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Investigation of Tribological Applications and Mechanical Properties of Zinc-Aluminium (ZA40)/Multi-Wall Carbon Nanotube (MWCNT) Composite Alloys

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Abstract: In this study, ZA40/ MWCNT composites were produced by using powder metallurgy technique and hot press method by adding 0,5-1-1,5-2% wt. MWCNT to ZA40 alloy. Powders made with mechanical alloys were sintered by hot pressing for 3 hours under 500 °C and 800 MPa pressure. Wear tests were carried out under 5N and 10N loads in a dry friction environment using the ball-on-disk technique. Weight losses, average friction force, and wear rate of the samples were calculated after wear tests. Morphology, internal structure images, and examination of worn surfaces of the samples were investigated using scanning electron microscopy (SEM). The wear test results show the coefficient of friction of ZA40-2wt. % MWCNT was 0,18 μ (lower than the coefficient of friction of 0,66 μ for ZA40 alloy). The wear rate of ZA40 alloy was almost 6 times higher than ZA40-2 wt. % MWCNT composite.

Keywords: Multi-Wall Carbon Nanotube; Powder Metallurgy; Wear; ZA40

1 INTRODUCTION

Zinc-Aluminium alloys are used successfully in many engineering applications today. Especially ZA8-ZA12-ZA27 and ZA40 alloys; due to their many properties such as durability, good thermal conductivity, good sintering, and rigidity, it is preferred more than aluminium, and bronze alloys in many industrial applications [1]. Zn-Al alloys; have higher tribological effects with low melting temperature and low cost; compared to that of cast iron, brass and aluminium. Especially in 1960 and 1970, ZA8-ZA12-ZA27-ZA33-ZA40 and ZA48 series Zn-Al alloys were developed. These alloys have limited applications due to the deterioration of some of their mechanical properties at operating temperatures above 100 °C. Since Zn-Al alloys are one of the most important alloying elements, it is possible to produce new materials with advanced engineering properties by adding ceramic-based reinforcement materials at different rates [2].

The most important task of a lubricant is to minimize wear in the wear environment. A suitable oil film significantly reduces the wear of the various parts in contact with each other. Composite alloys with appropriate lubricant additives are used in many applications according to operating conditions, pressure, load, and temperature of the system.

MWCNTs have been used as lubricant additives in various alloys due to their wear-reducing properties and thermal and electrical conductivity [3].

Li et al. obtained promising results in mechanical properties by adding yttrium (Y) in different ratios to ZA27, ZA35, and ZA40 alloys. Especially with 4% Y reinforcement, they observed significant increases in the elongation stress and hardness values of the composites [4].

A recent study investigated the wear behavior and mechanical properties of ZA27/SiC/Gr hybrid composites under 20-40 and 60 N loads in a dry friction environment in a pin on disc wear device by adding 1,5% SiC and 0,5% graphite to the ZA27 matrix. According to the results, the microhardness and breaking stress values increased. In addition, the weight losses in the samples after wear were less in hybrid composites than in the matrix material [5]. The composites formed by mechanical alloying (30 minutes) method by adding 2% MWCNT to AA 6061 aluminium matrix alloy were carried out with pin-on-disc (500, 1000 and 1600 m) wear tests in a dry environment with 5, 7 and 10 N loads. According to the results, it was seen that MWCNT reinforced composites have a lower wear rate, lower friction coefficient, and weight loss [6].

In a recent study, the wear behavior of the composites formed by strengthening the ZA27 matrix alloy SiC and Gr under different loads and at different sliding speeds in the dry friction environment was investigated. According to the results, it has been observed that SiC and Gr reinforcement have positive effects on the wear rate. [7]. Preethi et al. studied that mixtures reinforced with 500nm size of 1-1,5% and 2% CNT to Al6061 alloy produced by powder metallurgy technique with mechanical alloying at 150 rpm for 4 hours. The hardness value and wear data of the produced samples were examined under 10 N and 20 N loads, and according to the results obtained, an increase in hardness values, a decrease in density values occurred, and the best wear resistance was observed in the 2% CNT reinforced sample [8]. Aranke et al. investigated the wear behavior of composites formed by reinforcing 0,25-0,5-0,75 by % weight of multi-wall carbon nanotubes (MWCNT) to Al 7075 alloy under 20-40 N and 60 N loads at 200-300 and 450 rpm. The results showed that the best abrasion resistance was in 0.5 %wt. reinforced composite [9]. In a study, made with carbon nanotube, composites were formed by adding zircon, graphene and carbon nanotube to A_2O_3 alloy and sintering at 1600 °C. Composites were tested in ball on flat abrasion test setup and according to the results obtained, it has been observed that carbon nanotube reinforcement significantly reduces the wear rate and improves the wear resistance and mechanical properties of the composites [10].

