Research Article

Ismail Yıldız*

**Tribological properties and characterization of borided Co–Mg alloys**

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**Abstract:** In this study, tribological properties and characterization of borided Co–Mg alloys were investigated. Cobalt–magnesium (CM) alloys with 97% Co–3% Mg composition were borided at temperatures of 850–900°C and for 1.5–4.5 h with solid boriding. The properties of the resulting boride layers were measured and determined by microhardness, scanning electron microscopy (SEM), X-ray diffraction (XRD), density, and surface roughness testers. XRD analysis results after boriding found CoB, Co$_2$B, and Co phases. Depending on the boriding time and temperature, the thickness of the boride layer for the CM alloy varied from 51 to 138 µm. The boride layer had a hardness varying between 1,674 and 1,956 HV$_{0.05}$ for the CM alloy, while the Vickers hardness value of untreated Cobalt was 52 HV$_{0.05}$. The wear tests were carried out in a ball-disc arrangement under a dry friction condition at room temperature with an applied load of 10 N and with a sliding speed of 0.3 m/s at a sliding distance of 250 m. It was observed that the wear rate of borided and unborided CM alloy ranged from $25.89 \times 10^{-5}$ to $94.95 \times 10^{-5}$ mm$^3$/N m. As a consequence of the findings, the author reported that boriding CM alloys in the given conditions can make a difference for different application areas.

**Keywords:** Co–Mg alloys, surface roughness, borided, wear

1 Introduction

Magnesium and its alloys are evaluated in the aviation, transportation, electronics, biomedical, and energy sectors owing to their excellent physical and chemical properties such as low density, good damping performance, biocompatibility, and recyclability [1–4]. Despite their prevalence, there are many challenges that must be overcome before these advantages of magnesium and its alloys play an important role in large-scale industrial applications [5–8]. The low tensile strength, poor plasticity, and corrosion resistance of magnesium alloys hinder large-scale applications of magnesium and cobalt (CM) alloys as structural materials [9–11].

Boriding is a thermochemical treatment that consists of Ni, Co, Ti, and Mg alloys, and steels with a rich-boron material (solid, liquid, or gas phases) [12–14]. This method, which is exposed to temperatures of around 800–1,000°C to cause dissociation and diffusion of the boron atoms, improves the hardness and tribological properties of the surface of these alloys and steels [15–17]. Boriding is highly suitable for cobalt-based alloys where boride layers consisting of two phases (CoB and Co$_2$B) with high hardness are the typical outcomes obtained. Additionally, boronizing enhances the mechanical properties of steels by forming boron layers such as Fe$_2$B, FeB, Ni$_3$B, Ni$_2$B, and NiB on the surface [18–23].

Cobalt-based alloys have an excellent combination of mechanical strength and corrosion resistance that is well suited for a wide variety of aerospace, milling, and biomedical applications [24,25]. Nonetheless, some of its applications are limited due to its low hardness and wear resistance. Therefore, the boriding process is an effective method to improve the mechanical surface properties of CM alloys by diffusing boron atoms to the material surface [26,27].

The effects of the boriding method on different alloying elements have widely been studied in the literature. These elements include materials such as Al, Ni, Mo, Co, Fe, W, and WC [28–35]. Since Mg is a very specific element, it is rarely used in boriding methods. The main objective of this study is aimed at investigating the friction and wear behaviors of borided CM alloys. Structural and tribological properties were thoroughly investigated using a non-contact optical profilometer, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), microhardness tests, and a ball-on-disc tribotester. The findings were clearly given and discussed with the use of appropriate figures and tables as below.
2 Materials and methods

2.1 Boriding and characterization

Within the context of the present work, metal powders were used in 97% Co–3% Mg alloy materials. Co–Mg metal powders were homogeneously mixed for 24 h to obtain CM alloyed materials. The mixed powders were carefully poured into a cylindrical mold specially designed for shaping under 500 bar pressure in a uniaxial cold press which was followed by attentive pressing. The shaped samples were heat-treated in a conventional tube furnace at 530°C for 2 h in an atmosphere-controlled environment.

