www.dergipark.gov.tr
ISSN:2148-3736
El-Cezerî Fen ve Mühendislik Dergisi
Cilt: 6, No: 1, 2019 (31-42)

El-Cezerî Journal of Science and Engineering
Vol: 6, No: 1, 2019 (31-42)

DOI : 10.31202/ecjse.450204

ECJSE

Research Paper / Araştırma Makalesi

Friction and Wear Properties of T6 Treatment And As-Plated Duplex NiP/NiB Coatings on Az91d Magnesium Alloy

Kübra UÇAR, Uğur ŞEN

Department of Metallurgical and Materials Engineering, Sakarya University, Sakarya, Turkey
kubra.ucar4@ogr.sakarya.edu.tr, ugursen@sakarya.edu.tr

Received/Geliş: 01.08.2018 **Accepted/Kabul:** 13.11.2018

Abstract: Electroless nickel coatings can be preferred in wear resistant applications like firearms with good lubricity properties. In this study, a widely-used magnesium alloy, AZ91D both as-cast and precipitation-hardened conditions were coated with nickel phosphorus/nickel boron duplex coatings by the electroless deposition method. Solution treatment (W) of the alloy was carried out at 415 °C for 22 h in carbon powder followed by water quenched at 25 °C. Aging treatment (T6) of the solution-treated samples was performed at 216 °C for 6 h. The microstructures, elemental distributions and phase analysis of the obtained coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD) analysis. According to the XRD analysis, the obtained coatings have an amorphous character and subsequent to this, a crystallization process to the sample is carried out at 350 °C. The friction and wear properties of the coating are studied by means of ball-on-disc experiments at room temperature under 10N applied loads at 0.1 m/s sliding speed using alumina balls as counterparts. The friction coefficient of the sample was compared with each other from friction coefficient-distance graphics. The wear rates were determined by measuring the depth of the track with an 3D-optical microscope (3D-OM). Characterization of the wear tracks was performed by SEM and EDS.

Key words : Electroless nickel coatings, Wear, AZ91D .

T6 Işlem Görmüş ve Döküm Az91d Magnezyum Alaşımı Üzerine Dublex Nip/Nib Kaplamaların Sürtünme ve Aşınma Özellikleri

Öz: Akımsız nikel kaplamalar iyi bir kayganlık özelliğine sahip, ateşli silahlar gibi aşınmaya dayanıklı uygulamalarda tercih edilebilir. Bu çalışmada yaygın olarak kullanılan AZ91D magnezyum alaşımı, hem döküm hem de çökelme şertleşmesi koşullarında, akımsız kaplama metodu ile dublex Ni-P/Ni-B kaplamalar ile kaplanmıştır. Alaşımın çözelti işlemi 415°C'de 22 saat boyunca grafit tozu içerisinde gerçekleştirildi, ardından 25°C suda soğutuldu. Çözelti işlemine alınmış numunelerin yaşlandırma işlemi (T6) 216°C'de 6 saat boyunca gerçekleştirildi. Elde edilen kaplamaların mikroyapıları, elementel dağılımları ve faz analizleri taramalı elektron mikroskobu (SEM), enerji dağılım spektrometresi (EDS) ve X-ışınları difraksiyon analizi (XRD) ile karakterize edildi. XRD analizine göre, elde edilen kaplamalar amorf karaktere sahiptir ve bunun ardından numuneye 350°C'de bir kristalizasyon işlemi gerçekleştirildi. Kaplamanın sürtünme ve aşınma özellikleri, ball-on-disc vasıtasıyla deneyler alümina topa karşılık 0,1 m/s kayma hızında, 10N yük altında oda sıcaklığında çalışıldı. Numunenin sürtünme katsayısı, sürtünme katsayısı-mesafe grafiklerinden birbirleriyle karşılaştırıldı. Aşınma oranları, 3D optik profilometre (3D-OM) ile izin derinliği ölçülerek tespit edildi. Aşınma izlerinin karakterizasyonu SEM ve EDS ile gerçekleştirilmiştir.

Anahtar kelimeler: Akımsız nikel kaplama,Aşınma,AZ91D

How to cite this article
Uçar K.,Şen U., "*Friction And Wear Properties Of T6 Treatment And As-Plated Duplex Nip/Nib Coatings On Az91d Magnesium Alloy*", El-Cezerî Journal of Science and Engineering, 2019, 6(1); 31-42.

