

# The effect of boron nitride (h-BN) and silicon carbide (SiC) on the microstructure and wear behavior of ZA40/SiC/h-BN hybrid composites processed by hot pressing

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## Abstract

Within the scope of this study, silicon carbide (SiC) and hexagonal boron nitride (h-BN) powders were added as reinforcement into zinc-aluminum (ZA40) matrix powders, and the powder metallurgy (PM) method, which is an advanced technique in material production, was used to fabricate ZA40/SiC/h-BN hybrid composites. In the milling process, the as-received powders were mechanically milled at 400 rpm under a protective argon atmosphere for 2 h at room temperature. The hybrid composite powders were consolidated under 700 MPa pressure at 515°C for 3 h by hot pressing. Weight losses, friction coefficients, and wear rates were calculated by traveling 100 and 200 m at 250 rpm in a ball-on-disc abrasion test setup under 5 and 10 N loads. According to the results, it was seen that SiC and increased h-BN reinforcement changed the mechanical and physical properties of the composites and made significant contributions to the wear resistance and load-carrying capacity.

**Key words:** ZA40, silicon carbide, boron nitride, wear, hot pressing

## 1. Introduction

Zinc-Aluminum (Zn-Al) alloys stand out from brass, cast iron, and aluminum, attracting the attention of designers and engineers, considering their low melting temperature, good machinability, and superior tribological properties, especially their favorable economic value [1–3]. 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 exceeding 100°C. Since Zn-Al alloys are one of the most important nonferrous alloys, it is possible to produce Zn-Al metal matrix composites by adding ceramic reinforcement [4]. SiC has a higher elastic modulus and specific strength, as well as superior wear resistance and thermal conductivity. Therefore, SiC particles are used as a reinforcement material in parts such as piston rods, axle shafts, springs, transmission

boxes, beam support structures, and turbine blades, especially in the automotive and aerospace industries [5–7]. In a previous study, silicon-reinforced Al-40Zn-3Cu hybrid composite alloys were produced [8]. This study showed that the reason for their improved tribological properties was the hard silicon particles in the internal structure of these alloys and the distribution of these particles in the structure. In a study that examined the wear behavior of ZA27/B<sub>4</sub>C composites formed by the hot press method by reinforcing ZA27 alloy with B<sub>4</sub>C, the researchers observed that increasing B<sub>4</sub>C reinforcement decreased the hardness value of the composites, but significantly improved the wear resistance. In the pin-on-disc wear tests performed under 1, 2, 5, and 10 N loads, the least weight loss was observed in the composite sample containing 3 % B<sub>4</sub>C at all loads [9]. Literature studies have shown that this alloy can be reinforced with different reinforcement particles to improve mechanical properties. Dama et al. studied the microstructural and mechanical prop-

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erties of composites formed by adding 3, 6, and 9 % by weight  $B_4C$  into the ZA27 matrix. They reported an increase in the hardness values of the samples and a decrease in the elongation at break with increasing  $B_4C$  reinforcement [10]. Kumar et al. investigated the effect of SiC and graphite content on the mechanical properties and wear resistance of ZA27 matrix hybrid composites. The data indicated an increase in microhardness and breaking stress values. However, the weight losses after wear were less in hybrid composites than in the matrix material [11]. Miloradovic et al. studied the wear behavior of hybrid composites reinforced by the addition of SiC and graphite to the ZA27 matrix material in a dry friction environment. They found that the additive of SiC and graphite significantly improved the abrasion resistance of the composites [12]. Surya and Prasanthi et al. examined the tribological properties of Al7075 and SiC composites produced by the powder metallurgy method in the pin-on-disc wear mechanism. They stated that 15 wt.% SiC reinforcement was effective in both wear rate and friction coefficient [13].

h-BN is a ceramic material with a graphite-like layered structure which is used as a solid lubricant. Therefore, it has tribological properties such as excellent lubrication. h-BN has been used as an alternative lubricant in high-temperature, vacuum environments, and situations where it is not possible to use liquid lubricants and other lubricants. Previous research has shown that h-BN improves the wear behavior of composites [14, 15]. Rakshath et al. investigated the abrasive wear properties of Al7075 alloy reinforced with  $Al_2O_3$  and h-BN. They stated that 2.5 and 5 % by weight h-BN reinforcement improved the wear resistance and mechanical and morphological properties of the composites [16].

The most important reason limiting the use of ZA40 alloy due to the low melting temperature of zinc is that its mechanical and tribological properties are not at the desired level at high temperatures. Moreover, the above points deeply recommend that most of the studies on the abrasive wear behavior are determined to Zn-Al alloys, and minimal information is available regarding the wear behavior for Zn-Al-based hybrid composites. Because of the above, the present study aims to develop a new composite material with SiC and h-BN reinforcement to ZA40 alloy, which has not been studied up to now, and to examine its wear properties.