In the boriding process, nano-sized Ekabor II powder mixtures were poured under and over the samples in a stainless steel crucible. The top and lid of the box were properly sealed with chamotte mud to prevent samples from oxidizing by heat. The samples were heated in an oven at 850–900°C for 1.5–4.5 h. Figure 1 shows the placement of CM alloys both in the boring crucible and in the furnace. After this step, the samples were taken out of the oven and allowed to cool in the ambient air. The microstructures of the samples were determined by Nikon MA200 optical microscope. Boriding structures formed in the layers were revealed in Shimadzu XRD 6000. SEM analysis was performed with LEO 1430 VP model SEM instrument. Hardness measurements of the borided and unborided samples were carried out under 50 g loading on the Shimadzu HMV-2 Vickers hardness tester. The reason for preferring the Vickers microhardness test is to make use of its employment in the medium hardness group, thin steel sheet metal, hardened machine parts, cutting tools, mild steel, or all kinds of non-steel materials [36].

Furthermore, a wear test was applied to the boronized samples as a mechanical test. The abrasion test was carried out using a ball placed on a disk that rotates mechanically at a certain speed. In this mechanism, samples are tightly placed at the bottom. This table rotates and moves so that the ball touches the sample surface. In the experimental procedure, 8 mm diameter WC–Co-based balls were used for abrasion. Abrasion tests were carried out under 10 N load under dry friction conditions at room temperature atmosphere, 0.3 m/s sliding speed, and 250 m sliding distance (Figure 2).

Surface roughness measurements were performed on the samples. The averages \( R_a \) of these measurements were taken. \( R_a \) value is calculated according to the equation below.

\[
R_a = \frac{P_{\text{area}} + Q_{\text{area}}}{L} \times \frac{1,000}{V_q},
\]

where \( P \) and \( Q \) are the areas (mm²), \( L \) is the length (mm), and \( V_q \) represents the vertical magnification value. The measurement was carried out with the PCE-RT1100 instrument.

Before and after each wear test, every single sample and abrasion element was cleaned with alcohol. After the test, the wear volumes of the samples were quantified by multiplying the cross-sectional areas of the wear by the width of the wear track obtained from the Taylor–Hobson Rugosimeter Surtronic 25 device. The wear rate was calculated with the equation:

\[
W_k = \frac{W_v}{M \cdot S \cdot N \cdot m},
\]

where \( W_k \) is the wear rate, \( W_v \) is the worn volume, \( M \) is the applied load, and \( S \) is the sliding distance. Friction coefficients depending on sliding distance were obtained through a friction coefficient program. Surface profiles of the wear tracks on the samples and surface roughness were measured by a Taylor–Hobson Rugosimeter Surtronic 25.
3 Results and discussion

3.1 SEM analysis of boriding coatings

SEM analysis images of 97% Co–3% Mg alloys heated at 850–900°C for 1.5–4.5 h are shown in Figure 3a–d. As can be seen from the figures, the boride layers formed on the CM alloy base materials have saw-tooth morphology and these layer thicknesses are clearly seen to depend on the temperature and time increase. Due to the melting of the element Mg at high temperatures and its rapid deterioration in air, it has formed a partially porous structure in the microstructure.

In Figure 4, the layer thickness on the surface was obtained to be between 5,133–13,866 µm, depending on the chemical composition, time, and temperature after the boriding of 97%Co–3%Mg alloys. The saw-tooth morphology in the layer changes depending on the element Mg in CM alloys. The thickness of the boron layer varies with respect to temperature and time. Additionally, we found that Co and Mg elements move towards the matrix. As a result, it has been observed that the boride layers grow in this direction. Likewise, in our previous study, Yıldız et al. [38] also examined the boriding of the Fe–Mg alloy and found that after boriding, Mg forms pores in Fe and prevents the growth of the boride layer.

