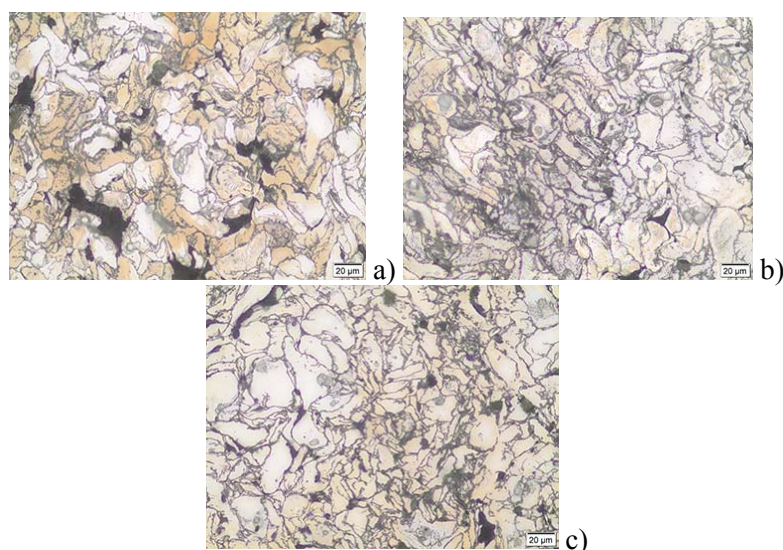


Fig. 2. Optical images of MgAl- 1.00% CNT composite for different sintering temperatures: (a) 450 °C, (b) 500 °C, and (c) 550°C.

Fig. 3 shows SEM images of the fracture surface of MgAl- 1.00% CNT composite at different sintering temperatures. Intergranular separation was observed due to sintering conditions of 450°C. The rupture was partially observed between Mg grains by waisting. This was associated the fact that matrix had a ductile structure and the samples were subjected to excessive plastic deformation and ruptured. In addition, it was understood that ductile fractures occurred since the hardness of magnesium was also low in zones where waisting was intense. There was a weak bonding at the interface of grains at 450°C. This is because when fracture surface images were examined, it was observed that there was a certain space between powder particles. When fracture surfaces of the composites sintered at 500°C and 550°C were examined, the fracture was found to be caused by the plastic deformation rather than being between grains. The fracture surface images showed that porosity also significantly decreased as sintering temperature increased.