## 2. Materials and methods

ZA40 alloy powders used as matrix material were obtained from İki-el Metal company in Turkey. SiC and h-BN powders were supplied by Alfa Aesar company. Sample codes are presented in Table 1. The

Table 1. Elemental composition (wt.%) and codes of the hybrid composites

Sample number	Milling time (h)	ZA40	SiC	h-BN
ZSB-0	2	100	0	0
ZSB-1	2	97	2	1
ZSB-2	2	96	2	2
ZSB-3	2	95	2	3
ZSB-4	2	94	2	4

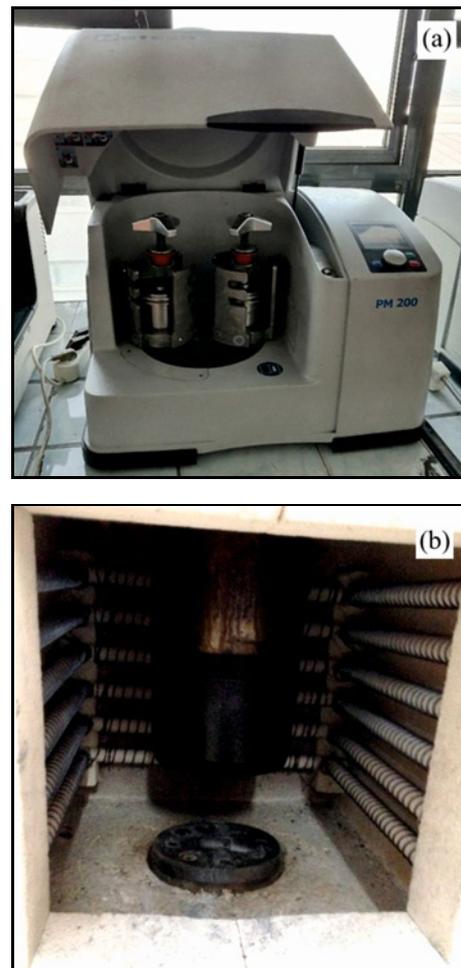


Fig. 1. (a) Ball milling, and (b) hot press.

prepared powders (Retsch PM 200) were milled in a planetary-type ball mill (Fig. 1a) at 400 rpm for 2 h under an argon atmosphere. Tungsten carbide balls with a diameter of 10 mm were used in the milling process. Ball to powder weight ratio was selected to be 5:1. XRD analysis of the mixed powders was performed between 10–20 °C. Cold pre-pressing was applied to the samples at 300 MPa pressure for 2 min. The addition of zinc stearate 0.5 % by weight was used to prevent agglomeration. Hybrid composite powders

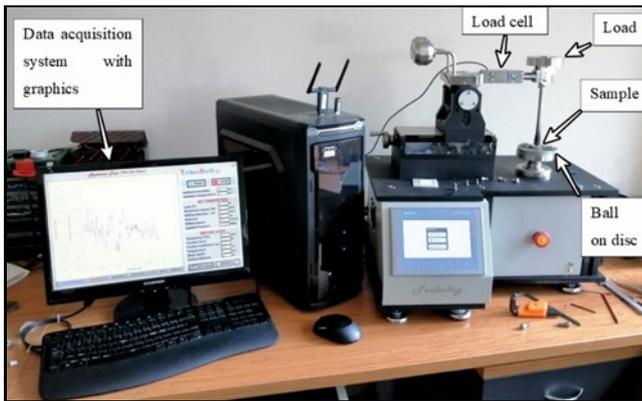


Fig. 2. Ball on disc wear tester.

were subjected to hot pressing (Fig. 1b) at 700 MPa and 515 °C for 3 h. Hardness measurements of the samples were determined by the Brinell hardness measurement method under a load of 31.25 kgf. Before the abrasion tests, the surfaces of the composites were sanded with 400, 800, 1000, 1200, 1500, and 2000

grit sandpapers, and smooth surfaces were obtained. Wear resistance tests were carried out on the ball-on-disc wear mechanism (UTS Tribology) shown in Fig. 2.  $A_2O_3$  balls with a diameter of 6 mm were selected as abrasive balls. Abrasion tests were carried out under 5 and 10 N loads, at 250 rpm speed and 100 and 200 m sliding distance. According to the results obtained, the friction coefficients of each sample along the eroded path were examined. After the wear tests, the SEM images of the samples were examined, and information was given about the types of wear.

### 3. Results and discussion

#### 3.1. Microstructure

In hybrid composite samples, a mechanical milling time of 2 h was chosen to ensure that the SiC and h-BN particles were dispersed as homogeneously as possible in the ZA40 matrix. Figure 3 clearly shows SiC and h-BN particles homogeneously distributed within the ZA40 matrix alloy at 1.00 K.X magnification. It was