This study, it was aimed to develop a new composite material with MWCNT reinforcement to ZA40 alloy and examine its microstructure, mechanical and tribological properties. Since ZA40 alloy is zinc-based, the biggest factor limiting its use in industrial applications is that its mechanical and tribological properties are not at the desired level at temperatures above 100 °C. For this reason, the effect of MWCNT reinforcement added to the ZA40 alloy at different rates on the microstructure, mechanical and tribological properties of the produced composites was investigated and it was aimed to produce a new advanced engineering material.

2 EXPERIMENTAL PROCEDURE

ZA40 alloy powders were used as matrix and MWCNT powders were used as reinforcement material. ZA40 powders were obtained from İki-el Metal Powders Company in 63 µm size. MWCNT powders used as reinforcement material were 30 nm in diameter with a purity of 90% (Graphene Chemical Industries). The chemical composition of the ZA40 alloy is shown in Tab. 1. In addition, the reinforcement ratios and coding of the samples are given in Tab. 2. Composite powders were ground in a planet-type ball mill (Retsch PM 200) with a milling speed of 350 rpm and a milling time of 2 hours. The milling process was carried out under an argon atmosphere. In the milling process, tungsten carbide balls with a diameter of 10 mm were used and the ball: powder weight ratio was found to be 5:1. Powder mixtures were placed in a 30 mm wide mold made of 4140 steel material and subjected to hot pressing (hot press, Fig. 1) at 800 MPa and 500 °C for 3 hours. Before hot pressing, the samples were subjected to cold pre-pressing under 350 MPa pressure for 1 minute. Zinc stearate was used at 0,5% by weight to prevent agglomeration. Theoretical densities of the produced samples were determined by applying the mixture rule. Archimedes method was applied in experimental intensities. The dimensions of the samples are ± 0,01 mg after measuring with a caliper to an accuracy of ± 0,01 mm. The measurements were made by measuring with precision scales. The hardness measurements of the samples were made using a 2,5 mm diameter penetrating tip under a load of 31,25 kgf, 8 measurements were made with the Brinell hardness measurement method and the arithmetic average was taken. The surfaces of the composites prepared for the abrasion tests were sanded with 400, 800, 1000, 1200, 1500 and 2000 sandpapers to obtain as a smooth surface as possible. Ball on disc wear mechanism was used in wear resistance tests (Fig. 2). Abrasive balls 10 mm diameter balls made of H11 hot work tool steel were used. Abrasion tests were carried out under 5 and 10 N loads, at 250 rpm speed and 100 meters distance. Abrasion tests were carried out with 5 samples 10 times. Morphologies and internal structure analyses of the ground composite powders were examined using a ZEISS LS 10 scanning electron microscope (SEM). The distribution of the reinforcements in the matrix, the porosity and the interfacial examinations of the samples were made in detail by SEM analyses. In the EDS analysis of the samples, the distribution of the additives in the matrix was examined by using Aztecone 3.3 SP1 program in the Oxford instrument x-act brand model device. After the wear tests in SEM, the wear type, surface condition, and the damages on the wear surface were examined.

Table 1 Composition of ZA40 (wt. %).

Al	Cu	Zn	Mg
43,29	1,92	54,79	0,01

Table 2 Samples code and ratio of MWCNT

Sample code	ZA40 (wt. %)	MWCNT (wt. %)
ZA40	100	0
ZC-0.5	99,5	0,5
ZC-1	99	1
ZC-1.5	98,5	1,5
ZC-2	98	2

Figure 1 Hot press

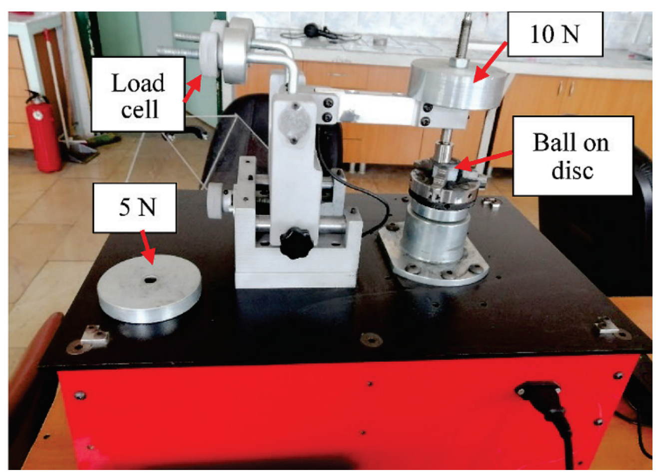

Figure 2 Ball on disc wear tester

3 RESULTS AND DISCUSSION

The data obtained from the production of ZA40/MWCNT composite powders by T/M method and the microstructure, hardness, porosity, wear, friction and worn surface examinations are analysed and discussed below.

