Original Article

Effect of CNT on microstructure, dry sliding wear and compressive mechanical properties of AZ61 magnesium alloy

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Carbon nanotubes (CNTs) reinforced AZ61 magnesium alloy was successfully fabricated through stir casting method with the concentration of (0, 0.1, 0.5, 1) wt.% CNTs followed by age heat treatments. The influence of the CNTs concentration on compressive mechanical properties, dry sliding wear behavior and microstructure of synthesized composites have been investigated using compression test, hardness, block on wear apparatus, scanning electron microscope and X-ray diffraction (XRD) respectively. The comparative study of as-cast and aged CNTs/AZ61 composites have been analyzed. The experimental results reveal that the addition of CNTs content in AZ61 magnesium alloy causes the decrease in mass wear loss and coefficient of friction, improves grain refinement and compressive strength. Three dominant wear mechanism (i.e. abrasion, oxidation, and delamination) have been observed. The compression strength of composites increases with the increase in CNTs contents for both aged and as-cast composite. The addition of CNTs contents has very small effects on fracture strain of as-cast composites and aging has remarkable effects to increase fracture strain which increases up to 0.5 wt%CNTs/AZ61 and then decrease for 1 wt%CNTs/AZ61. Evaluation of microstructure revealed that CNTs have grain refining eligibility and cause the diffusion of secondary phases to improve the strength. The diffusion of phases in aged CNTs/AZ61 composites causes the formation of shallow cavities at grain boundaries.

Results analysis indicated that aged-CNTs/AZ61 composites exhibit enhanced wear and mechanical properties with load-bearing capacity, grain refinement and modification at grain boundaries than as-cast composites.

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1. Introduction

Magnesium alloys are lightest metallic structural materials owing to their high specific strength and good castability [1]. Magnesium is 35% lighter than aluminum and 77% lighter than steel [2], which leads to an alternative candidate for applications in aerospace components, computer parts, electronic industries, automobiles, mobile phones, sporting goods, and household goods resulting in considerable weight reduction and economic advantages [3]. Magnesium alloys would not be a candidate for bearings, gears, piston and cylinder bores but there are some situations in which their surfaces come in contact with other materials which makes wear and friction behavior of interest. Sliding wear is important in automotive brakes and engine components [4]. Tribological properties are dependent on a specific material, reinforcement, counterface materials, loading conditions and experimental conditions [5,6]. To improve mechanical and wear properties of magnesium alloys, the selection of reinforcement plays a key role to produce a composite with unique microstructure and uniformly distributed in a matrix using conventional casting techniques.

Magnesium alloys have poor wear and corrosion resistance [4,7]. Particle reinforced metal matrix composites exhibit improved mechanical and wear properties as compared to base metals due to the presence of hardened reinforced particles which resist the continuous removal of material at tribo-contact [8]. The increase in the concentration of particles leads to an increase in wear resistance of metal matrix composites (MMCs) as inter-particle spacing influence the tribological properties of composites. Micro/nano-sized particles SiC, B4C, Al2O3 are commonly used reinforced particles which improve the hardness and elastic modulus but limit the wear resistance [9–12]. Researchers have tried many other techniques i.e. High energy ball milling, squeeze casting, friction stir processing, spread dispersion method and spray deposition for uniform distribution of particles. Stir casting has great interest and attractive for its simplicity, complex geometry of products uniform distribution of reinforcement. However, due to the higher surface area to volume ratio, nano-sized particles exhibit better properties than micro-sized. Few contents of nanoparticles exhibit better compressive mechanical properties and superior wear resistance compared with composites reinforced micro-sized particles [13,14].

In past decades, carbon-based nanoparticles have been used as preferred reinforcement to improve mechanical and wear performance of metal matrix composites [15]. Generally, carbon nanotubes, graphene which are allotropes of carbon are used as nanoparticle reinforcement [16]. Carbon nanotubes are rolled carbon sheets with a 1–2 nm diameter having excellent mechanical and wear properties [17]. CNTs have high strength, high density, high elastic modulus and high aspect ratio which make CNTs as ideal reinforcement [18]. The strength of improving the property of CNTs would be sustained by homogeneous distribution and maintain structural integrity [19]. Previous studies show that up to 1.3 wt% CNT addition leads to an increase in mechanical properties of magnesium [18]. However, carbon nanotubes may cause agglomeration due to van der Waals attraction between carbon atoms. There are many applications in which different materials come in contact via sliding. The Mg5Si medium carbon steel is one of the most widely used materials which are used in automotive parts, in springs, washes, clutch parts and bearing and has sliding contact with different materials.

