



Mechanical and Optical Properties of Multiwall Carbon Nanotube-Reinforced ZA27- Al_2O_3 Hybrid Composites Fabricated by Powder Metallurgy Routine

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Abstract

In this study, multiwall carbon nanotubes (MWCNT) were employed as reinforcement elements in the hybrid composites of ZA27- Al_2O_3 produced through a powder metallurgy routine. The MWCNTs were incorporated at concentrations of 1%, 3%, and 5% in the samples. The preparation involved planetary ball milling for 4 hours, utilizing 10-diameter steel balls, followed by pressing the powders using a 20-ton capacity manual press machine after sintering at 400 °C. The composites' microstructures were analyzed using an optical microscope, and their densities were measured following the principle of Archimedes. Furthermore, the mechanical properties were evaluated by conducting Vickers hardness tests. The results indicate that the addition of MWCNTs resulted in an increase in hardness values. The sample with ZA27- Al_2O_3 -5% MWCNT exhibited the highest hardness scale value

Keywords: Mechanical alloying, hybrid composites, ZA-27 zinc alloy, carbon nanotube.

1. Introduction

Zinc-Aluminum (ZA) alloys have gained popularity as metal matrix composites due to their exceptional strength, hardness, and wear resistance. These qualities position them as viable alternatives to traditional materials such as aluminum, brass, bronze, or iron for designers working on structures and machine parts. Consequently, the increasing utilization of ZA alloys across various industrial applications (,such as automotive, building, sporting goods, toys, hardware, decoration and white goods[1]) is becoming a notable trend[2]. Moreover, ZA-27-based composites have emerged as a cutting-edge generation of metal matrix composites, showcasing the potential to fulfill the evolving demands of advanced engineering in bearing and bushing applications[3]. Nevertheless, the alloyed system does exhibit certain limitations, notably its diminished performance at elevated temperatures exceeding 120°C and a relatively high coefficient of thermal expansion[4]. One of the possible solutions for overcoming these deficiencies is the reinforcement of the ZA alloy by incorporation of a thermally stable second phase[5]. To address these shortcomings, one potential approach is the incorporation of a thermally stable second phase to reinforce the ZA alloy. This strategy has proven successful in enhancing the properties of aluminum-based alloys through the addition of ceramic particles. Consequently, a growing number of researchers have been drawn to explore the production and analysis of ceramic-reinforced composites[6-10].

Incorporating hard and thermally stable ceramic reinforcements into ZA alloys significantly enhances their hardness[11], elastic modulus[12], and reduces the coefficient of thermal expansion at ambient temperature. Furthermore, as the content of the reinforcing phase increases, there is a continuous improvement in the properties of the composite material. The increase in



hardness could be accompanied by[5] or without a decrease in strength[13]. Kumar et. al[14] reported zirconium diboride (ZrB_2) reinforced zinc aluminum-based alloys. Results indicate the mechanical properties of the composites were improved. At 9 vol% of ZrB_2 , the matrix grains are refined by 48%, and the hardness value is improved by 68% compared to pure ZA alloy. Khan et al[15] studied titanium carbide (TiC)-reinforced ZA-27 alloy composites prepared by using the powder + liquid metallurgy route. It was observed that increasing the TiC reinforcement content from 5 wt % to 10 wt % results in improved wear resistance in the ZA-based composite[16].

Hybrid metal matrix composites (HMMCs) are second-generation composites where more than one type, shape, and size of reinforcements are used to obtain better properties[17]. Hybrid composites possess better properties compared with single-reinforced composites as they combine the advantages of their constituent reinforcements. A study conducted by Marigoudar[18] depicts an experimental model for investigating the mechanism and nature of chip formation during the machining of silicon carbide (SiC)-reinforced mono and SiC and graphite-reinforced ZA43 HMMCs. It was observed that hybrid composite being more brittle than mono composite material produces short segmental chips. the work is concentrated on the production of ZA-27 alloy and hybrid composite reinforced with 1.5 weight percentage of SiC and 0.5 weight percentage of graphite (Gr). The ultrasonic-assisted stir casting method is used for the preparation of the ZA-27/SiC/Gr hybrid metal matrix composite. The mechanical properties of the hybrid composite increase as compared to the base metal.