Bu makaleye atıf yapmak için
Uçar K.,Şen U., "*T6 Işlem Görmüş Ve Döküm Az91d Magnezyum Alaşimi Üzerine Dublex Nip/Nib Kaplamalarin Sürtünme Ve Aşınma Özellikleri*", El-Cezerî Fen ve Mühendislik Dergisi 2019, 6(1); 31-42.

1. Introduction

Magnesium alloys have an important place in the defense industry and transportation sector due to their lightness and high specific strength properties (Strength / density). When unalloyed, magnesium alloys have low strength and toughness values, thus it is used by alloying. AZ91D is composed of three main phases according to Al distribution found in the structure of magnesium alloy, these are primary α phase, eutectic α phase (Al-rich), β phase which is chemical and heterogeneous depending on. β phase eutectic α is more cathodic than primary α phase. Several studies have shown that the accumulation of Ni-P coating is nucleated on the position of β phase and that eutectic-α and primary-α phase are dispersed in the coating process. The initial accumulation in the electroless plating bath is severely affected by the galvanic couple between β phase and α phase. Hence, the aging process results in the precipitation of β phase along the grain boundaries of the homogenized AZ91D magnesium alloy, and β phase acts as a physical barrier against the active cathode or corrosion. Clark reported an aging mechanism in the AZ91 series magnesium alloy, and found that both continuous and discontinuous β precipitates occurred [1]. For this, T6 treatment was deemed suitable before plating. The most difficult and critical part of the magnesium alloy is pre-treatment to obtain high anti-corrosion resistance, substrate surface adhesion performance, mechanical properties and high-performance coating. Therefore, the oxide layer should be removed before the electroless plating process. In general, there is a superior adhesion strength when electroless coatings are applied in comparison with the electroplating method which is due to the presence of a strong metal-metal bond during plating. Electroless Ni-P alloy coating on magnesium is an effective method to change the wear and corrosion resistance of substrate materials as it shows good corrosion resistance. The Ni alloy is cathodic to the magnesium alloy base and acts as a physical barrier against corrosion of the bottom layer. However, electroless Ni-P coatings have superior properties such as high hardness, high abrasion resistance, excellent solderability and good conductivity in comparison with the Ni-B coatings. Electroless Ni-B coatings are less porous compared to electrolytic coatings. Ni-B coatings are obtained by reduction of borohydride ions or amine-borane ions, the structure and properties vary depending on the amount of boron incorporated into the coating.

For any tribology-based application, the purpose of the coating is to reduce friction coefficient and improve abrasion resistance by imparting smoothness and hardness to the surface. Since boron is one of the most important amorphous elements, it is prepared to look for superior qualities in various alloys.

Vitry et al. thoroughly investigated the wear behaviours of extruded Ni-B coatings, but they have been extensively focused on Taber abrasion and scratching [2].

The procedure we have developed in this study is to obtain a smooth, well adherent and abrasion-resistant layer with electroless Ni-B process using uncoated T6 alloyed AZ91D and AZ91D cast alloy with coating. It has been shown that the findings improve the wear rate and durability life of the coating. Furthermore, the coating obtained on the AZ91D alloy base has a better abrasion resistance than the T6 treated uncoated alloy.

2. Experimental Methods

2.1 Sample preparation

AZ91D magnesium alloy was used in the substrate of 30x20x5 mm^3 dimensions. Before the pre-treatment, substrate was ground with metallographic operation up to by 1200 grid SiC emery paper and polished with 0.3 μm alumina**.** When magnesium contacts with air or water, oxide and hydroxide layer on the surface of the magnesium alloys form due to the fact that it is one of the most active metals, electrochemically. Therefore, in this study AZ91D Mg alloy was cleaned with acetone for 5 minutes, then followed by alkaline solution for 15 minutes. However, these cleaners are not enough to remove oxide and similar layers on the surface of the AZ91D Mg alloy. Hence, surfaces of samples were treated with 20 s HCl/H_3PO_4 and 40 s HF acids in second stages. Thus, AZ91D Mg alloy matrix corrosion can be prevented by this pre-treatment.