In last decades many researchers have been trying to develop new techniques for uniform dispersion of CNTs in the matrix. Generally, morphology and processing route has a great effect on the uniform distribution of CNTs in a composite matrix which effects the mechanical and wear behavior of fabricated composite [20]. CNTs with a larger diameter and smaller length are stiffer and easy to disperse but on the other hand, CNTs with a smaller diameter and larger length are angled and difficult to distribute in matrix [17,20]. The structural integrity and uniform distribution of reinforcement possess much better wear resistance and influence elastic modulus. The uniform inter-particle spacing of harden reinforcement will lead to enhanced wear resistance and better mechanical behavior under compressive wear applications. The structural integrity must be maintained in CNTs reinforced composites to maintain morphology [21]. To get uniform distribution and maintain structural morphology, stir casting techniques have been developed to manufacture composites. It has been reported that magnesium alloys reinforced with homogenously distributed CNTs improve the hardness which contributes the excellent wear resistance.

In the present work, dry sliding wear behavior and compressive mechanical properties of CNT reinforced AZ61 magnesium alloy have been investigated using Ring on Block wear apparatus against S45C steel counterpart. The effects of CNT contents on porosity, wear and compressive mechanical properties under fixed loading conditions including the applied load and the sliding velocity on the wear transitions. The microstructures of composites are characterized by scanning electron microscopy (SEM) equipped with energy dispersive spectroscope (EDS). The mechanical properties, strengthening mechanism and wear mechanism of each composite have been discussed.

2. Experimental procedures

2.1. Synthesis of CNTs-reinforced AZ61 magnesium alloy composites

AZ61 magnesium alloy was selected as a matrix with the chemical composition (wt%) of Al-5.95, Zn-0.64, Mn-0.24, Fe-0.005, Cu-0.0008 and Mg balance. Multiwalled carbon nanotubes (MWCNTs) with a diameter of 9.5 nm and 1.5 nm length have been selected as reinforcement. Stir casting method was adopted to developed AZ61/CNT metal matrix composites as shown in Fig. 1. The temperature was increased up to 760 °C with a gradual increment of 100 °C having 15 min stabilizing time for uniform heat distribution.

A mixture of carbon dioxide (CO2) and sulfur fluoride (SF6) was supplied at 400 °C to prevent from burning and argon was used at 700 °C to avoid oxidation. After 30-minutes stabilization at 760 °C, the molten slurry was stirred at 300 rpm for 5 min for uniform distribution of CNT in the matrix. Finally, the mixture was poured into steel ingot placed in a lower
chamber under gravity. Four kinds of composites with 0 wt%, 0.1 wt%, 0.5 wt%, and 1 wt% CNTs were fabricated. Samples were heated up 400 °C in a controlled furnace for 24 h, after quenching in water for two seconds and artificially aged at 200 °C for 10 h.

2.2. Density and porosity

The actual density was obtained using the Archimedes principle. The square-shaped samples were weighed in the air (W_a) and in distilled water (W_w) using photoelectric weight balance with 0.01 mg accuracy. The actual density of samples was measured as follow Eq. (1) [22].

\[ \rho_a = \frac{W_a}{W_a - W_w} \times \rho_w \]  

(1)

where \( \rho_a \) and \( \rho_w \) are the actual density of samples and the density of water respectively.

The theoretical density of composites was measured by dividing the mass of the sample to its volume. The theoretical density of five samples was measured and average was taken in final results. The porosity of samples was measured as by Eq. (2)

\[ P = \left[ 1 - \left( \frac{\rho_a}{\rho_t} \right) \right] \times 100\% \]  

(2)

where \( \rho_a \) and \( \rho_t \) are skeletal density and apparent density of samples respectively. Four samples were tested for each kind of composite and average was taken into final results.

2.3. Hardness test

Microhardness was measured using a Vickers hardness testing machine (Akashi MVK-H1) equipped with diamond indenter under the load applied of 300 N and dwell time of 10 s. The average of five indentations for each sample was taken in results.