Specifically, carbon nanotubes can be utilized as reinforcing elements in composites due to their exceptional properties[19-28]. A carbon nanotube is a unique form of carbon structure, exhibiting both elasticity and flexibility, yet possessing remarkable hardness, being ten times stronger than steel. It also boasts excellent electrical conductivity and an impressive melting point exceeding 3550°C , which piques interest for its diverse applications in mechanical, electrical, and thermal realms. Leveraging its exceptional mechanical properties, carbon nanotubes serve as an ideal reinforcement in metal composites.

In this study, we present the first-ever production of multi-wall carbon nanotube (MWCNT)-reinforced zinc-based hybrid composites through a mechanical alloying routine. We investigate the impact of varying MWCNT ratios on the resulting HMMCs. Additionally, we conduct microstructural, density, and mechanical analyses to gain comprehensive insights into the performance of these innovative materials.

2. Materials and Method

To create MWCNT-reinforced zinc-alumina-based hybrid alloys, elemental powder precursors of Al, Zn, Cu, Al_2O_3 , and MWCNT were initially employed. The composition of the zinc alloy resembled ZA-27 zinc alloy. The mechanical alloying process was carried out using a Retsch PM-100 model planetary high-energetic ball mill with 120 mL stainless steel grinding jars rotating at 250 rpm. The milling direction was reversed after every 7 minutes, and the total milling duration was 4 hours. The ball-powder weight ratio was maintained at 7:1, with 10 mm diameter stainless steel balls. To prevent overheating, the planetary mill was paused for 2 minutes after every 5 minutes of operation. Additionally, 5 ml of water was used as a wet medium agent. To achieve a homogenous distribution, the powder samples underwent 10 minutes of mechanical stirring and were then cold pressed in a steel die at 200 MPa to form bulk alloys. The bulk samples were subsequently sintered at 400°C for 2 hours, followed by immediate cooling at room temperature.

3. Results and Discussion

Aluminum (99.9% purity, ~44 μm), zinc (99.8% purity, ~44 μm), and copper (99.9% purity, ~44 μm) powders were procured from Nanografi, while Al_2O_3 powders (99.9% purity, ~44 μm) were supplied by EGE Nano A.Ş. The chemical composition of the ZA-27 alloy is outlined in Table 1.

Table 1. Bulk chemical composition of ZA-27 alloy

<i>Al</i> (%)	<i>Cu</i> (%)	<i>Zn</i> (%)
27	2.5	70.5

In this experimental study, a powder mixture of ZA-27 and Al_2O_3 was employed as the matrix material, while multi-wall carbon nanotubes (MWCNT) served as the reinforcing element. The technical properties of the MWCNT can be found in Table 2. The weight ratio of ZA-27 alloy to Al_2O_3 was maintained at 10:1.

Table 2. Some technical properties of MWCNT

Multiwalled carbon nanotubes	
Purity (%)	>96
Density (True) (g/cm^3)	2.4
Outer diameter (nm)	8–18
Surface area (m^2/g)	>210
Inner diameter (nm)	5–10
Length (μm)	10–35
Density (tap) (g/cm^3)	0.3