3.1 Microstructure

In ZA40/MWCNT composites, a milling time of 2 hours was determined to ensure that the MWCNT powders were homogeneously dispersed into the ZA40 matrix powders and at the same time sufficiently embedded. The distribution of MWCNT in the ZA40 matrix is seen at 500× magnification in Fig. 3a. To achieve high performance in ZA series composite materials, it is necessary to ensure a homogeneous distribution of the reinforcement particles in the matrix and to establish a good interfacial bond between the reinforcement particles and the matrix [11]. Fig. 3b clearly shows that the MWCNT particles are well embedded in the ZA40 matrix alloy. It was determined that MWCNT particles were heterogeneously dispersed in the matrix.

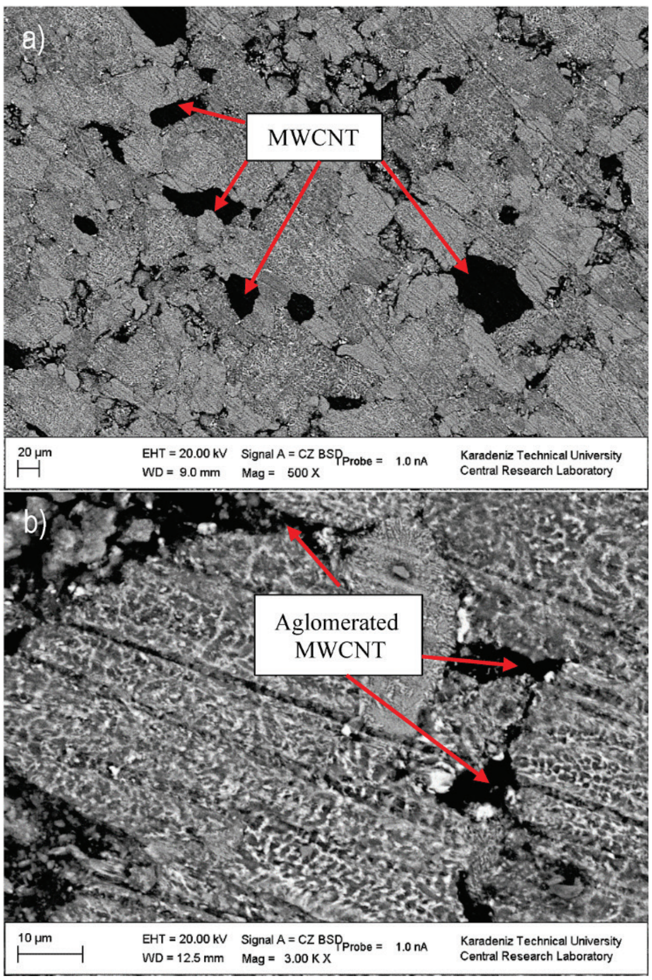

Figure 3 SEM image of ZC-2; a) at 500× magnification, b) at 3000× magnification.

An increase in MWCNT particle aggregation resulted in an increase in MWCNT agglomeration. As a result, the MWCNT distribution in the ZA40 matrix was not homogeneous. It can be concluded that more MWCNT particle aggregates would adversely affect the mechanical properties, wear and corrosion behavior of ZA40/MWCNT composites. In particular, the increase in the amount of reinforcement increased the agglomeration of the powders and led to the enlargement of the grain boundaries [12]. To increase the homogeneity, the mechanical alloying time can be increased and the ball: powder ratio can be changed, but at this time, undesirable problems such as low hardness and poor wear resistance may occur in the mechanical and tribological properties of the composites [13]. In Figure 4, the element distributions of the SEM-EDS analysis of the composites are shown. The red, green, yellow and blue regions of these microstructures show the distribution of Zn, Al, C and Cu elements, respectively. It seems there is no adequate homogeneous distribution. It was observed that the C elements clustered towards the grain boundaries.