2.4. Wear test

Dry sliding wear tests were performed with S45C counterface using the ring on block wear apparatus as shown in Fig. 2. Specimens with dimensions (12.2 mm x 12.5 mm x 12 mm) were used for wear tests. All specimens were tested under 50 N load, 140 rpm speed for 10 min. The maximum contact area was considered for wear. The counterface ring was cleaned with acetone using an ultrasonic cleaner for 5 min. The mass loss was determined by measuring sample weight before and after each experiment using photoelectric weight balance. The volume loss was calculated by dividing mass loss to the density of each composite. The wear response for each sample was evaluated by Archard’s law Eq. (3) [23].

\[ \frac{V}{L} = K \left( \frac{F}{H} \right) = kF \]  

(3)

where \( V \) is the wear volume loss, \( L \) is the sliding distance, \( F \) is the applied load, \( H \) is the hardness, \( k \) is the specific wear rate and \( K \) is Archard’s constant. The average coefficient of friction was calculated for distance traveled.

The tangential force exerted on the holder was measured and from that the coefficient of friction (COF) was calculated and recorded as a function of distance/time/laps. The vertical position of the holder was measured in order to monitor the displacement due to material removed by wear. Three samples were tested for each type of composite and average was taken in final results.

2.5. Compression test

Uniaxial compression tests were performed on samples with dimensions (10 mm x 10 mm x 10 mm) using MTS100 universal testing machine with a strain rate of 0.5 mm/min. The average of three specimens was considered for obtained results. The compressive strength was determined from the stress-strain curve and absorbed energy was calculated from the area under the curve up to fracture strain by Eq. (4)

\[ E = \int_{0}^{\epsilon} \sigma d\epsilon \]  

(4)
Average of three sample tests were taken into account for final results.

2.6. Microstructure and X-ray diffraction (XRD) analyses

Specimens were ground using 200, 400, 1000, 2000 and 4000 grit sized emery papers and the polished using aluminate solution to make the mirror-like surface. Samples were etched with 75 ml ethanol, 10 ml DI water and 10 ml nitric acid solution for 25 s. The microstructure of samples was studied using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The phase composition was analyzed using X-ray diffraction (XRD) on polished samples exposed to CU Kα radiations generated at 45 kv and 0.8 mA. during stirring and pouring process, the vertex formed during turbulent which resulted in entrapment of air resulting in higher porosity. Another reason for increased porosity can be attributed to poor wettability with matrix and shrinkages during solidification [26,27] resulting in pore nucleation of surface and larger pore size. During the fabrication process of metal matrix composites, porosity can be normal because there are multi-walled nanotubes which increase the contact area.

Porosity, its volume fraction and its distribution in cast composites play a vital role in controlling mechanical and wear properties of composites. Porosity cannot be avoided but can be controlled.

3.2. XRD analysis

To clarify the constituent phases, present at as-cast and aged CNTs/AZ61 interface, X-ray diffraction analysis was performed as mentioned in methodology and results are shown in Figs. 4 and 5 respectively. The standard procedures have been adopted to analyze the diffraction peaks in the XRD pattern. The analysis of peaks in XRD results indicates that
major phases present in CNT/AZ61 composites are $\beta$-Mg$_{17}$Al$_{12}$, Al$_4$Mn, MgZn, Mg$_2$Al$_3$, and Al$_4$C$_3$.

The chemical composition and elemental peaks in EDS analysis (Figs. 7 and 9) affirm the XRD results. The presence of aluminum carbide indicates the reaction product at CNTs-AZ61 interface leading to the strengthening of CNTs/AZ61 composites [18]. The intensity of Mg$_{17}$Al$_{12}$ is reduced with the increase CNTs concentration, this is because carbonaceous particles regulate precipitates during cooling after the casting process.

CNTs are active in manipulating the $\beta$-Mg$_{17}$Al$_{12}$ phase leading to the development of new secondary phases adjacent to reinforcement particle [28]. When the rate of formation of new second phases from activation of CNTs is higher than previously formed phases results in refinement of $\beta$-Mg$_{17}$Al$_{12}$ phases in composites.

MgZn phase has been observed in 0.5 wt%CNTs/AZ61 composite which eliminated with the further addition of CNTs.