3.2 XRD analysis

Figure 5a–d shows the XRD patterns of 97% Co–3% Mg alloys borided after changing temperatures of 850–900°C and different times of 1.5–4.5 h. XRD results show that cobalt-structured boron layers are predominantly formed. These results mean that CM alloys contain CoB, Co<sub>2</sub>B, and Co phases with boride layers after boriding. CoB and Co<sub>2</sub>B phase values increase due to the increase in boriding temperature and time. In this case, it strengthens the diffusion
bond between the base material and the boride layer and therefore it affects the strength of the alloy material. In the recent literature, Oh et al. [39] focused on producing cobalt–boron alloys by mixing cobalt and boron powders under the gas atmosphere of Ar–N₂ and Ar–H₂ in the thermal plasma jet system. Their report revealed various structures such as Co, CoB, and Co₂B phases in nanoparticle synthesis. Similarly, Delgado-Brito et al. [40] conducted a powder package boriding process on the surface of ASTM F1537 alloy at 1,273 K for 6 h. They found that CoB and Co₂B layers were formed on the alloy surface after boriding. As can be appreciated from some recent investigations, CoB and Co₂B phase structures emerged as 45–50 as the 2θ angle at most. A detailed view of the CoB and Co₂B phases is given in Figure 6b and c.

3.3 Microhardness test

Figure 7 shows the microhardness values of borided 97% Co–3% Mg alloy materials at a temperature of 850–900°C for 1.5–4.5 h. After this process, the results were obtained by the average of the microhardness measurements made from at least eight different regions along the cross-section of each sample. Based upon the findings, one can state that an increase appears in parallel with the increase in the temperature and time variables.

Accordingly, the lowest value was obtained as 1,674 HV₀.⁰⁵ after 1.5 h at 850°C, while the highest value was found as 1,956 HV₀.⁰⁵ at 900°C after 4.5 h. On the other hand, Vickers hardness value of unboried 97% Co–3% Mg alloys was found to be 52 HV₀.⁰⁵. When it comes to comparing these findings with some literature studies, Johnston et al. [41], for instance, obtained a 2,549 HV hardness value on borided cobalt–
Figure 6: CoB and Co₂B XRD phase structures revealed in the literature. Detailed view of figure 6–b CoB, CoB and Co₂B phases in Figure 6–c [39,40].

Figure 7: The variation in hardness depth of borided CM alloys depending on the applied temperature and time.
chromium alloys by plasma boriding method. Further, Cuao-Moreu et al. [42] figured out the hardness values of 1,835–2,243 HV after processing at the temperatures of 1,223, 1,248, and 1,273 K for periods of 6, 8, and 10 h on the borided Co–Cr–Mo alloys. For these reasons, we can say that our findings are promising for enhancing microhardness values.

3.4 Surface roughness and density

A surface roughness test was performed on the samples after the boriding method. As a result of the surface roughness test, $R_a$ values of CM alloys are found between 0.3 and 0.62 $\mu$m. In addition to this test, a density test was also performed using Archimedes’ principle. The results vary between 7.32 and 7.57 g/cm$^3$. It is apparent that both parameters increase with the changing parameters. The reason for this increment can be associated with the evaporation of magnesium elements in the alloy at high boriding temperatures creating porosity in the structure. Such phenomenon can also be referred as due to the low melting temperature of the element Mg [43,44].

3.5 Wear test

In Figure 8, the friction coefficients emerge after the wear test was performed on borided and unborided CM alloys. The surface roughness values of the materials have increased due to the increase in the boriding temperature and time. In this case, the friction coefficients have increased, as well.