2.2 Bath Preparation and Operating Conditions

Ni-P was coated in the solution of the nickel sulfate 14 gr/L, sodium hypophosphite, 15 gr/L, sodium acetate 12 gr/L, ammonium bi fluoride 8 gr/L, HF 1,8 mL , thallium acetate 0,02 gr at the temperature of 65°C for 20 min. and then Ni-B coatings was realized on the pre-NiP coated samples in the solution of nickel chloride 20 gr/L, sodium borohydride 1,05 gr/L, ethylenediamine 13.5 mL , sodium hydroxide 100 gr/L, thallium acetate 0,11 gr/L at 90°C for 90 minutes at 400 rpm magnetic stirrer. In an alkaline bath, sodium borohydride is used as a reducing agent and nickel chloride is used as a nickel source to prepare a electroless Ni-B bath. Nickel source and sodium borohydride as well as the appropriate amount of coating binder ethylenediamine is included to the coating bath. Thallium acetate is used as the stabilizer. Reduction of sodium borohydride is much higher than that of sodium hypophosphite and dimethylamine borane. The pH value of the alkaline coating bath has been increased to 12, due to the easy dissolution of sodium borohydride easily in the acidic or neutral environment.

Table 1. Solution concentration and operation conditions of electroless coating Ni-P

Bath composition	
Nickel Sulfate	14 gr/L
Sodyum Hipofosfit	15 gr/L
Sodium Acetate	12 gr/L
HF	1,8 mL
Ammonium bifluoride	8 gr/L
Thallium acetate	0,02 gr
Temperature	65°C
pH	6-6,5

Therefore, pH value of electroless Ni-B coating bath was chosen as Zhang et.al. used thiourea as the stabilizer in Ni-P / Ni-B coating on AZ91D magnesium [3]. In the present study, thallium acetate was used in both baths and seen the same effect in the shorter time.

Table 2. Solution concentration and operation conditions of electroless coating Ni-B

Bath composition	
Nickel chloride	20 gr/L
Sodium borohydride	1,05 gr/L
Ethylenediamine	13,5mL
Sodium hydroxide	100 gr/L
Thallium acetate	0,11 gr/L
Operating conditions	
pH	13
Temperature	90°C

2.3 Coating Characterization

SEM was used to assess the surface microstructure of Ni–P/NiB duplex coatings. Wear tracks of coatings were performed by SEM and EDS. Phase analysis of samples performed at heat treatment 350 °C for 1 h. was characterized by XRD. A ball-on-disk method was used to determine the friction and wear characteristics of un-coated and Ni-P / Ni-B dublex coated surfaces. Applied load was 10 N and sliding distance was 250 m. Sliding speed, wear scar diameter and the rotational speed of the disc was fixed at 0.1 m/s. The experiments were performed at about 35% relative humidity and 25°C heat degree. After the wear test, the surfaces of the sample was cleaned in an ultrasonic agitator for approximately 8 minutes in acetone to remove abrasive particles on the surface.

In addition, wear volume realized on the worn sample was calculated from the wear track cross-section area determined by optical profilometer and sliding distance using by eq.1

$$V = lxA \tag{1}$$

where, l is the circumference of the wear track and A is the cross-sectional wear track area.

Table 2 Electroless Ni-B coating conditions of the wear test.

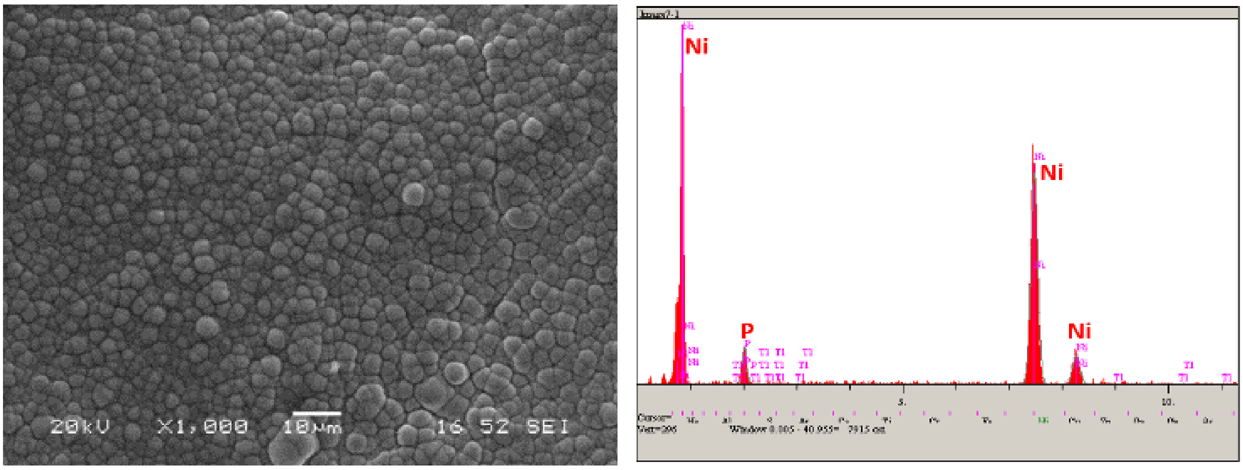
Parameter	Ball-on-disk test
Ball diameter (mm)	10.45
Moving sample	Sample
Applied force (N)	10
Sliding velocity (m/s)	0.1
Humidity	35
Motion	Unidirectional
Temperature	25
Test length (m)	250
Test Ball	Al_2O_3