To fabricate the MWCNT-reinforced Al-Zn-Mg-Cu composites, MWCNTs were incorporated at weight percentages of 1%, 3%, and 5%. The densities of the investigated materials were determined using the Archimedean principle. The measured density of the composites with varying MWCNT weight percentages is illustrated in Figure 1, showcasing a decrease in density with the addition of MWCNTs. These findings align with a similar study conducted by Garg et al.[29]. The incorporation of graphene into aluminum composites resulted in a reduction in their density values. This phenomenon can be attributed to the decreased intergranular friction forces between graphene and other elements. Interestingly, the density values exhibited a further decrease after the sintering process (refer to Figure 1). This behavior can be rationalized by considering the densification stage, where the elimination of unstable materials creates opportunities for the formation of internal pores with varying volumes and shapes. During this process, small pores and/or concave surface morphologies have the ability to shrink through mass transfer via inward atomic diffusion from the particle's bulk towards the pore surface. This mechanism effectively fills the pore space. In contrast, large pores and/or convex surface morphologies are unable to shrink as mass transfer is dominated by outward atomic diffusion from the pore surface towards the particle's bulk. This dominance enlarges the pore space, resulting in what is commonly referred to as the foaming process, ultimately leading to a reduction in density.

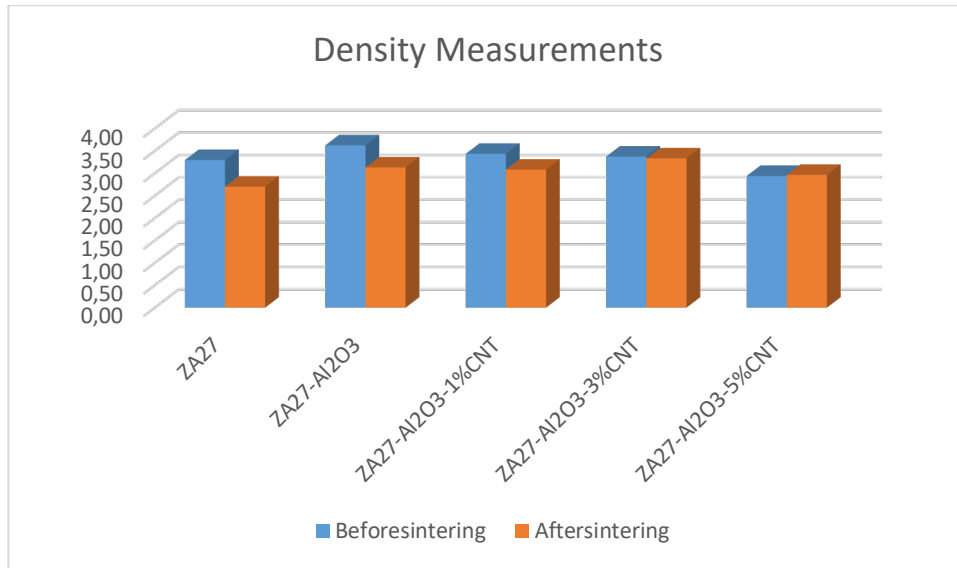


Fig. 1. Measured density of the given materials

The metallographic processes, including sanding, polishing, and etching, were employed sequentially. The sanding technique involved the use of 1000 and 2000 mesh sanders to treat the material surfaces. Subsequently, the specimens were polished using 6 μ diamond suspension followed by 3 μ diamond suspension to achieve a smoother finish. Finally, the samples underwent the etching process using diluted nitrate solutions.

For hardness testing of the studied composites, measurements were performed using an AOB Vickers Microhardness tester with a load of 0.5 kgf and a dwell time of 15 seconds. Five indentations were made for each sample, and the mean hardness values were recorded. The Vickers hardness values are presented in Figure 2. Notably, the hybrid composite (ZA27-Al₂O₃) exhibited a 7% higher hardness compared to the pure alloy. The addition of MWCNTs significantly increased the hardness values. However, it was observed that the MWCNTs were not uniformly distributed throughout the structure, particularly evident in the ZA27-Al₂O₃-3% MWCNT composite (refer to Figure 2), where a decrease in hardness value was observed in comparison to the ZA27-Al₂O₃-1% MWCNT composite.