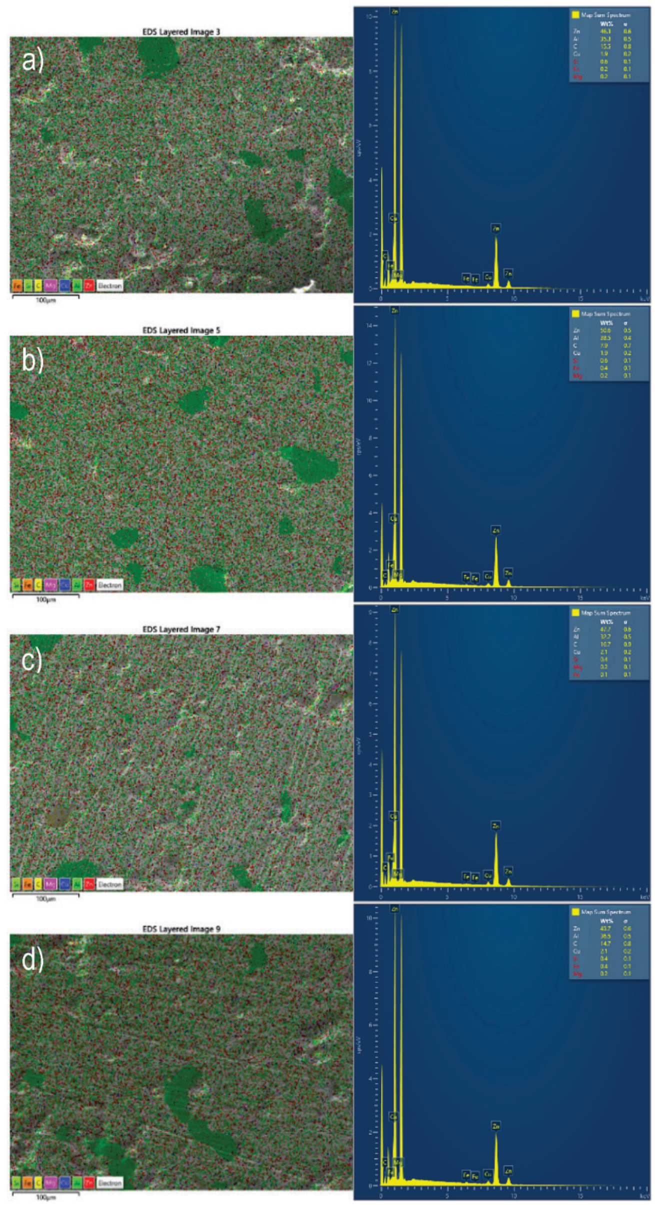

Figure 4 EDS mapping of composites a) ZC-0,5 b) ZC-1 c) ZC-1,5 d) ZC-2

3.2 Porosity and Hardness

As can be seen in Tab. 3 and Fig. 5, the porosity ratio between matrix and composites increased with the increase in MWCNT reinforcement. The highest porosity value was observed in the ZC-2 sample with 13,55 %. While the porosity was measured as 11.19% in the ZA40 matrix, it immediately increased to 12,01% in the ZC-0,5 sample, and the ZC-0,5 sample had less agglutination in the composites. Here, the effect of the packing factor and the agglomeration of the powders to the grain boundaries and the growth of the grain boundaries increased the porosity. The densities decreased with the increase in the amount of reinforcement. It was determined that the hot press technique decreased the densities of the samples and increased the porosities.

Brinell hardness values of the samples are shown in Tab. 3 and Fig. 5 While the hardness value was measured at 150 HB in the matrix material, the lowest hardness value was measured in the ZC-2 sample with 92 HB with the increase in the amount of MWCNT. The most significant decrease was between ZC-1 and ZC-1,5. The addition of graphene-based particles such as MWCNT to the matrix reduced the hardness of the samples linearly. However, it improved the wear resistance and mechanical properties of the samples positively. Particularly, the 2-hour mechanical alloying time facilitated sintering and the distribution of MWCNT reinforcement in the matrix was an important factor in the reduction of hardness.

Table 3 Porosity and hardness value of samples

Sample code	Porosity content (%)	Hardness Brinell (HB)
ZA40	11,19	150
ZC-0.5	12,01	148
ZC-1	12,21	142
ZC-1.5	12,28	113
ZC-2	13,55	92