The formation of Al$_4$Mn phase represents the reaction product of Aluminum with manganese causing the ductility of as-cast composites. Low melting phase ($\beta$-Mg$_{17}$Al$_{12}$) has a key role in determining mechanical properties and grain structure. It can be seen from XRD results that heat treatment affects the formation and diffusion of $\beta$-Mg$_{17}$Al$_{12}$ phase in the matrix [29].

Fig. 8 shows that $\beta$-Mg$_{17}$Al$_{12}$ has been dissolved during the aging process causing the grain refinement. The increased in Mg$_2$Al$_3$ peaks in aged 1 wt% CNTs/AZ61 represents the diffusion of $\beta$-phase and leading to the strengthening of composites. The sharp magnesium peaks are present in XRD pattern of aged CNTs/AZ61 composites than as-cast which indicates crystallinity has been improved during aging process.

The formation of heterogeneous crystalline phases are dependent on heat-treatment process and aging time. The phase quantification has been presented in Table 1. The quantity of each phase has been determined using the reference intensity ratio (RIR) method which most suitable method used in X-ray diffraction analysis of bulk samples. The method uses the ratio of the strongest peak of unknown phase to the strongest peak of standard phase and the sum of under consideration phases should be equal to 1 as described in Eq. (5).

\[
\sum_{k=1}^{n} W_k = 1
\]  
(5)

The weight percentage of unknown phases can be determined by Eq. (6).

\[
W_u = \frac{I_u}{RIR_{uc}} \times \left( \frac{\sum_{k=1}^{n} I_k}{RIR_{uc}} \right)^1 \times 100\%
\]  
(6)

where $W_u$ is weight percentage of unknown phase, $I_u$ is the maximum peak of ith phase.

The phase quantification analysis is important when the weight fraction of each created phase affects the properties under consideration as each phase has different mass absorption capacity. The phase Mg$_{17}$Al$_{12}$ produced in as-cast 0 wt% CNTs/AZ61 composite has highest weight fraction even

<table>
<thead>
<tr>
<th>Materials</th>
<th>Major phases</th>
<th>Quantitative value (%)</th>
<th>Crystalline structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>71.35</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn,</td>
<td>25.0</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn, Al$_4$Mn,</td>
<td>2.3</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Al$_4$C</td>
<td>1.35</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>0.1 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>87.29</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn,</td>
<td>9.53</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn, Al$_4$Mn,</td>
<td>1.9</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Al$_4$C</td>
<td>1.29</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>0.5 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>96.64</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn,</td>
<td>2.5</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn, Al$_4$Mn,</td>
<td>0.99</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Al$_4$C</td>
<td>1.01</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn</td>
<td>1.28</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>1 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>96.75</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn,</td>
<td>0.07</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn, Al$_4$Mn,</td>
<td>1.92</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_4$C</td>
<td>1.26</td>
<td>Rhomb.h. axes</td>
</tr>
<tr>
<td>0 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>9.01</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn,</td>
<td>1.09</td>
<td>Cubic</td>
</tr>
<tr>
<td>0.1 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>98.05</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn, Al$_4$C,</td>
<td>1.05</td>
<td>Cubic</td>
</tr>
<tr>
<td>0.5 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>98.06</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Al$_2$, MgZn, Al$_4$Mn, Al$_4$C,</td>
<td>1.04</td>
<td>Cubic</td>
</tr>
<tr>
<td>1 wt%CNT/AZ61</td>
<td>Mg$<em>{60.97}$Zn$</em>{0.03}$, Mg$_{17.12}$</td>
<td>96.06</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn, Al$_4$Mn, Al$_4$C,</td>
<td>3.01</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>Mg$_2$Zn</td>
<td>1.03</td>
<td>Rhomb.h. axes</td>
</tr>
</tbody>
</table>
though it has a low peak in XRD pattern (Fig. 4). The Table 1 indicates the diffusion and generation of phases with aging and CNTs content addition.

3.3. Microstructural characterization

Figs. 6 and 8 show the SEM images of as-cast and aged CNTs/AZ61 metal matrix composites respectively. According to the Fig. 6(a), the microstructure of as-cast monolithic AZ61 magnesium alloy mainly consists of Mg17Al12, MgZn, Mg2Al3 and Al4Mn phases which are confirmed by EDS and XRD results. Phases are distributed and are present in whole composites. The β-phase precipitates are formed in continuous and discontinues at the grain boundaries and with the addition of CNTs, these phases start to be concentrated at grain boundaries and grain boundaries are started to be prominent. For as-cast 1 wt% CNT/AZ61 metal matrix composite, Mg17Al12 have been diffused in matrix leaving behind shallow cavities at grain boundaries. The pores are also visible in 1 wt% CNT/AZ61 composite which confirms the results discussed in the porosity section.