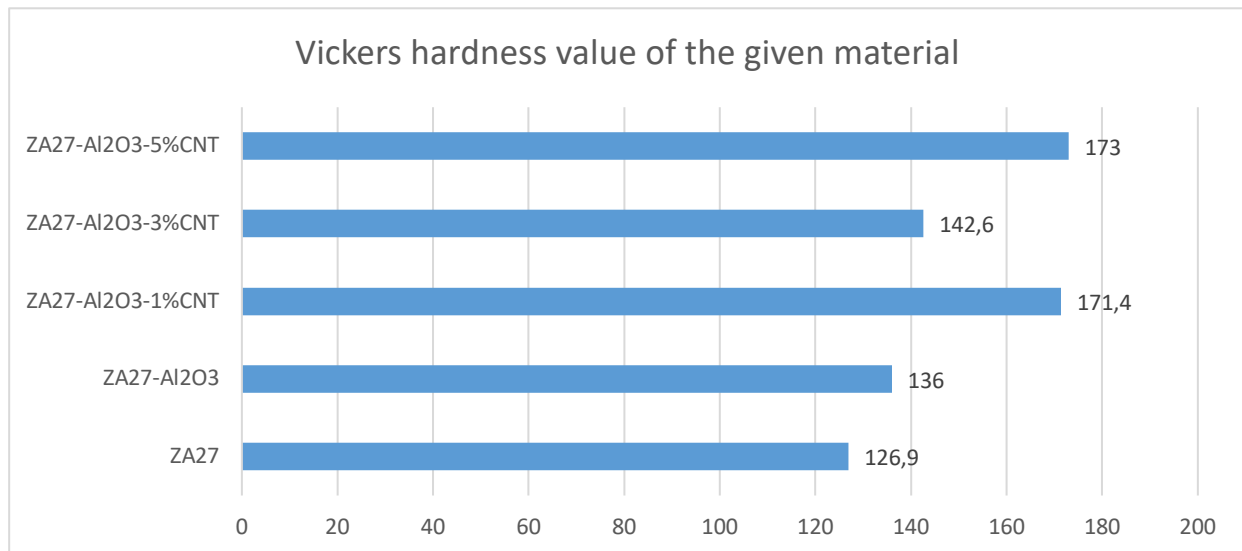


Fig. 2. Vickers hardness values of the given materials

Figure 3 presents the optical images of the analyzed structures. A comparison with Figure 6 (c-e) reveals a noticeable refinement of the grain boundaries. This observation aligns with previous studies on the subject [30]. Furthermore, it can be observed that agglomerations are present in several regions, with dense MWCNT reinforcement particles clustering around and adhering to the surfaces of ZA27 and Al₂O₃ particles. These agglomerations have a detrimental effect on the mechanical properties of the materials, which is consistent with the findings from the Vickers hardness tests.