Figure 9 reveals the wear rate of the unborided and borided CM alloys. It is clear from the figure that wear rates have decreased in borided samples. The hardness values of the samples after boriding have also increased; therefore, the wear rates have decreased. The main reason for this situation is shown as the emergence of CoB and Co$_2$B phase structures within the structure. Because these phases have rigid and strength structures, lowest wear rate is observed in the alloys subjected to boriding at 900°C temperature for 4.5 h. While the rate of wear is measured as $94.95 \times 10^{-5}$ mm$^3$/N m in the unborided alloy, this value is found to be $25.89 \times 10^{-5}$ mm$^3$/N m in the borided alloy. In the wear region of the borided 97% Co–3% Mg alloy samples, debris, delamination wear, surface grooves, and cracks on the surface can be observed (Figure 9a, c, e, and g). First, micro-cracks occur in the boride layers. These formations are occurred due to the load and friction applied to the sample surfaces. These broken boride layers increase the formation of abrasive wear in the wear zone of the sample. As a result, delamination eventuates. Chipise et al. [45] examined the slip and wear of WC–VC–Co alloys by adding Ru at different rates, and they obtained a decrease in the wear rates on the material surface as the additive rates increased. Therefore, our findings are in good agreement with the literature reports.

Figure 10 displays the abrasion surfaces and cross-sectional surface (CS) in samples of the wear mark acquired from the wear area by analyzing multiple profilometry surface line scans using the Nanovea ST-400 non-contact optical profiler. It is observable that the conditions such as abrasion and voids on the surfaces of the samples decreased due to the increase in the boriding temperature and time (Figure 10b, d, f, and h).

The results of EDX analysis performed after the wear test on 97% Co 900°C-1.5 h and 97% Co 900°C-4.5 h borided alloys are shown in Figures 11 and 12. As a conclusion of the linear analysis performed after the wear test, Mg and O elements are revealed beside the Co element. As a result of EDX analysis applied to the wear zone of the borided CM alloy, oxide and heat occur on the surface of the sample as a result of the ball rotating and rubbing on the sample during wear. Therefore, Co$_3$O$_7$ and Mg$_2$O$_3$ phases were formed in EDX analysis.
Figure 10: The SEM micrograph and CS of the worn out surfaces of the compositions; (a) 850°C-1.5 h, (b) 850°C-1.5 h CS, (c) 850°C-4.5 h, (d) 850°C-4.5 h CS, (e) 900°C-1.5 h, (f) 900°C-1.5 h CS, (g) 900°C-4.5 h, and (h) 900°C-4.5 h CS.
Figure 11: The EDX analysis obtained from 97% Co 900°C-1.5 h borided alloys.

Figure 12: The EDX analysis obtained from 97% Co 900°C-4.5 h borided alloys.
4 Conclusion

The following conclusions may be derived from the present study:

- Boride types formed on the surface of the CM alloys have a smooth and flat morphology. XRD results on borided alloys showed that boron layers formed on CM alloys contain CoB, Co2B, and Co phases.
- Depending on the chemical composition of the alloys, and the time and temperature of the boriding, the thickness of the boride layer formed on the surface of 97% Co–3% Mg alloys ranged from 51 to 138 μm.
- While the hardness of the borided layer formed as a result of boriding due to temperature and time depending on the CM alloys varied between 1,674 and 1,956 HV0.05. Vickers hardness value of the unborided CM alloys was 52 HV0.05.
- Surface roughness values of borided samples vary between 0.3–0.62 μm and their density between 7.32 and 7.57 g/cm³. The friction coefficient of values (between 0.54 and 0.7) for the boriding samples were lower than the coefficient of friction values (0.9) of the unborided alloys sample.
- The wear rate of the unborided sample was 94.95 × 10⁻⁵ mm³/N m; however, this value dropped to 25.89 × 10⁻⁵ mm³/N m as a result of the boriding process. In the wear region of the borided sample was observed debris, adhesion, abrasive, delamination wear, surface grooves, and cracks on the surface.

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