Wear track was examined using by Jeol 6060 Lv scanning electron microscopy (SEM). Table 2 presents the parameters used in the wear test. 3D imaging of the wear track was performed using the Huvitz HR-SPLG4 profilometer.

3. Results and Discussion

3.1 Coating characteristics

The surface morphology of the Ni-P coating is shown in the Figure 1. The Ni-P coating is very compact and it has even been seen that there are no defects such as halls and cracks on the surface. As shown from the Figure 1, Ni-P coating on AZ91D magnesium alloy has been successfully carried out. There are significant boundaries in the nodules. As shown from the Figure 1 (b), coating layer includes Ni and P elements.



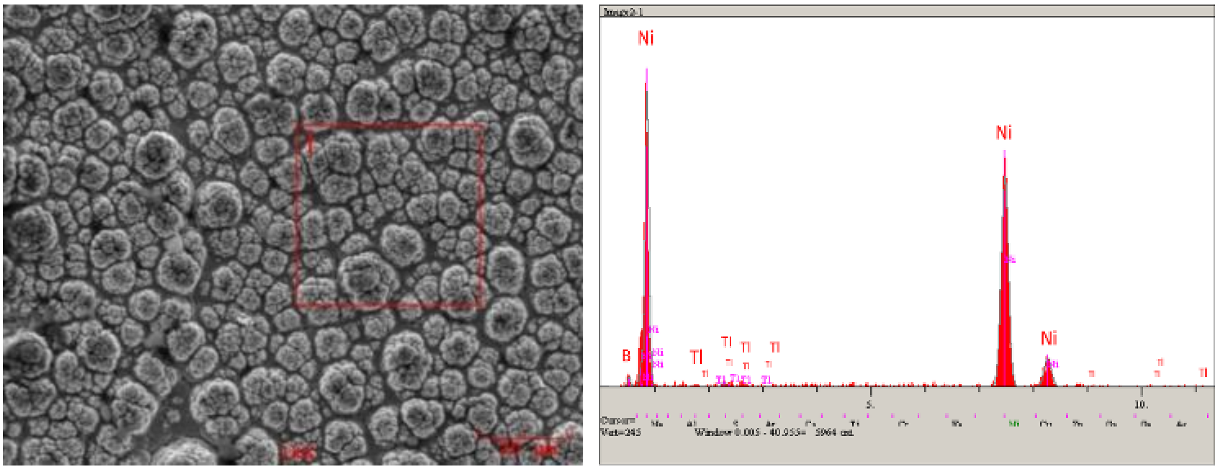
(a) (b)

Fig. 1 (a) SEM images and (b) EDS analysis of the electroless Ni–P deposition on AZ91D substrate

A typical 'nodular-like' structure or 'cauliflower' -like structure provides a natural slippery texture in scanning electron microscopy images of the electroless double layer Ni-P / Ni-B coatings as shown in Figure 2.

It exposes a properly coated surface that includes nodules whose dimensions ranging between a few microns. On the morphological surface of the duplex coating, the Ni-B coating dominates, but the Ni-P adheres very well to the bottom layer. As can be seen from the SEM-images, the double-layer coating seems to have less porosity and rough surface. Kanta et al. observed that after coating, the surface roughness of the electroless coating was significantly higher [4].

EDS analysis was performed to determine the chemical composition of the coatings. The electroless Ni-P / Ni-B coated sample includes Ni, Tl and B elements as shown in Figure 2 (b).



(a) (b)

Fig. 2. (a) SEM image and (b) EDS analysis of Ni-B coatings realized on pre-NiP coated AZ91D magnesium alloy

Cross-sectional SEM image of the Ni-P / Ni-B coating formed on the AZ91D Mg alloy was shown in Figure 3. The coating layer was compact, porosity-free and rough. The coating layer were well bonded on the AZ91D alloy. The coating layer average thickness was 29.3±4.2 µm.