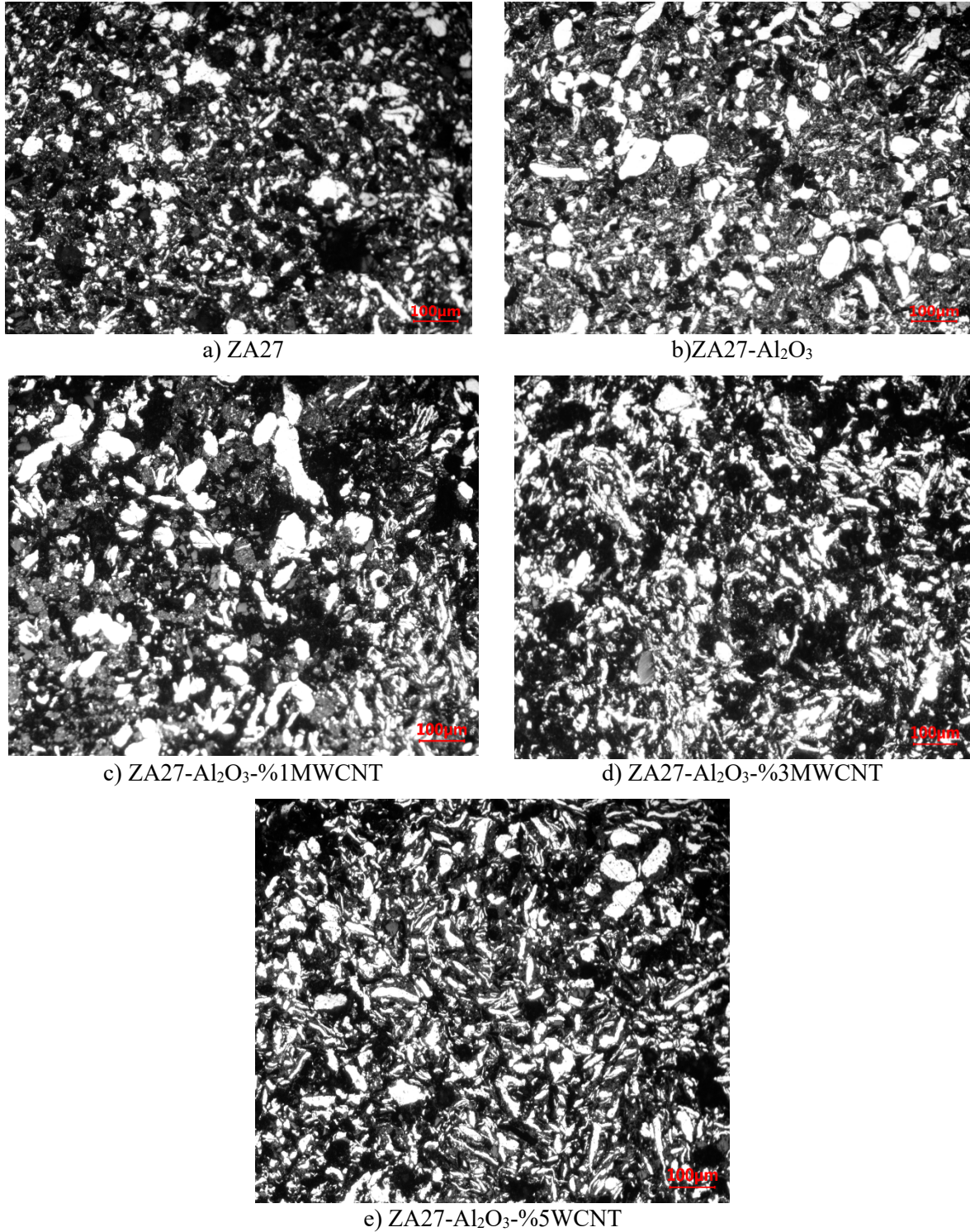


Fig. 3. Optical microscope images of the given materials

4. Conclusion

This study focused on the fabrication of zinc-based hybrid composites reinforced with multi-wall carbon nanotubes (MWCNTs) using a powder metallurgy routine. ZA-27 and Al₂O₃ were chosen as the matrix materials, while MWCNTs were employed as the reinforcing element. The primary objective was to investigate the impact of varying MWCNT ratios on the properties of the hybrid metal matrix composites.

The incorporation of MWCNTs resulted in a reduction in density values, which can be attributed to the diminished intergranular friction forces between the MWCNTs and other elements within the composite. Surprisingly, the sintering process further contributed to decreased density, contrary to its intended purpose. This phenomenon can be explained by the loss of unstable materials during densification, leading to the formation of internal pores with distinct volumes and shapes.

To evaluate the hardness properties of the composites, measurements were conducted using an AOB Vickers Microhardness tester with a load of 0.5 kgf and a dwell time of 15 seconds. The hardness values of the ZA27-Al₂O₃ composites were found to be 7% higher compared to those of the pure alloy, highlighting the reinforcing effect of alumina. Additionally, the introduction of MWCNTs significantly enhanced the hardness values.

Optical examination of the studied structures revealed that an increase in the MWCNT ratio resulted in finer grain boundaries. Furthermore, prominent agglomerations of dense MWCNT reinforcement particles were observed in various regions, adhering to the surfaces of ZA27 and Al₂O₃ powders. These agglomerations contributed to a decrease in the hardness values of the powders, consistent with the findings from the Vickers hardness tests.

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