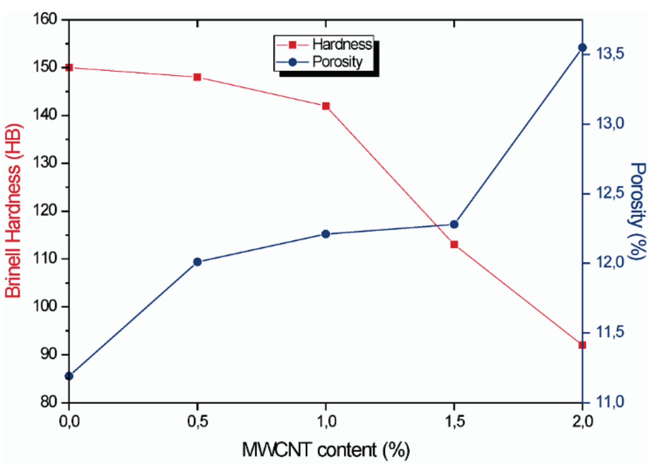

Figure 5 ZA40 and its composites hardness and porosity values

3.3 Wear

The samples that have passed the wear tests are shown in Fig. 6 When the wear data is examined, in Tab. 4 and Fig. 7, the weight loss of 0,0529 mg in the matrix material under 5 N load was measured as 0,021 with the addition of 0,5% MWCNT. This can be explained by the lubricating property of MWCNT. While the weight loss of the matrix material was 0,1032 under 10 N load, the weight losses decreased with increasing MWCNT supplementation. However, it was minimized with 2% MWCNT supplementation. The least weight loss was observed in the ZC-2 sample under 5 N load. In addition, it was observed that the weight losses of the composites under 5 N load were less than the matrix material. The most significant decrease under 10 N load occurred between ZC-1.5 and ZC-2 composites. The least weight loss occurred in ZC-2 composite in all composites and under all loads. These findings suggested that 2% MWCNT supplementation is the ideal rate. For metal matrix composites, one of the most important factors is the reinforcement content; because as the microstructure reinforcement content increases (% by weight), it transforms from metal to ceramic matrix [14]. Although the hardness of the composite samples decreased, their wear resistance increased. Because it is known that carbon-derived additives settled on the grain boundaries form a lubricating film on the surface with the effect of friction and reduce the contact of the abrasive ball with the material, and also fill the grooves formed on the surface of the sample during the wear test [15].

Figure 6 Wear specimens

Table 4 Weight loss of ZA40 and its composites

Sample Number	5 N Weight Loss (mg)	10 N Weight Loss (mg)
ZA40	0,0529	0,1032
ZC-0.5	0,021	0,0916
ZC-1	0,0181	0,0708
ZC-1.5	0,01	0,0588
ZC-2	0,005	0,0168

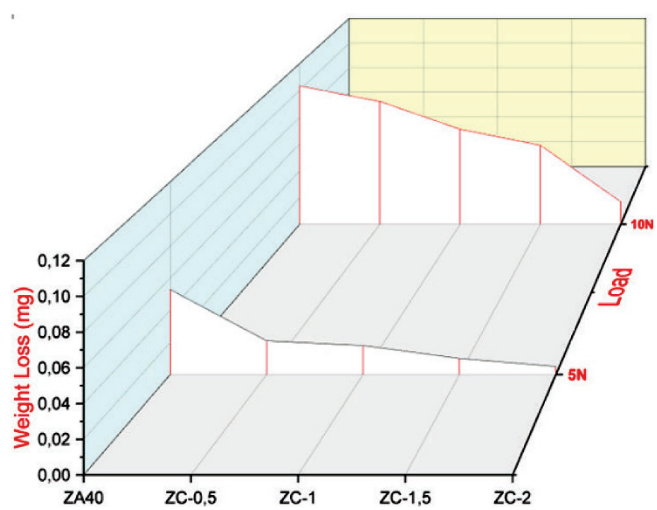

Figure 7 Weight loss of ZA40 and its composites

3.4 Average Frictional Coefficient and Wear Rate

Yan et al. studied ZA27, ZA33, ZA40 and ZA48 zinc aluminium alloys in oily environments. Their results showed that ZA27 and ZA48 exhibited similar properties in friction coefficients in experiments carried out under a load of 400 to 1000 N, but the friction coefficient of ZA40 alloy decreased with increasing loads [2]. As can be seen in Tab. 5 and Fig. 8, the lowest average friction coefficient is seen in the ZC-2 sample under 5 N load. It is clearly seen that increasing MWCNT reinforcement decreases the friction coefficient value. The increased MWCNT reinforcement from 0,5 %wt. to 2 %wt. reduces the friction coefficient from 0,56 µ to 0,18 µt at 5N load and its lubricating property. The highest coefficient of friction was obtained in the ZA40 matrix material for each load. Also it was observed that 2% MWCNT reinforcement had a significant effect on the coefficient of friction at 5 N and 10 N loads. It can be concluded that better distribution of the MWCNTs in the ZA40 matrix causes a lower friction coefficient for the composites. Throughout wear, the friction between the hard ball and the ZA40-MWCNT composites was fewer due to the multilayer structure of the reinforcement, which offers a lubricating influence on the ZA40 matrix subsequent in a decreased friction coefficient [16].