The precipitates shown in Fig. 6(a–c) have the dendritic morphology. The accumulation of solute phases and heat ahead of the interface can lead to circumstances in which liquid in front of solidification front is super-cooled. The interface becomes unstable and solidification becomes dendritic. The dendrites tend to branch because of interface instability. The Fig. 6(c) shows that some phases are being diffused leading to the generation of cracks like grain boundaries shown with yellow arrowheads.

Comparing Figs. 6 and 8, it is believed that aging affects the diffusion and generation of phases in the matrix. It is clearly visible that β-Mg17Al12 has been completely dissolved and some granular shaped intermetallic compounds have been produced in the vicinity of grains and at grain boundaries. Thermodynamically stable phases, diffusion of β-Mg17Al12 as
well as reduction in grain size causes the improvement in mechanical strength. Fig. 7 shows the EDS elemental analysis of area A, B which confirms the presence of Mg$_2$Al$_3$ and Al$_4$Mn$_3$ which are confirmed from XRD results. The larger amount of Mg peaks is because of the larger amount of Mg at interface.

The Fig. 10 shows the effects of CNTs concentration on the average grain size of CNTs/AZ61 composites.

It can be noticed that the addition of CNTs causes a reduction in grain size and refinement of grain structure. Grain size reduces with increase in CNTs contents but the degree of reaction is pretty limited. The grain refinement is attributed to two major reasons. CNTs distribution at grain boundaries inhibits the grain boundaries and heterogeneous nucleation occurring due to the addition of CNTs. Aging has effects in grain refinement along with CNTs contents [30]. The aged composites indicate more refined grains which are attributed to dynamic recrystallization during heat treatments process. Secondary phases (Al$_4$Mn, Mg$_2$Al$_3$) are distributed along the grain boundaries which could pin the grain boundaries and can hinder grain growth [31].

3.4. Hardness

The microhardness of as cast and aged CNT/AZ61 composites is presented in Fig. 11. It can be seen that microhardness of aged composites is higher than as-cast which is the attributed to phenomenon of dynamic recrystallization and grain refining during the aging process [32]. The presence of reinforcement in matrix facilitates the nucleation at early stage caused by dynamic recrystallization process and reduces the average grain size [33]. In general, continuous dynamic recrystallization is most common recrystallization mecha-
nism in magnesium alloys. The dynamic recrystallization improves the grain size during aging [34], which leads to enhance the precipitates has been dissolved and dispersed along the grain boundaries, leading to refine the grains. The hardness increases with the increase in CNTs concentration until it reaches the maximum value of HV = 58.28 then decreases. The increase in hardness is attributed to constraint localized matrix deformation during indentation due to homogeneously dispersed hard and tough CNTs and grain refining characteristics of CNTs [18]. The presence of CNTs agglomeration and lower densification of composites leads to deterioration of hardness [35].

3.5 Wear behavior

Mass wear loss and volume wear loss of CNTs/AZ61 metal matrix composites are shown in Fig. 12(a, b) respectively. It can be observed that mass loss decreases with the increase in CNT concentration so as the volume loss under the same loading conditions. The reduction in mass loss is attributed to Archard’s principle in which hardness is inversely proportional to mass loss, thus increase in hardness of composites decreases the ploughing effect and reduces the mass loss [23].

Another reason for the reduction in mass loss is the self-lubricating effect of CNTs and the formation of CNT layer on the surface during sliding which corresponds to lower coefficient of friction. The CNTs are pinned up at grain boundaries and retard the grain growth leading to grain refinement of composites thus improving the strength. Reinforcing CNTs act as a bonding agent in the matrix. The strengthening and bonding behavior of CNTs leads to a reduction in mass loss.

The variation of coefficient of friction with CNT concentration is shown in Fig. 5(c) which indicates that the decrease in coefficient of friction with the increase in weight fraction of CNTs under the same loading condition. The similar trend has been observed for aged samples also and the difference in coefficient of friction is attributed to enhanced strength and refined microstructure. The CNTs are pulled out during wear tests and form carbon film between matrix and counter material which act as solid lubricant and reduces the coefficient of friction and thus the mass loss [36]. The studies indicate that CNTs are more significant at higher loads in reducing the weight loss by making the thick film at the interface to reduce the ploughing effect [37].