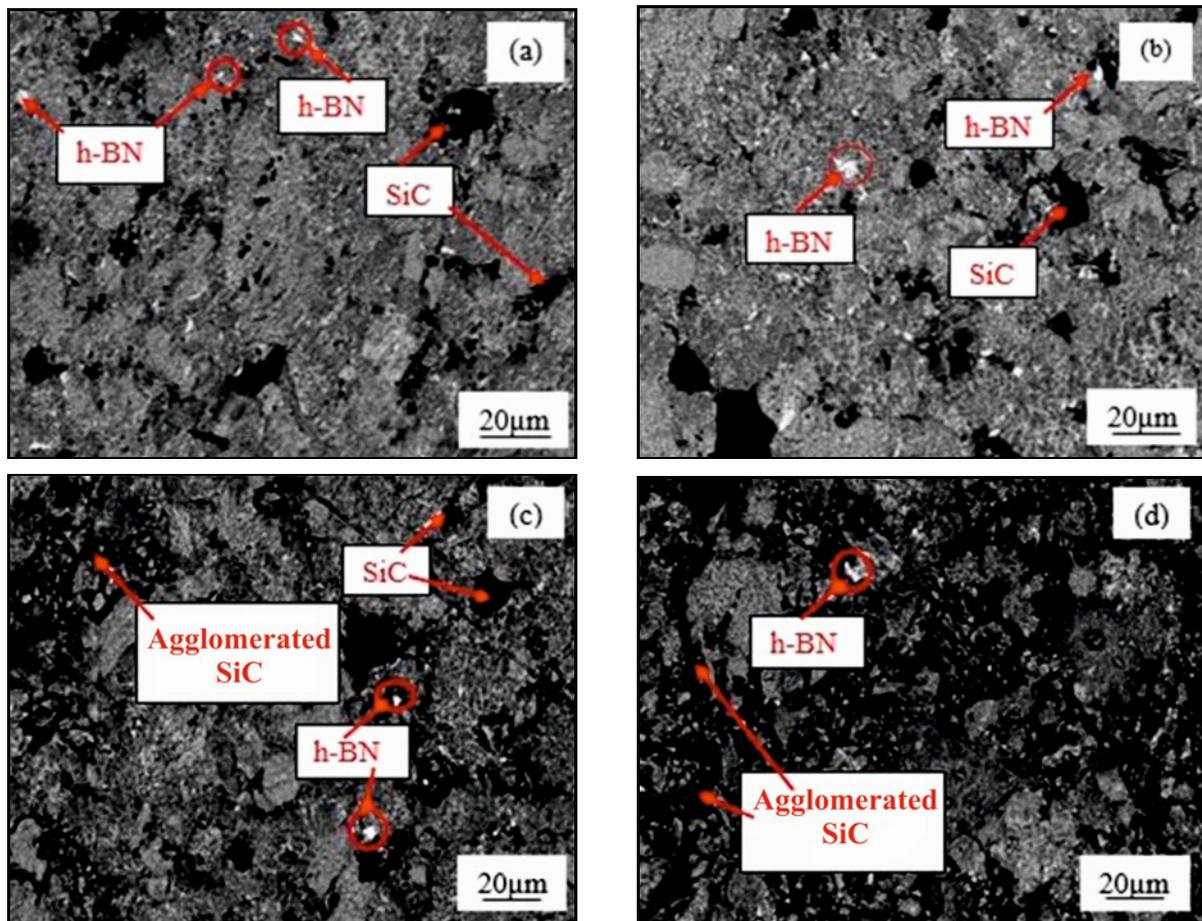


Fig. 3. SEM images (1.00 K.X) of hybrid composites: (a) ZSB-1, (b) ZSB-2, (c) ZSB-3, and (d) ZSB-4.

observed in previous studies that if the silicon ratio in Zn-Al alloys exceeds 2 %, the silicon particles grow and cluster in the structure and cause agglomeration [17]. If it is desired to achieve high performance and a good working range in Zn-Al alloy series composites, the reinforcement particles should be distributed as homogeneously as possible in the matrix, and a good interface bond should be also formed between the re-

inforcement particles and the matrix [18, 19].

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, poor sintering, and poor wear resistance may occur in the mechanical and tribological properties of the composites [20]. In Fig. 4, the element distributions of the SEM-EDS analysis of the