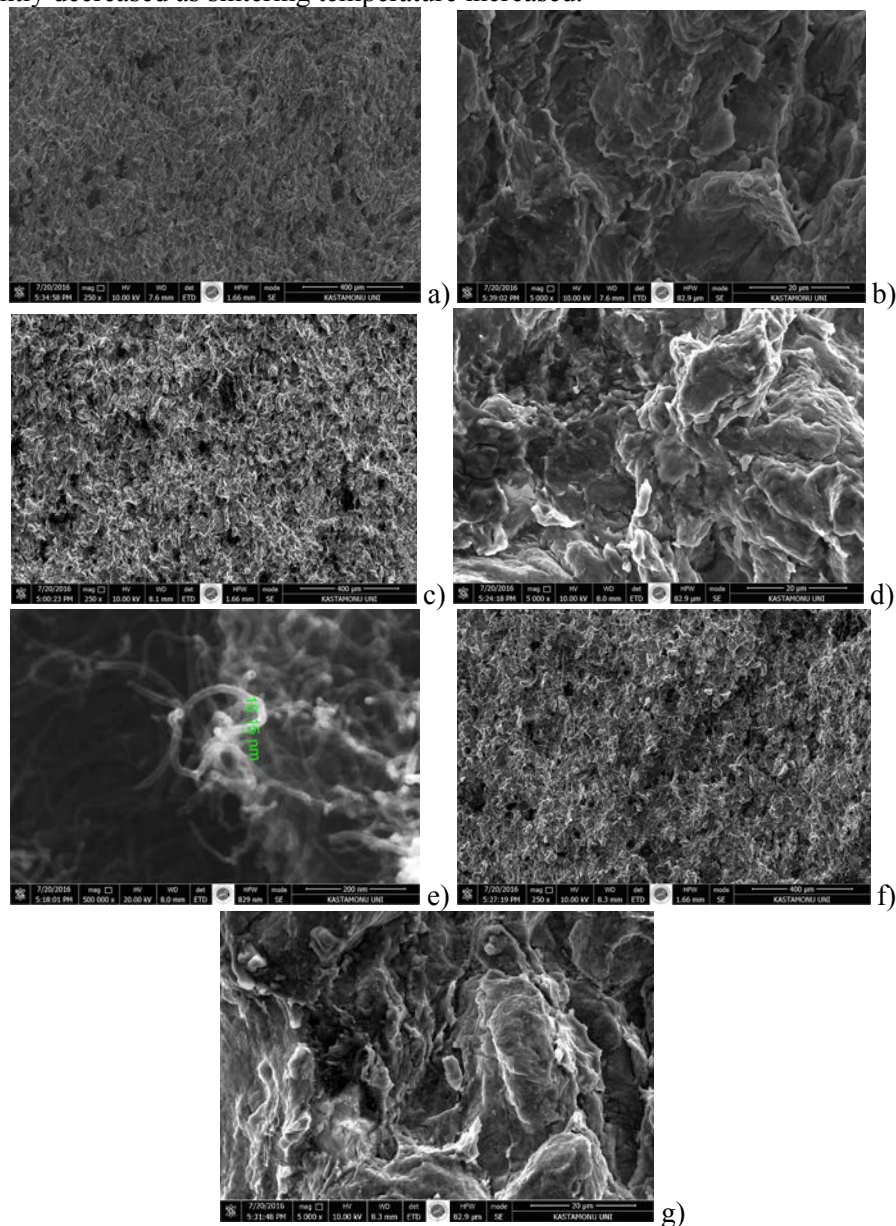


Fig. 3. Fracture surface images for MgAl- 1.00% CNT: (a) and (b) 450°C, (c), (d) and (e) 500°C, (f) and (g) 550°C.

Fig. 3 shows the view of the carbon nanotube. Its diameter was approximately 15 nm. In addition, locations of carbon nanotubes were seen more evidently from fracture surfaces

(Fig. 4). As we mentioned above, CNTs were located in clusters.

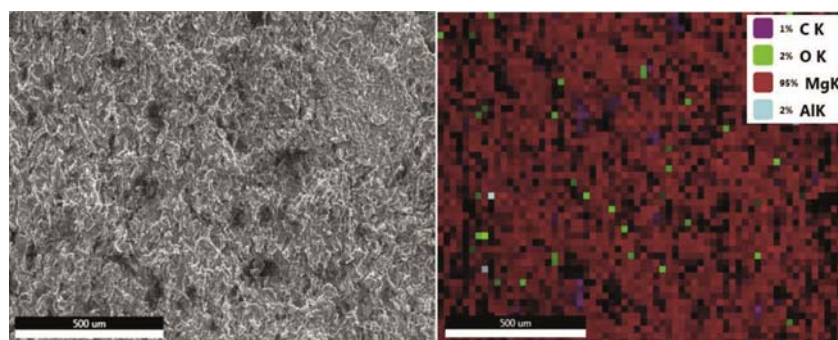


Fig. 4. MAP analysis of fracture surface for MgAl- 1.00% CNT sintered at 500°C.

Fig. 5 and Fig. 6 show EDS analysis of undoped MgAl and MgAl- 1.00% CNT sintered at 500°C. CNT was hardly determined in the structure. EDS analysis clearly revealed that composites were oxidized. It was also obvious that oxidation was present in joint points of powder particles. Generally, this negatively influenced sintering, as well.

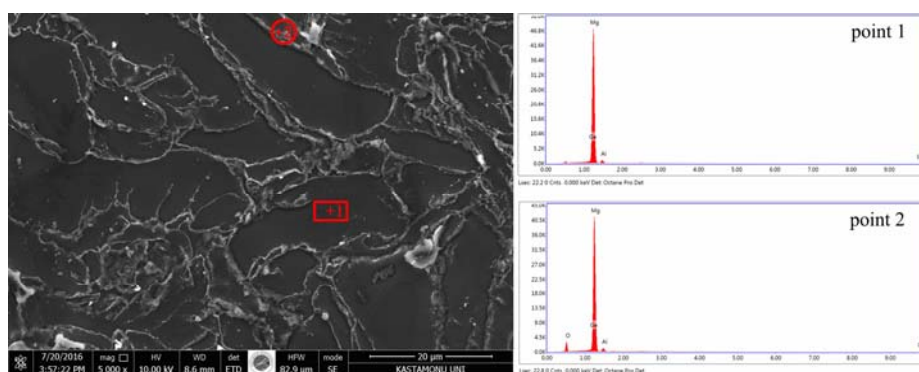


Fig. 5. EDS analysis of undoped MgAl sintered at 500°C.