The stabilized coefficient of friction with a higher concentration of CNTs reinforcement is attributed to sliding attitude of CNTs. It has been also proven that when CNTs concentration exceeds the 2 wt%, agglomeration effects are dominant which leads to a sudden increase in pores and weaken the strengthening effect [18]. CNTs provide higher aspect ratio which enables to dragged directly into the contact zone to effect the tribological behavior of composites [38].

From Ramezani and Ripin’s friction model, the coefficient of friction is inversely related with to resistance. Thus the reduction in coefficient of friction leads to decline in wear loss [39]. The aged composites have less mass loss and coefficient of friction as compared to as-cast composites under same loading conditions which is attributed to increased hardness and refined microstructure of aged composites.

The low strength Mg12Al12 phases are dissolved in aged composites which leads to higher strength causing a reduction in wear rates. The mass wear rates have been reduced to 7% and 20% for 1%CNT/AZ61 composite when compared with unreinforced as-cast and Aged composites respectively.

3.6 Wear mechanisms

Scanning electron microscope examination of worn surfaces identifies the three kinds of wear mechanisms operating under the same loading conditions. Abrasion, oxidation and delamination type of wear have been observed in CNTs/AZ61 composites.

The grooves and scratches are evident (Fig. 13(a)) along the sliding direction which are produced when hard particles are entangled between counterpart and samples acting as plough to remove the fragments. The size of voids varies from 10-35 μm. Generally, abrasion is caused by wedge forming without removal of materials and it dominates at interme-
diate load and speed. The Fig. 13(b) shows the SEM images of oxidation wear of CNTs/AZ61 composites.

EDS analysis of surfaces indicates the presence of oxygen peaks along with magnesium peaks which indicates the oxidative wear in which frictional heating during sliding wear causes oxidation of surfaces. A compact oxygen layer is developed on the surface leading to a reduction in wear loss. Freshly produced surfaces are exposed to air and get oxidized. The sign of transferred materials on wear track is an indication of adhesive wear which is clear from all figures but mass loss due to adhesive wear was negligible so that it cannot be considered the main wear mechanism. While the tracks at lower temperatures have a regular shape with constant depth along the circumference, in the tracks made at higher temperatures a pattern of valleys and ridges starts to form. This suggests that besides abrasion, which is dominant at the lower temperature, combination of abrasion and adhesion are dominant mechanisms at the higher temperature (occurs leading to so-called slip-stick phenomenon). In the beginning occasional sticking of the pin and sample and subsequent slipping leads to formation of changes in the track depth, which then causes repetition of adhesive and abrasive wear [40].

In delamination wear, short cracks appear on surface perpendicular to sliding direction (Fig. 13b, c). The intersection of these cracks leads to detachments of sheet-like wear particles. The delamination of the subsurface which may exist earlier or get nucleated due to stress concentration propagate during sliding wear. As a result of propagation of cracks and extend to pinned surfaces leading to detachment of wear layers. The delamination crater becomes wider and deeper, indicating the severity of delamination. It has been reported that the existence of earlier subsurface cracks also contributes to delamination. Consequently, resistance to delamination has been weakened for granted. Delamination wear is a type of wear which appears at stage transition from mild to severe wear.

3.7. Mechanical properties

The compressive mechanical properties of as-cast and aged CNT/AZ61 at room temperature are shown in Figs. 14 and 15 respectively. It is clearly depicted that CNTs have dominant effects on compressive strength and ductility. Fracture strain and ultimate compressive stress (UCS) are enlisted in Table 2. It is clear from Fig. 14 and Table 2 that the addition of CNTs has drastic effects on UCS of as-cast AZ61 magnesium alloy. It can be noticed that UCS for monolithic AZ61 is 310 MPa and with the addition of 0.1 wt%CNTs causes the 33.5% increase
strength. It can also be visualized that CNTs has a linear relationship with compressive strength but with the addition of 1 wt% CNTs, decrease in strength has been noticed which is attributed to increase in porosity and shallow effects when secondary phases are dissolved. The CNTs contents have very small effects on the ductility of AZ61 magnesium alloy in as-cast conditions.