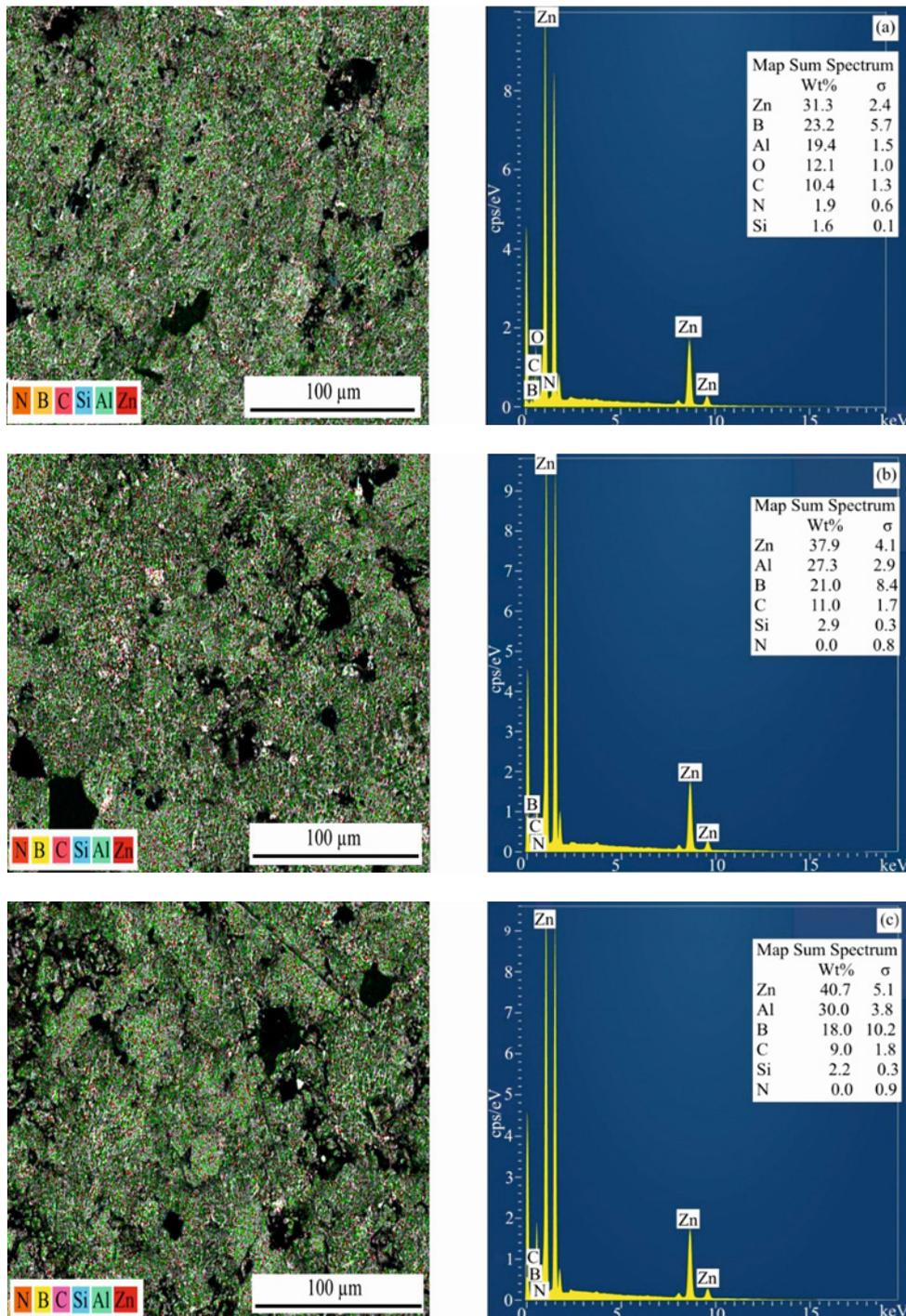


Fig. 4a–c. SEM-EDS mapping of hybrid composites: (a) ZSB-1, (b) ZSB-2, (c) ZSB-3.

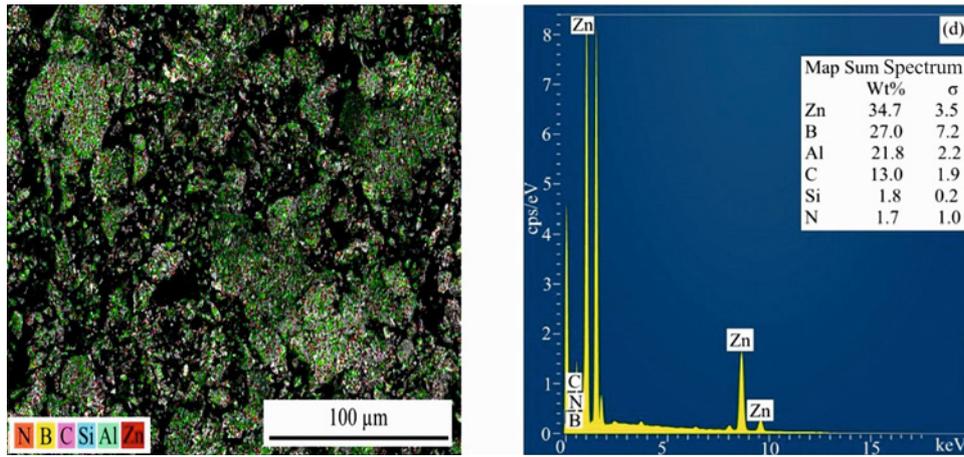


Fig. 4d. SEM-EDS mapping of hybrid composites: (d) ZSB-4.

Table 2. Values: porosity, relative density, and hardness of samples

Sample number	Porosity content (%)	Relative density (%)	Hardness Brinell, HB
ZSB-0	7.57	92.42	134.3
ZSB-1	8.58	91.41	130.4
ZSB-2	9.64	90.35	112.8
ZSB-3	10.10	89.89	108.2
ZSB-4	12.90	87.09	95

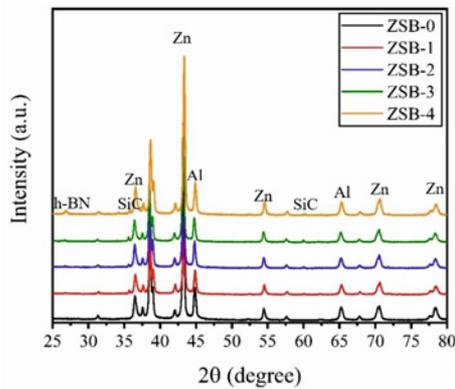


Fig. 5. XRD analysis of matrix and hybrid composites.

composites are shown. The red, green, blue, pink, yellow, and orange regions of these microstructures show the distribution of Zn, Al, Si, C, B, and N elements, respectively. It seems there is no adequate homogeneous distribution. It was observed that the Si and B elements clustered towards the grain boundaries.