Table 5 Average friction coefficient of ZA40 and its composites

Sample Number	5 N Average Friction Coefficient (µ)	10 N Average Friction Coefficient (µ)
ZA40	0,66	0,62
ZC-0.5	0,56	0,58
ZC-1	0,52	0,56
ZC-1.5	0,37	0,33
ZC-2	0,18	0,28

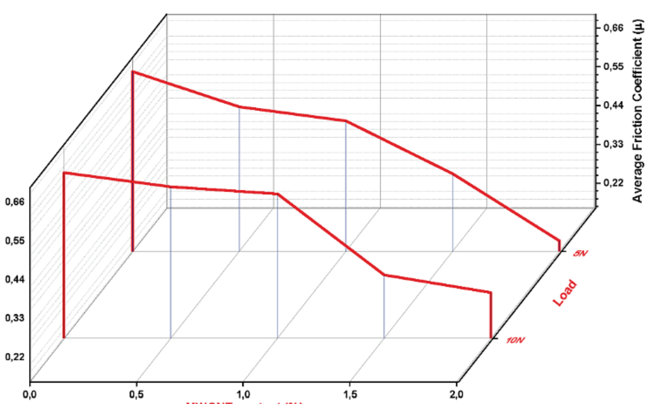

Figure 8 Average friction coefficients of ZA40 and its composites

The results obtained in the wear tests showed that, the increased load and reinforcement rates changed the wear rate of the matrix alloy and composites. When Fig. 9 and Tab. 6 are examined, the lowest wear rate is seen in ZC-2 composite alloy under 5 and 10 N loads. In particular, a significant decrease in the wear rate between ZC-1,5 and ZC-2 under 10N load was noted. This decrease is in parallel with the decrease in weight loss between ZC-1,5 and ZC-2. The highest wear rate was seen in the unreinforced ZA40 alloy. These findings indicated that the MWCNT reinforcement acts as a lubricant between the H11 ball and the surface during wear.

Table 6 Wear rate of ZA40 and its composites

Sample Number	5 N Wear Rate (10^{-4} mm^3/N·m)	10 N Wear Rate (10^{-4} mm^3/N·m)
ZA40	1,391	2,71
ZC-0.5	0,559	2,438
ZC-1	0,484	1,894
ZC-1.5	0,267	1,574
ZC-2	0,136	0,458

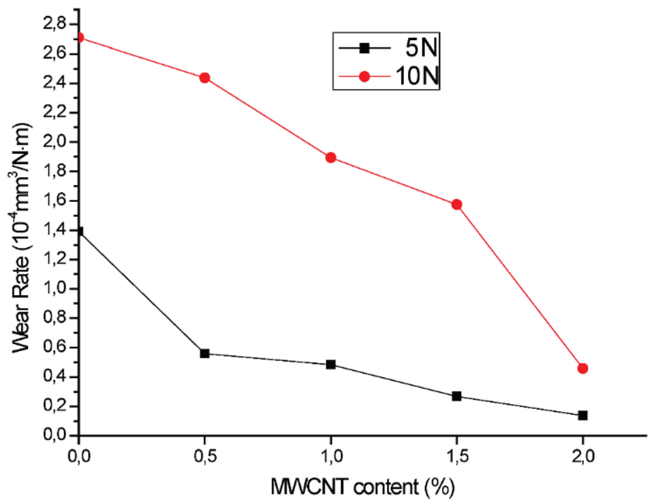

Figure 9 Wear rate of ZA40 and its composites

3.5 Worn Surface Analysis

When the wear surfaces in Fig. 10 were examined, it was seen in the SEM pictures that there was adhesive and sliding wear in ZA40/MWCNT composites. Shear stresses are transferred to the material below the contact zone during wear testing for metal matrix composites. Wear particles are formed due to high deformation and wear in the surface area. A layer is mechanically formed between two sliding surfaces. During the wear test of ZA40/MWCNT composites, a plastic hardening matrix phase is formed on the surface with fine reinforcement particles on the inner surface. The brittle region breaks off from the matrix during the delamination process. The presence of reinforcement particles in the matrix increases its mechanical strength in micro-spaces with its homogeneous distribution [12]. Fig. 10k shows less wear. In the current study, it was found that MWCNT particles changed the wear mechanism to sliding wear, especially under 10 N load. The trace diameter formed on the sample surface of the 10 mm diameter H11 abrasive tip in the ball on disc wear device was measured. When Fig. 11 and Fig. 12 are examined, the trace diameter, which was measured as 3,254 mm in the ZA40 matrix material under 5N load, was found to be 1,640 mm in the ZC-2 sample. Likewise, when we reduced the load by 10 N, the trace diameter was measured as 3,331 mm in the ZA40 matrix material and 2,147 mm in the ZC-2 composite. As a result, the increase in load increased the scar diameter in the composites, as expected. Increasing the MWCNT ratio led to a decrease in the scar diameter of composites. In Fig. 11b and Fig. 12b, the wear mark and wear were observed to be decreased with the lubricating property of MWCNT reinforcement.