As it has been mentioned before that heat treatments have tremendous effects on microstructure so has on mechanical properties. Fig. 15 and Table 2 depict that increase in CNTs contents causes the increase in strength and ductility. The increase of 35.5% in UCS for aged – 1 wt% CNTs/Az61 has been noticed. The enhanced compression strength and compressive ductility are due to the presence of reinforcement.
particles and secondary phases present in matrix alloy [41]. The compressive ductility also increases with the increment in CNTs concentration but for 1 wt% CNTs/AZ61 strength is increases at the cost of ductility. The decrease in ductility can be attributed to pores and voids present in composite [42].

The energy absorbed (E) have been measured by area under the curve for each composite samples and presented in Table 2. Table 2 shows that toughness increases with the increase in CNTs contents but slightly decreased in aged 1 wt% CNTs/AZ61 and as-cast 0.5 wt% CNTs/AZ61 which can be attributed to a small decrement in ductility of corresponding samples.

Generally, strengthening mechanism is explained by theories of (a) Orowan strengthen, (b) Hall–Pitch strengthen (c) load transfer strengthening from soft matrix to hard and tough reinforcement (d) dislocation generation due to difference in coefficient of thermal expansion (CTE) and elastic modulus (E) between matrix and reinforcement which is enhance by dislocation density, grain size reduction and load-bearing capacity of reinforcement respectively. Orowan strengthening is a key mechanism in improving strength in which nanoscale reinforcement act as an obstacle which restricts the dislocation movement. The dislocations are piled up during movement when more obstacles come across. These dislocation bows and bypass the reinforcement by forming loops around them known as Orowan strength looping [43] and can be described as

\[ \sigma_{\text{Orowan}} = \frac{Gb}{2\pi(1-v)\left(\sqrt{\frac{0.779}{f}} - 0.785\right)d} \]

where G is shear modulus, b is burger vector, v is Poisson ratio, d is the grain size, f is volume fraction of reinforcement. From Eq. (7), samples with 1 wt% CNT/AZ61 obtained higher strength. It is proposed that the improvement in mechanical properties [44] are due to the reduction in grain size of matrix caused by CNTs which creates good interfacial bonding between and heterogeneous nuclei.

Strengthening in CNTs/AZ61 is also induced by the difference in coefficient of thermal expansion between matrix and reinforcement [45] which can be ascribed as Eq. (8)

\[ \sigma_{\text{CTE}} = \alpha Gb \sqrt{\frac{12\Delta T\Delta C}{bd}} \]

where \( \alpha \) is constant and b is burger vector, \( \Delta T \) is the difference in processing temperature and ambient temperature, d is grain size and \( \Delta C \) is the difference in coefficient of thermal expansion. The coefficient of thermal expansion for CNTs and AZ61 is \( 10^{-6} \text{ K}^{-1} \) and \( 22.2 \times 10^{-6} \text{ K}^{-1} \) respectively. In addition, CNTs has elastic modulus 1.2 TPa and AZ61 has 80 GPa. This huge difference of coefficient of thermal expansion and elastic modulus between matrix and reinforcement leads to the formation of dislocation at the interface [46]. These dislocations resist the fracture under compressive loading leading to improve in strength. From Eq. (8), the aged 1 wt% CNTs/AZ61 composite has higher strength than other composites because in addition to a mismatch in CTE and elastic modulus it has a higher volume fraction of reinforcement and reduced grain size.

CNTs/AZ61 composites are also strengthened by load transfer strengthen mechanism which describes a load transfer phenomenon from soft matrix to hard and tough reinforcement [47]. The model can be expressed by the following formula

\[ \sigma_{\text{LT}} = \sigma_{m}\left[1/(2m)\right] \]

where \( \sigma_{m} \) is yield stress of matrix and m is volume fraction of reinforcement. From Eq. (9) it can be derived that 1 wt% CNT/AZ61 has higher strength than other composites. According to shear log model, better reinforcement can be achieved by a higher aspect ratio. Thus samples with larger aspect ratio have higher strength.

Another strengthening mechanism is Hall–Pitch effect which describes the grain size on strength of composites [48]. The strength is improved with the decrease in grain size of matrix as explained by relationship as given in Eq. (10)

\[ \sigma_{y} = \sigma_{0} + k_{y}d^{-1/2} \]

where \( \sigma_{y} \) is yield strength of composite, \( \sigma_{0} \) and \( k_{y} \) are the constants of corresponding materials and d is grain size.