### 3.2. XRD analysis

When we examine the XRD graph given in Fig. 5, Zn, Al, SiC, and h-BN peaks can be seen. In particular, the ZA40 matrix and the highest reinforced ZSB-4

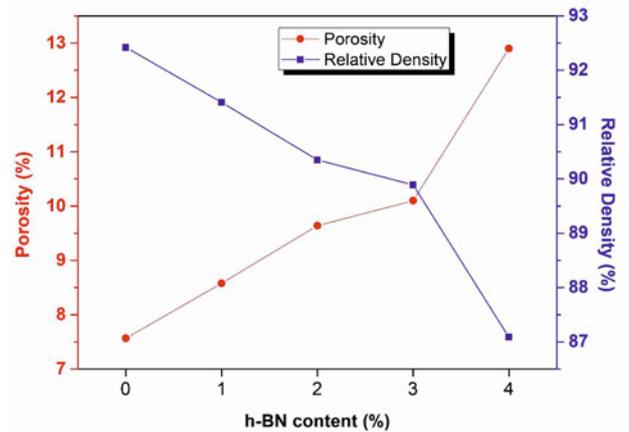


Fig. 6. Porosity and relative density values of matrix and hybrid composites.

hybrid composite were compared. The h-BN peak is observed at 27 degrees. SiC peaks are seen at 36 and 60 degrees. The Zn and Al peaks were seen at higher diffraction peaks. A decrease in Zn and Al peaks was determined with SiC supplementation and increasing h-BN supplementation.

### 3.3. Porosity, relative density, and hardness

The porosity and relative densities of ZA40 and re-

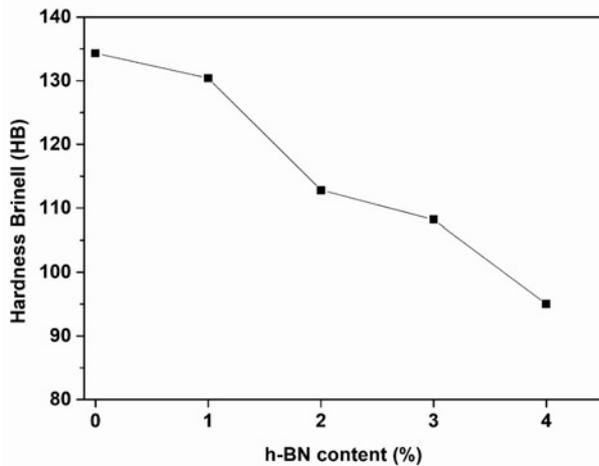


Fig. 7. Hardness value of matrix and hybrid composites.

inforced composites are given in Table 2 and Fig. 6. It is seen that the amount of porosity in hybrid composite samples increased with the addition of SiC and h-BN reinforcements. The amount of porosity was measured as 7.57% in the matrix material, and it increased to 8.58% with 2% SiC and 1% h-BN reinforcement (ZSB-1). The highest porosity amount was measured as 12.9% in the ZSB-4 sample. Here, the ZSB-1 sample was the sample with the lowest amount of porosity among the composites. From this, it can be deduced that the ZSB-1 sample had less agglomeration compared to other composites. In particular, an increase in the amount of reinforcement increases the agglomeration of the powders, which causes the enlargement of the grain boundaries [21]. While the relative density value of the ZA40 matrix was measured as 92.42%, it tended to decrease with increasing reinforcement amount. When hardness values were investigated in Table 2 and Fig. 7, it was seen that the hardness value of the matrix, which was measured as 134.3 HB, decreased linearly with the increase of reinforcement ratios. The lowest hardness value was observed in the ZSB-4 sample with 95 HB and the highest amount of porosity. These results suggested that the increase in the amount of porosity reduced hardness values. In particular, the difference in the amount of increased porosity between the ZSB-3 and ZSB-4 samples was inversely proportional to the decrease in the hardness values of these composites.

### 3.4. Wear

Table 3 and Fig. 8 show weight losses of matrix and hybrid composites under 5 and 10 N loads for 100 and 200 m sliding distances. The weight losses of the composites were less than that of the matrix material for both load and shear distances. This can be attributed

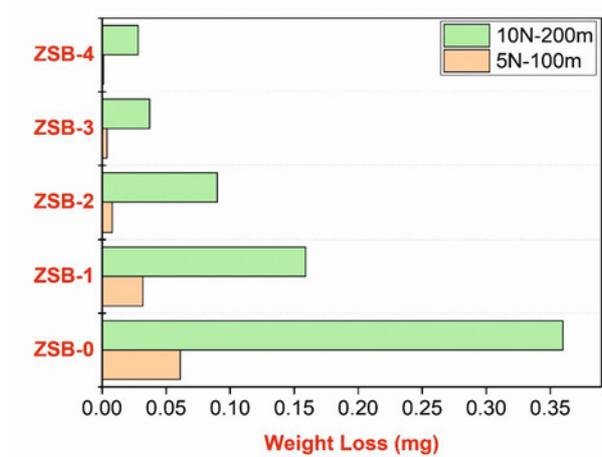


Fig. 8. Weight loss of samples.