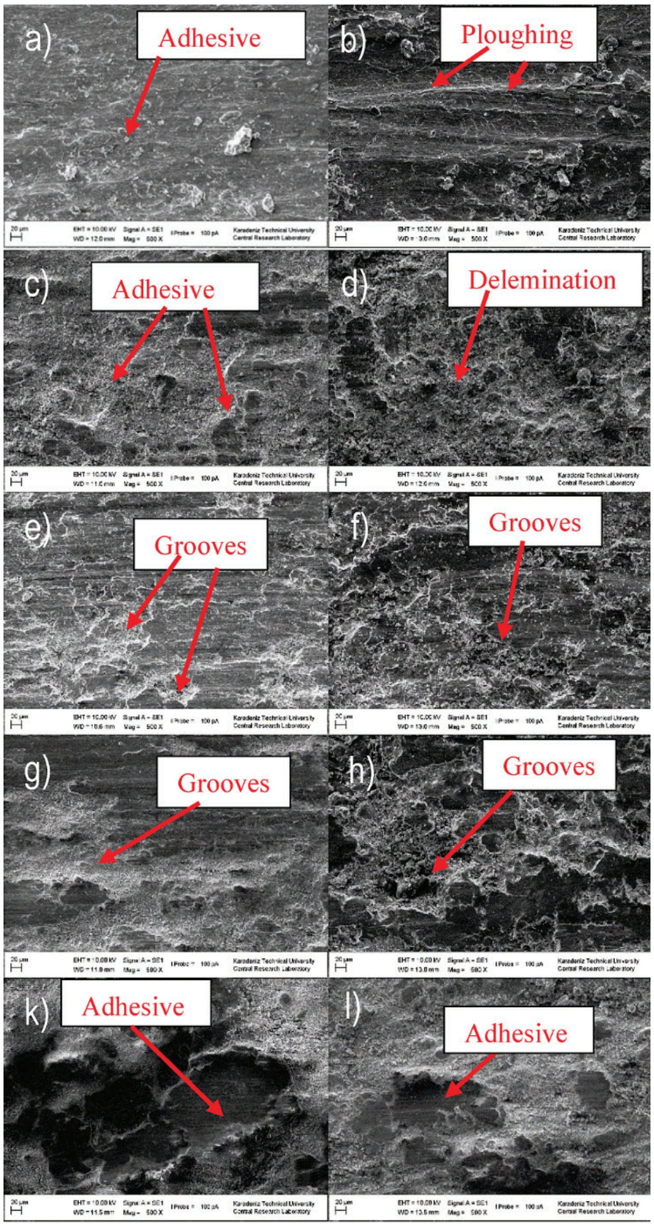

Figure 10 SEM of images ZA40/MWCNT composites (5-10 N): (a-b) ZA40; (c-d) ZC-0,5; (e-f) ZC-1; (g-h) ZC-1,5 and (k-l) ZC-2

4 CONCLUSIONS

In this study, composite samples were produced using the powder metallurgy method by reinforcing ZA40 matrix material with MWCNT. The density, hardness, microstructure, wear and friction behaviours of the samples produced were investigated. The findings obtained can be listed as below:

1) MWCNT reinforced composite materials with ZA40 matrix were produced by the mechanical alloying and hot pressing method, which is a good technique in the powder metallurgy method.