**Fig. 14** – Compressive stress-strain relationship for as-cast.

**Fig. 15** – Compressive stress-strain relationship for aged CNTs/AZ61 composites.
The fracture strengthening is another candidate for strengthening the composites and quantification of its effects on materials response [49]. The specific microstructures are design to improve the fracture toughness which lead to enhance the strength. The interface debonding is one two major (interface debonding, particle cracking) fracture mechanisms which alleviates the stress concentration promote the micro crack initiation [50]. The fracture toughness is effected by combine effect of plastic dissipation and energy spent to start crack. When stress level reaches ultimate stress, crack starts in particles [51]. After the crack starts, fracture energy behavior can be described by post-failure behavior. The crack normal displacement \((U_n)\) at which complete loss of strength takes place can be determined Eq. (11) [52].

\[
U_n = \frac{2G_f^I}{\sigma_I^f} \tag{11}
\]

where \(G_f^I\) is the energy required to open unit area of Mode I crack and can be determined by Eq. (12).

\[
2G_f^I = \frac{K_{IC}^2}{E'} \tag{12}
\]

where \(K_{IC}\) and \(E'\) are the fracture toughness and effective Young’s modulus of CNTs, respectively.

The plastic deformation can be determined by using Johnson-cook constitutive model equation (13) [53].

\[
\bar{\sigma} = A + Be^\varepsilon \tag{13}
\]

where \(\bar{\sigma}\) is the effective stress, \(\varepsilon\) is plastic strain, \(A\), \(B\) and \(n\) are the yield strength, hardening modulus and coefficient of hardening respectively.

The studies have proven that CNTs has a larger effect on compressive mechanical properties than tensile which may be attributed to large strain fields near CNTs because of tangled dislocations occurred in fine-grained CNTs/AZ61 composites during plastic deformation.

At room temperature, the ductility and mechanical strength of magnesium alloy are dependent on activation of secondary phases and their crystal structures.

From Table 1 and Fig. 13, it can also be derived that crystallographic structure, active secondary phases, and grain refinement are one of the most attractive method to improve mechanical properties in polycrystalline magnesium alloy [54].

4. Conclusion

In summary, CNTs reinforced AZ61 magnesium alloy metal matrix composites were manufactured by stir casting method followed by aging heat treatments. The influences of CNTs on dry sliding wear behavior, compressive mechanical properties and microstructure of AZ61 magnesium alloy have been investigated. Based on the analysis, the following conclusion can be drawn

1. The CNTs reinforced AZ61 magnesium alloys can successfully be fabricated using stir casting method with a uniform dispersion of CNTs in the matrix.
2. The porosity of CNTs/AZ61 metal matrix composites increases with the addition of CNTs contents.
3. The addition of CNTs in AZ61 causes the significant decrease in coefficient of friction and mass loss which is due to self-lubrication effects of CNTs and formation of carbon film on the wear surface. Aged-CNTs/AZ61 composites have better wear resistance as compared to as-cast composites. The wear behavior is affected by modification in microstructure and mechanical properties of composites which is attributed to diffusion effects primary and secondary phases of aging heat treatments.
4. The wear mechanisms of abrasion, oxidation, and delamination have been identified during the sliding of CNTs/AZ61 metal matrix composites.
5. The room temperature mechanical characterization revealed that there is a significant increase in ultimate compressive strength and hardness has been noticed for both as-cast and aged composites.
6. The compressive ductility is increased with the addition of CNTs contents for aged CNTs/AZ61 composites and it is decreased for aged 1 wt% CNTs/AZ61 composites.
7. The enhancement in ultimate compressive strength of CNTs/AZ61 composites is attributed to Orowan mechanism, mismatch of coefficient of thermal expansion, efficient load transfer and Hall–Petch effects. The excellent tribological and mechanical properties have been achieved for aged-CNTs/AZ61 composites as compared to as-cast composites due to grain refinement and hardening of composites.
8. Mechanical characterization of manufactured composites revealed that addition of CNTs has grain refining effects and further processing of age heat treatments leads to diffusion of all intermetallic phases produced in as-cast composites leaving behind shallow cavities at grain boundaries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES