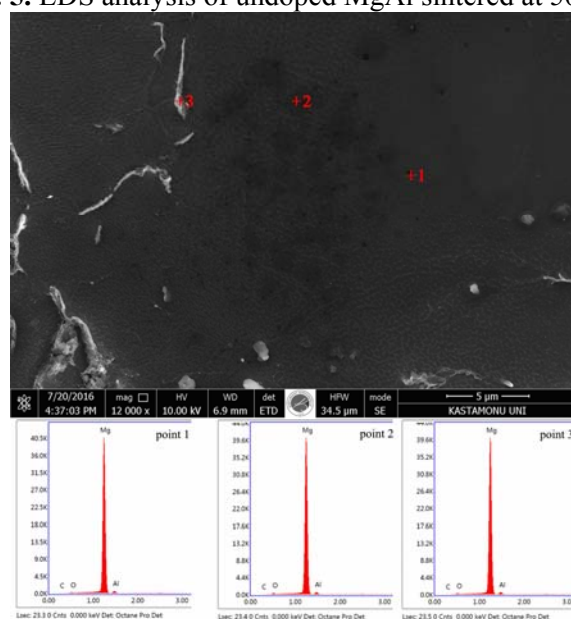


Fig. 6. EDS analysis of MgAl- 1.00% CNT sintered at 500°C.

XRD analysis was carried out in order to determine whether or not a phase occurred to provide a bonding in the interface of powder particles depending on sintering parameters and how the the condition of current phases changed. Fig. 7 shows XRD graphics of MgAl, MgAl- 0.5% CNT and MgAl- 1.00% CNT composites. Generally, Mg, $Mg_{17}Al_{12}$ and MgO phases were observed in all graphics. $Mg_{17}Al_{12}$ phase formed in the parent of magnesium alloy as it was reported by Bhingole et al. [17] in their study of $MgO-Al_2O_3-MgAl_2O_4$ dispersed magnesium alloy composites. The reason for the absence of Al in graphics was that Al formed the solid solution by being dissolved in Mg. Also, the C peak could not be determined for CNT. This is because it is difficult to detect the CNT signal by XRD when dealing with structures [18]. $Mg_{17}Al_{12}$ phase occurred between Mg and Al. The content of this phase was detected approximately 3%. The matrix of the composite consisted of Mg+ $Mg_{17}Al_{12}$.

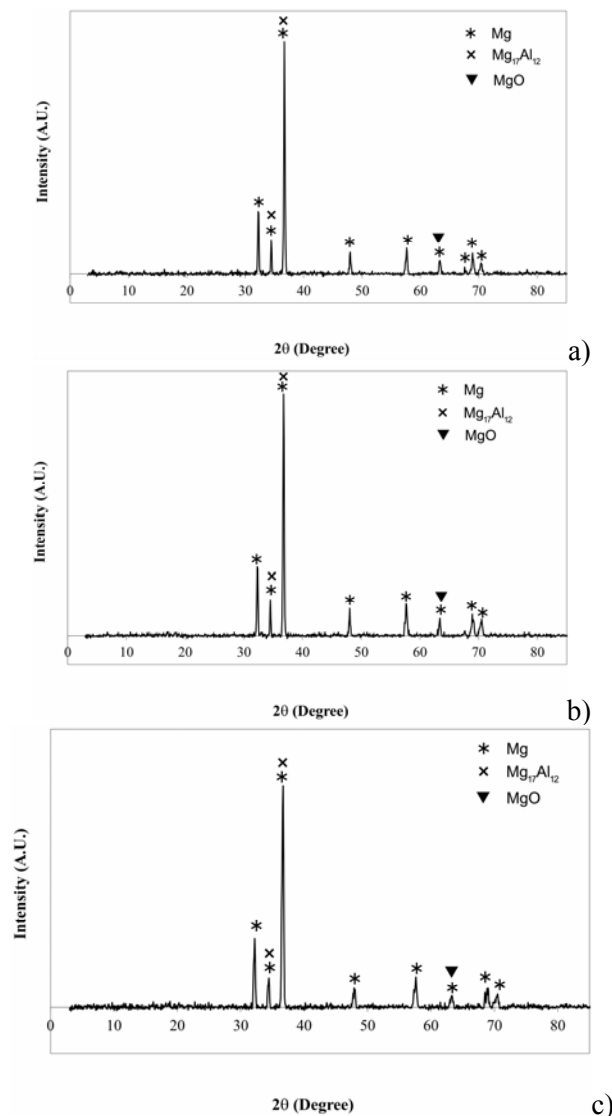


Fig. 7. XRD graphics: (a) MgAl, (b) MgAl- 0.5% CNT and (c) MgAl- 1.00% CNT.