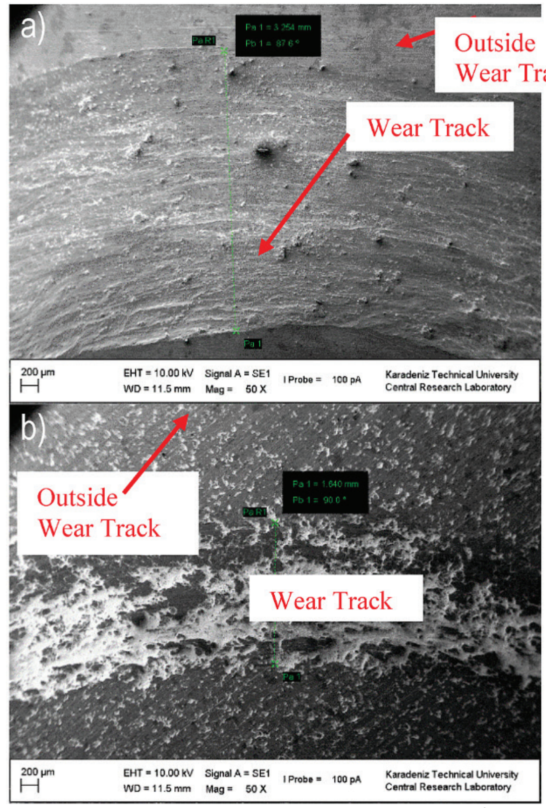

Figure 11 Wear scar diameter measurement under 5 N load at 50X magnification a) ZA40 and b) ZC-2

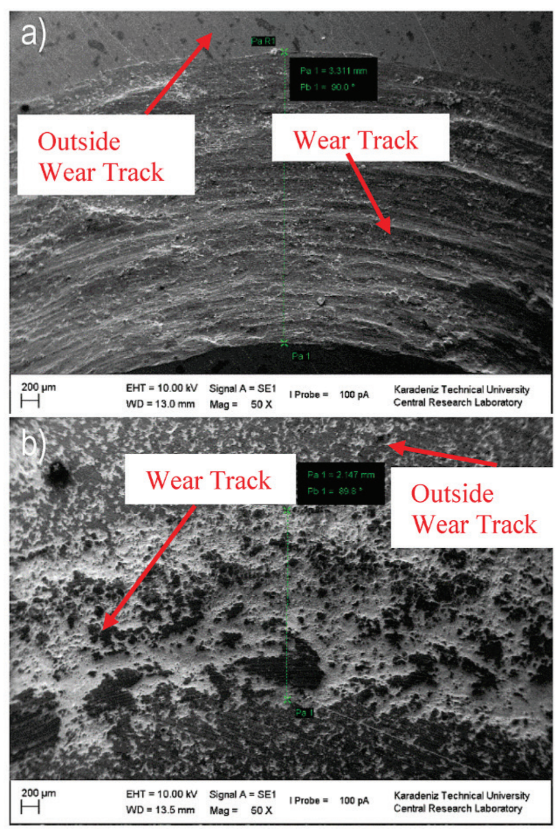

Figure 12 Wear scar diameter measurement under 10 N load at 50× magnification a) ZA40 and b) ZC-2

2) According to the characterization results of the microstructures of ZA40/MWCNT composite powders obtained after mechanical alloying, it can be concluded that the milling time during which the MWCNT particles were ideally dispersed in the ZA40 matrix was determined as 2 hours.
3) The density values of ZA40/MWCNT composites decreased with increasing reinforcement ratios, but the porosity ratio increased. The highest porosity ratio was seen in the ZC-2 sample containing the highest MWCNT supplement.
4) The hardness values of ZA40/MWCNT composites decreased with increasing reinforcement ratios, and the highest hardness value was measured in the ZA40 matrix sample with 150 HB, and the lowest hardness value was measured in the ZC-2 sample with 92 HB.
5) The wear mechanisms observed as a result of the ball-on-disc wear test for all composite materials were determined to be adhesive and abrasive wear. Wear losses increase with increasing load. The greatest weight losses were observed in wear tests under 10 N load. The highest weight loss; 0,1032 mg under 10 N load in ZA40 matrix material. The lowest weight loss is 0,005 mg under 5 N load in the ZC-2 sample was measured.
6) All composites showed a higher wear resistance than ZA40 matrix alloy.
7) A lower coefficient of friction was measured in all composite samples compared to the ZA40 alloy. The highest coefficient of friction was measured as μ = 0,66 in the ZA40 matrix alloy under 5 N load, while the lowest was measured as μ = 0,18 under 5 N in the ZC-2 composite. MWCNT reinforcement reduced friction in wear tests and lowered the coefficient of friction.
8) A lower wear rate was measured in all composite samples compared to the ZA40 alloy. The wear rate increased with increasing load and decreased with increasing MWCNT reinforcement. It has been clearly seen that MWCNT reinforcement reduces the wear rate in composites.

Based on the results of the study, the following recommendations can be tried:

1) In wear tests, wear behaviors can be examined more broadly by applying different speeds, different loads, different durations and longer travel distances.
2) Wear tests carried out in a dry friction environment can be performed in a full oil environment and intermittent oil environment, and the wear behaviour of materials can be examined from different angles.
3) The mechanical properties can be re-examined by applying various heat treatments to the produced samples.

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