Table 3. Weight losses of samples

Sample number	5 N-100 m weight loss (mg)	10 N-200 m weight loss (mg)
ZSB-0	0.061	0.36
ZSB-1	0.032	0.159
ZSB-2	0.008	0.090
ZSB-3	0.004	0.037
ZSB-4	0.001	0.028

to the hard SiC particles and the self-lubrication of h-BN particles within the ZA40 matrix. When the wear load increased, the weight losses also showed a linear increase. The ZSB-4 sample was determined as a hybrid composite with the least weight loss of 0.001 mg at 5 N load for a 100 m sliding distance. Doubling the applied load and the distance traveled significantly increased the weight losses in all samples. The difference in weight loss between the ZSB-3 and ZSB-4 samples was quite close to each other. The distribution of SiC and h-BN particles in the ZA40 matrix alloy is a quality factor that affects the wear behavior, except for the interface reactions between the matrix material and the reinforcement particles.

### 3.5. Average frictional coefficient and wear rate

When the friction coefficient results are compared to the matrix material (Fig. 9), it is seen that the friction coefficient decreases by increasing SiC and h-BN content. An increase in friction coefficients was observed with increasing load and increasing distance. The decrease in the coefficient of friction with increasing h-BN ratios also supports each other with decreasing weight losses. Doubling the load and the

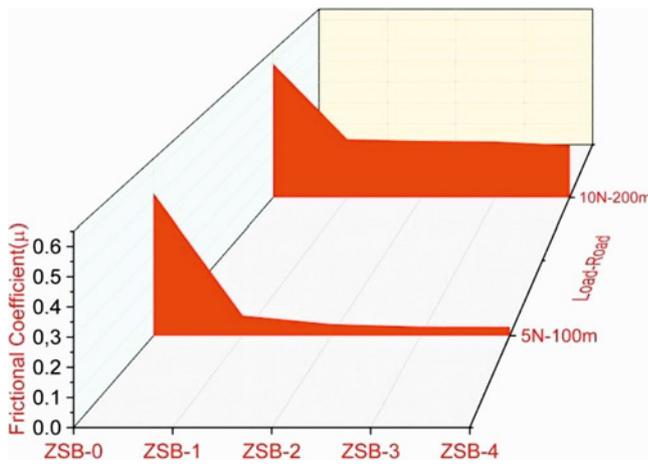


Fig. 9. Frictional coefficient of samples.

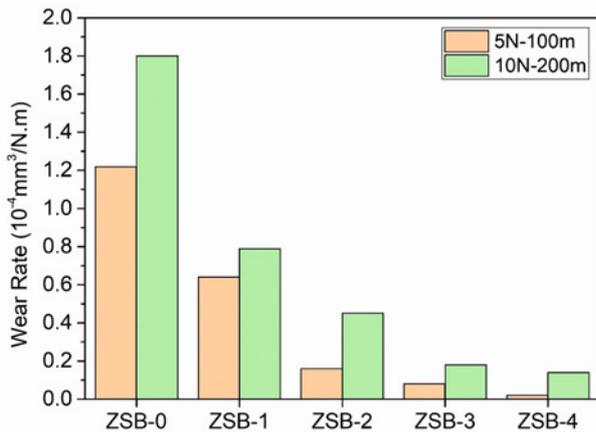


Fig. 10. Wear rate of samples.

distance produced a significant increase in the ZA40 matrix and the friction coefficients of the hybrid composites. The friction coefficients of the ZA40 matrix alloy were higher than all hybrid composites. This showed that hybrid composites were successful in wear resistance. The lowest coefficient of friction was observed in the ZSB-4 sample under 5 N load and was measured as  $0.0315 \mu$ . ZSB-4 composite showed the lowest friction coefficient values in both parameters. It is known that the load-carrying capacity of SiC particles reduces the amount of wear [22]. From this point of view, it is possible to say that the SiC reinforcement, which was the hard particle in the matrix, increased the load-carrying capacity of hybrid composites, and reduced the friction coefficient of hybrid composites by acting as a lubricant in the increased h-BN reinforcement. While the aluminum and copper-rich phases in the internal structures of the Zn-Al series alloys undertake the load-bearing task, the softer

zinc-rich  $\eta$  phase facilitates slippage and reduces the friction coefficient [23]. In a similar study, SiC and h-BN nanoparticles within the Al6063 matrix significantly reduced the wear rate and friction coefficient of the hybrid composites, and the 5 % SiC-1.5 % h-BN doped hybrid composite showed the best wear resistance [24].

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. 10 is examined, the lowest wear rate is seen in ZSB-4 composite alloy under 5 N-100 m and 10 N-200 m conditions. In particular, a significant decrease in the wear rate between ZSB-1 and ZSB-2 under a 5 N load was noted. The decrease in wear rates and the decrease in weight losses supported each other. The highest wear rate was seen in the unreinforced ZA40 alloy. These findings indicated that h-BN reinforcement acted as a lubricant between the  $A_2O_3$  ball and the surface during dry sliding wear. In a similar study, it was observed that SiC and graphite reinforcement improved the wear properties of ZA27 hybrid composites and reduced the specific wear rate [12].

### 3.6. Worn surface analysis

Traces of abrasive and adhesive wear were observed on the surfaces of hybrid composite and matrix samples. It was stated in similar studies that abrasive and adhesive wear types are the main mechanisms in Al-containing composite materials [25–27].