The density of each sample was measured in order to determine the effect of sintering parameters and CNT addition on compressibility properties of powders. Fig. 8 shows both experimental density values and relative density values of MgAl and MgAl-CNT at different sintering temperatures. According to Fig. 8a, the addition of CNT increased density of the

composite, which was caused by the fact that density of CNT was higher than Mg. As the sintering temperature increased, the densities increased. The difference between theoretical and experimental densities decreased with the increase of sintering temperature since according to the equation $D = D_0 \exp(-Q/T)$, diffusion between powder metal particles varied depending on sintering temperature. Where D is diffusion coefficient, Q is activation energy, R is Boltzmann coefficient, and T is temperature. Increasing sintering temperature increased the formation of solid binding between particles and accelerated diffusion between particles. Relative densities also increased with increasing addition of CNT at constant sintering temperature and relatively decreased in addition of 1.00% CNT (Fig. 8b). This might be explained by the fact that CNTs filled micro pores. On the other hand, coagulations highly occurred with the addition of 1.00% CNT. This was also understood from fracture images. Relative densities were observed to increase at increasing sintering temperatures due to high diffusion rates [19, 20].

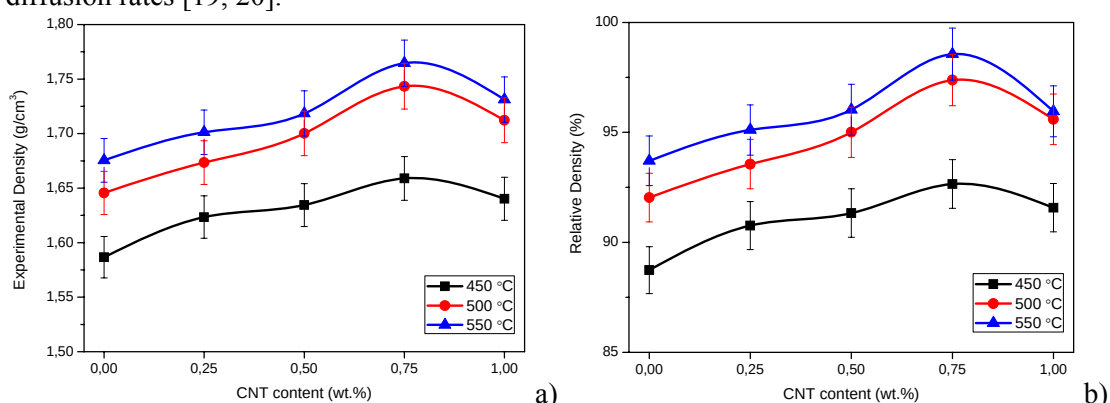


Fig. 8. Density graphics of composites: (a) experimental density and (b) relative density.

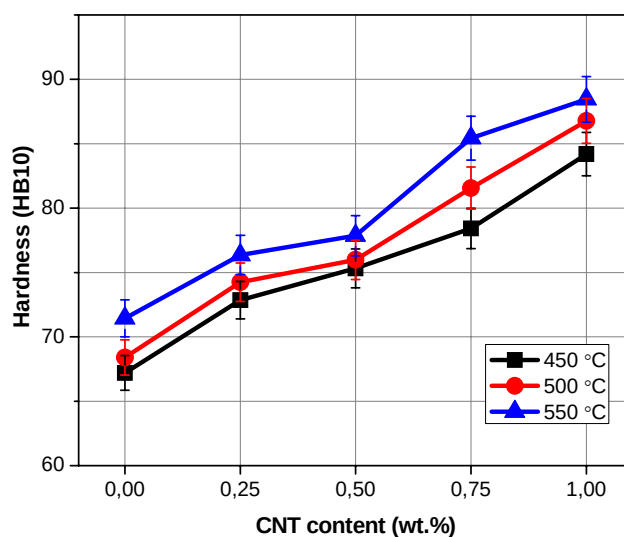


Fig. 9. The effect of sintering temperature and carbon nanotube addition on the hardness values.

The hardness of MgAl and MgAl-CNT composites was measured by using brinell hardness test device. Fig. 9 shows changes of hardness based on sintering temperature and CNT quantity. The hardness of the samples was observed to increase with the increase of sintering temperature. This was associated with a good binding occurring between neighboring particles through solid phase diffusion with the increasing temperature [21, 22]. According to another opinion, MgAl matrix is easier to get compact due to the improvement

of the plastic deformation capability of MgAl matrix at higher temperatures, which results in higher hardness [23]. The hardness of the samples produced with the addition of CNT significantly increased. This hardness increase can be asserted to be caused by the distribution of CNT within the matrix. In other words, the increase of hardness can be explained with the rule of a mixture [24, 25]. The rule of mixture for materials with high relative density is as follows:

$$H_k = H_m f_m + H_t f_t$$

Where H_c is the hardness of composite, H_m is the hardness of matrix, H_t is the hardness of reinforcing element, and f_m and f_t are volume ratios of the matrix and reinforcing element, respectively. In addition, CNTs contributed to increasing of strength and hardness of a material by preventing dislocations' movement [26, 27]. Moreover, it was argued that the hardness of the CNT composite samples increased because CNTs filled the micro-voids of the matrix particles [28].

4. Conclusion

Following information, results, and conclusions were obtained in this study aims to examine the effect of sintering temperature and carbon nanotube on some properties of MgAl-CNT composites.

1. CNT was observed to distribute relatively homogeneously within the matrix in produced samples based on SEM and optical studies. It was found that as sintering temperature increased, the number of the pores in the structure decreased. In addition, CNT addition caused a decrease in a number of pores.
2. According to XRD analyses, Mg, $Mg_{17}Al_{12}$ and MgO phases were observed in composites. The reason for the absence of Al in graphics was that Al formed the solid solution by being dissolved in Mg. Also, the C peak could not be determined for CNT. This was associated with the fact that mass of CNT was low.
3. Providing that the ratio of CNT remained constant at different sintering temperatures, relative densities of composites increased with increasing sintering temperature. As temperature increased, diffusion between powder particles accelerated, which increased densification. The highest densification occurred with the value of 98.6% in MgAl - 0.75% CNT sample sintered at 550°C.
4. As sintering temperature and the addition of CNT increased, the hardness of matrices increased. The hardness of MgAl sintered without the addition of CNT was measured to be 67.20 HB10 at 450°C, 68.40 HB10 at 500°C, and 71.44 HB10 at 550°C. This was associated with obtaining a more compact structure as a result of pores decreasing with increasing temperature. The highest hardness value was measured as 88.45 HB10 in the addition of 1.00% CNT at 550°C. Free distribution of CNT in matrix caused this hardness increase.

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Садржај: Магнезијум и његове легуре се сматрају битним компонентама за израду модерних лаких материјала и, због тога, имају широку примену, посебно у електроници, авио- и ауто-индустрији. Његова употреба је проширена и коришћењем у производњи композитних материјала. У овом раду, композитни материјал састављен од MgAl ојачаног угљеничним нанотубама је произведен методом врућег пресовања. Додавано је 0.25 wt%, 0.50 wt%, 0.75 wt%, and 1.00 wt% угљеничних нанотуба, а температуре од 450°C, 500°C и 550°C су одабране за синтеровање. Испитан је утицај температуре синтеровања и садржаја угљеничних нанотуба на неке од својстава композита. Микроструктура и фазни састав материјала су испитани оптичком микроскопијом, скенирајућом електронском микроскопијом (СЕМ), дифрактометријом X-зрака и електронском дисперзионом спектроскопијом X-зрака (ЕДС). Тврдоћа композита је мерена у бринелима. Релативне густине материјала су одређене помоћу Архимедовог принципа. Помоћу СЕМ-а и мерења густине утврђено је да је структура густа и има малу порозност.

Дифрактометријска мерења су утврдила присуство Mg, $Mg_{17}Al_{12}$, и MgO кристалних фаза у композиту. Одсуство Al је објашњено формирањем чврстог раствора са Mg, док пик угљеника који би потицао од угљеничних нанотуба није уочен. Тврдоћа композита се повећава са повећањем температуре синтеровања и удела угљеничних нанотуба. Највећа измерена вредност је 88.45 HB10 при 1.00 wt% угљеничних нанотуба и синтеровању на 550°C. Повећање тврдоће је изазвано слободним распоредом угљеничних нанотуба у MgAl структури.

Кључне речи: MgAl легуре, угљеничне нанотубе, композити, вруће пресовање.

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