Detailed SEM images of ZA40 and hybrid composites under 5 and 10 N loads are given in Fig. 11. In particular, the wear marks at increased loads are in the same direction as the wear direction and are more clearly and distinctively determined in the images. Cracks and cold tears were observed at loads less than 5 N, while adhesive wear and plastic deformations were observed at 10 N loads. SEM images, which show wear surfaces under 10 N load, indicated that more particles were detached from the sample surfaces along the 200 m road, but the broken particles strongly adhered to the surface of the composite samples and performed cold welding within the wear mechanism. It is suggested that there was an abrasive wear mechanism in the ZA40 matrix alloy. The alumina pin determined the wear mechanism by breaking off large pieces from the matrix surface, which is softer than itself. When a hard material is pressed against a much softer material by applying force, the abrasive surface of the hard material creates localized plastic flow on the soft material [28]. In summary, the SiC ratio and the increasing h-BN ratio in the composites changed the wear mechanism from abrasive wear to adhesive wear.

#### 4. Conclusions

ZA40/SiC/h-BN hybrid composites were successfully produced with different reinforcement ratios by hot press and powder metallurgy method, and their tribological properties were investigated in the study.

In the SEM and EDS analyses, a homogeneous distribution was observed in the microstructures of the

hybrid composites during the milling for 2 h. In XRD analyses, the peak changes between the matrix and the reinforced hybrid composite sample were seen in the specified intervals.

Increasing load and traveling path increased the wear rate and friction coefficient of the matrix and hybrid composites, while the wear rate and friction coefficient decreased linearly with increasing h-BN con-

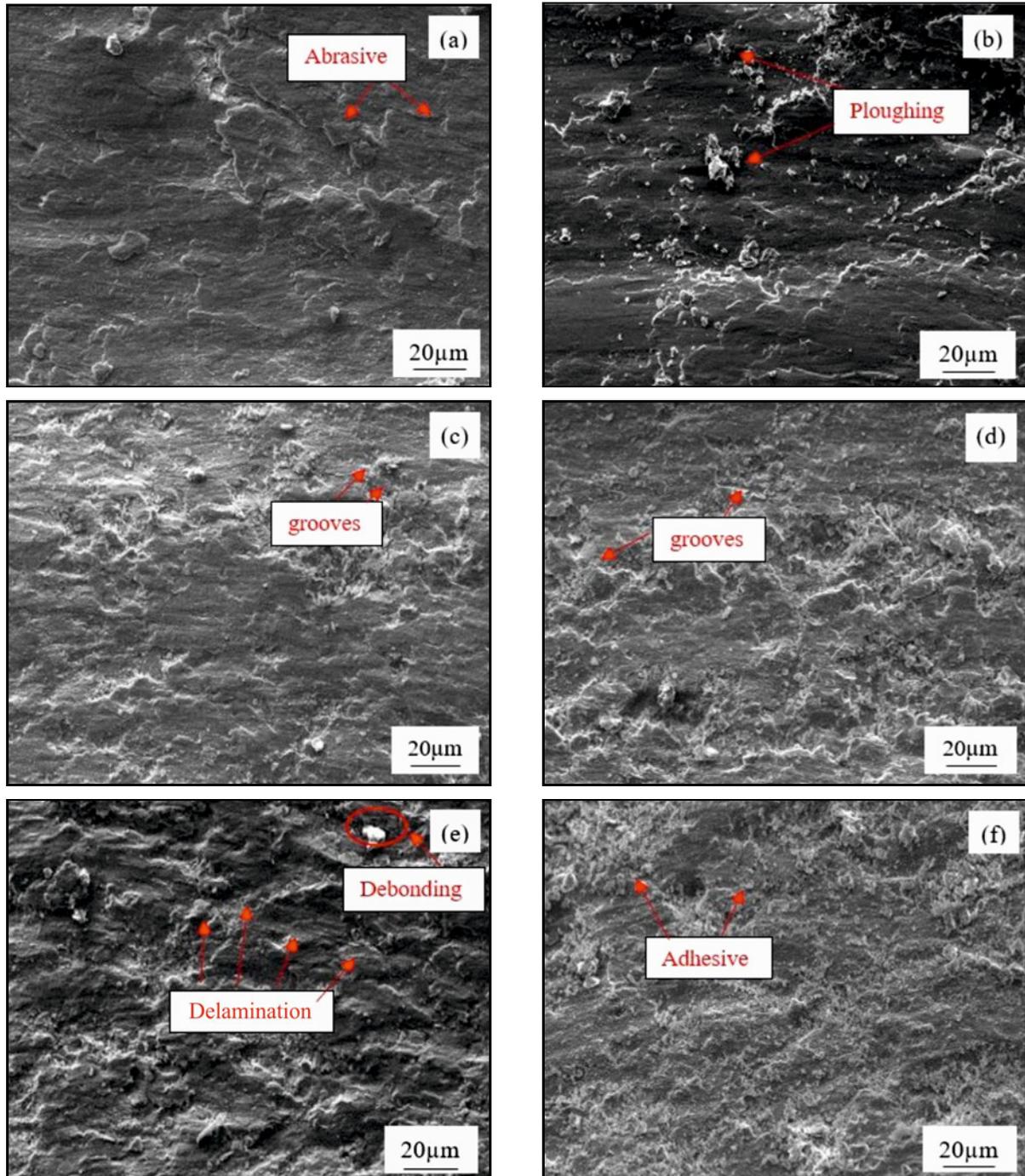


Fig. 11a–f. Worn surface SEM images of matrix and hybrid composites (5 N-100 m, 10 N-200 m): (a) and (b) ZSB-0, (c) and (d) ZSB-1, (e) and (f) ZSB-2.

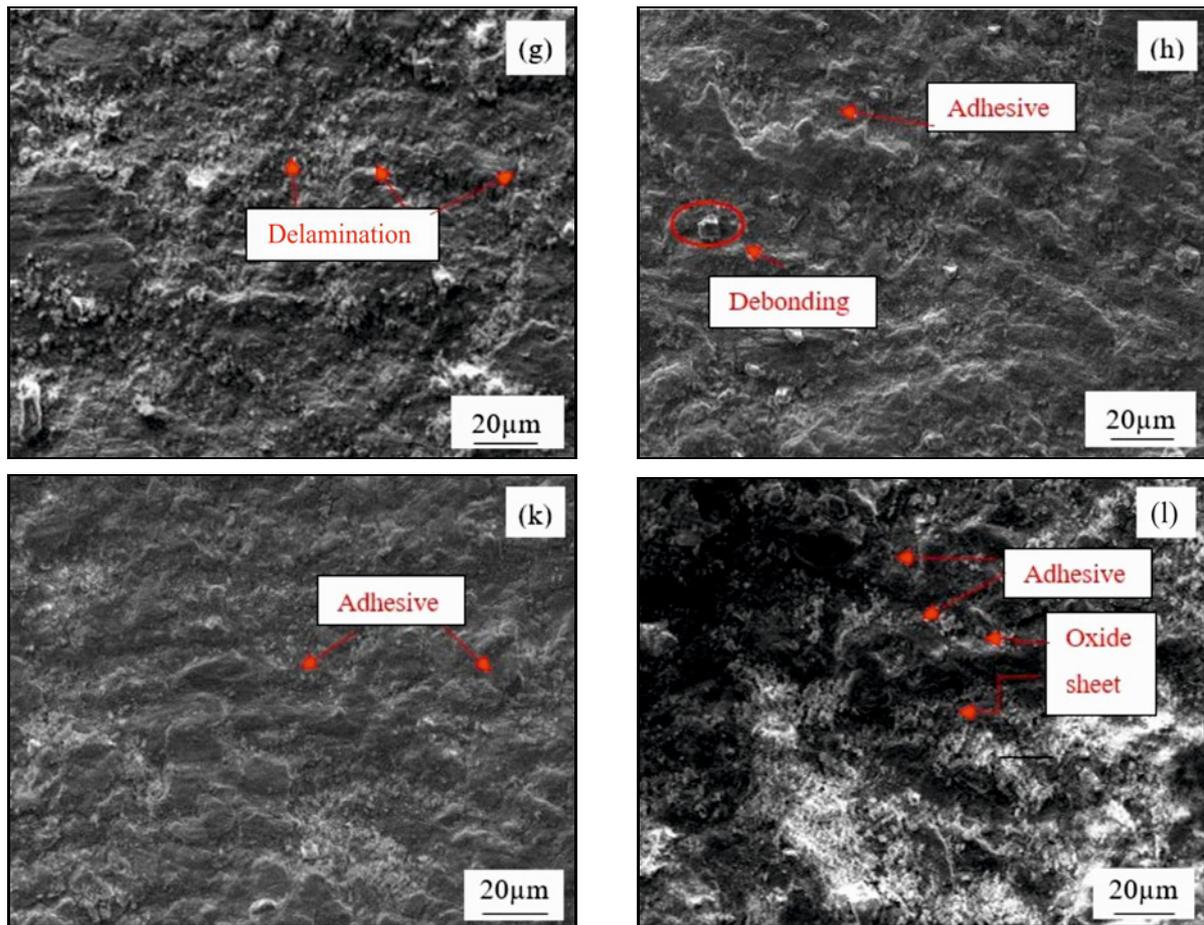


Fig. 11g–l. Worn surface SEM images of matrix and hybrid composites (5 N-100 m, 10 N-200 m): (g) and (h) ZSB-3, (k) and (l) ZSB-4.

tent. The lowest coefficient of friction was observed in the ZSB-4 sample under 5 N load and was measured as  $0.0315 \mu$ . While the wear rate of the matrix material was  $1.22 (10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1})$ , it was measured as  $0.02 (10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1})$  in the ZSB-4 sample (5 N-100 m), while the wear rate of the ZBS-0 sample was measured as 1.8 and 0.14 in the ZBS-4 sample (10 N-200 m).

The hybrid composite with the highest wear resistance was ZSB-4 (2 % SiC and 4 % h-BN). Adhesive, abrasive, and delamination wear was observed on the wear surfaces of matrix and hybrid composites. It was observed that especially hard SiC and self-lubricating h-BN particles improved the wear resistance of hybrid composites by showing lubricity.

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