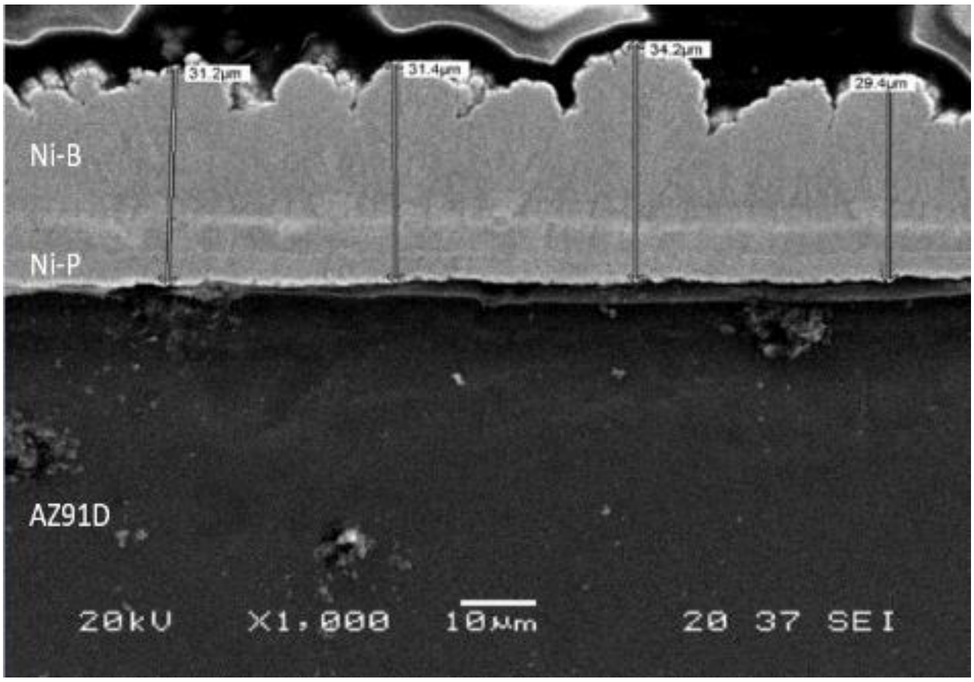


Fig. 3. The cross-sectional image of the dublex NiP/NiB coating.

The X-ray diffraction pattern of the electroless Ni-B coating shows a single broad peak indicating the amorphous nature of the coating as coat. Theoretically, an irregularity in the ordering of the atoms also manifests itself as a broad peak at the XRD.

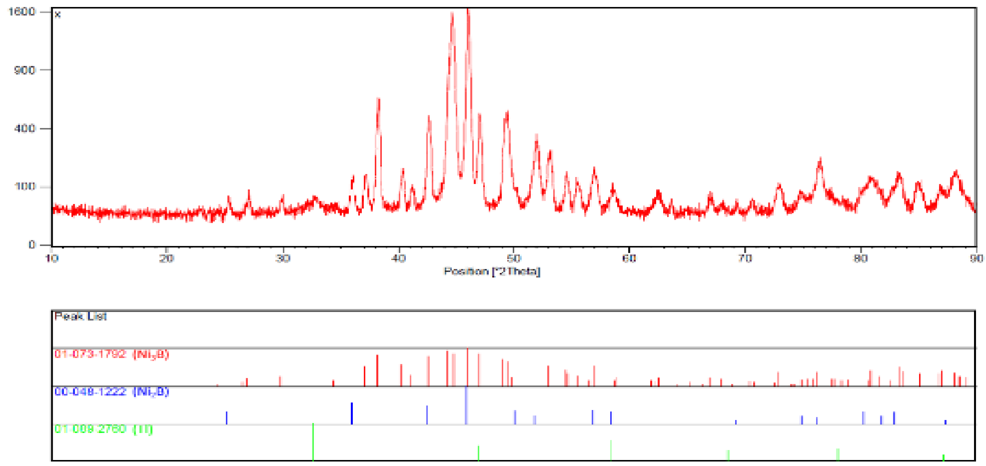


Figure 4. XRD analysis of electroless Ni–B coatings.

Post crystallization heat treatment caused to crystallization of the amorphous coating to be formed composite structure includes Ni matrix and Ni_3B precipitates.

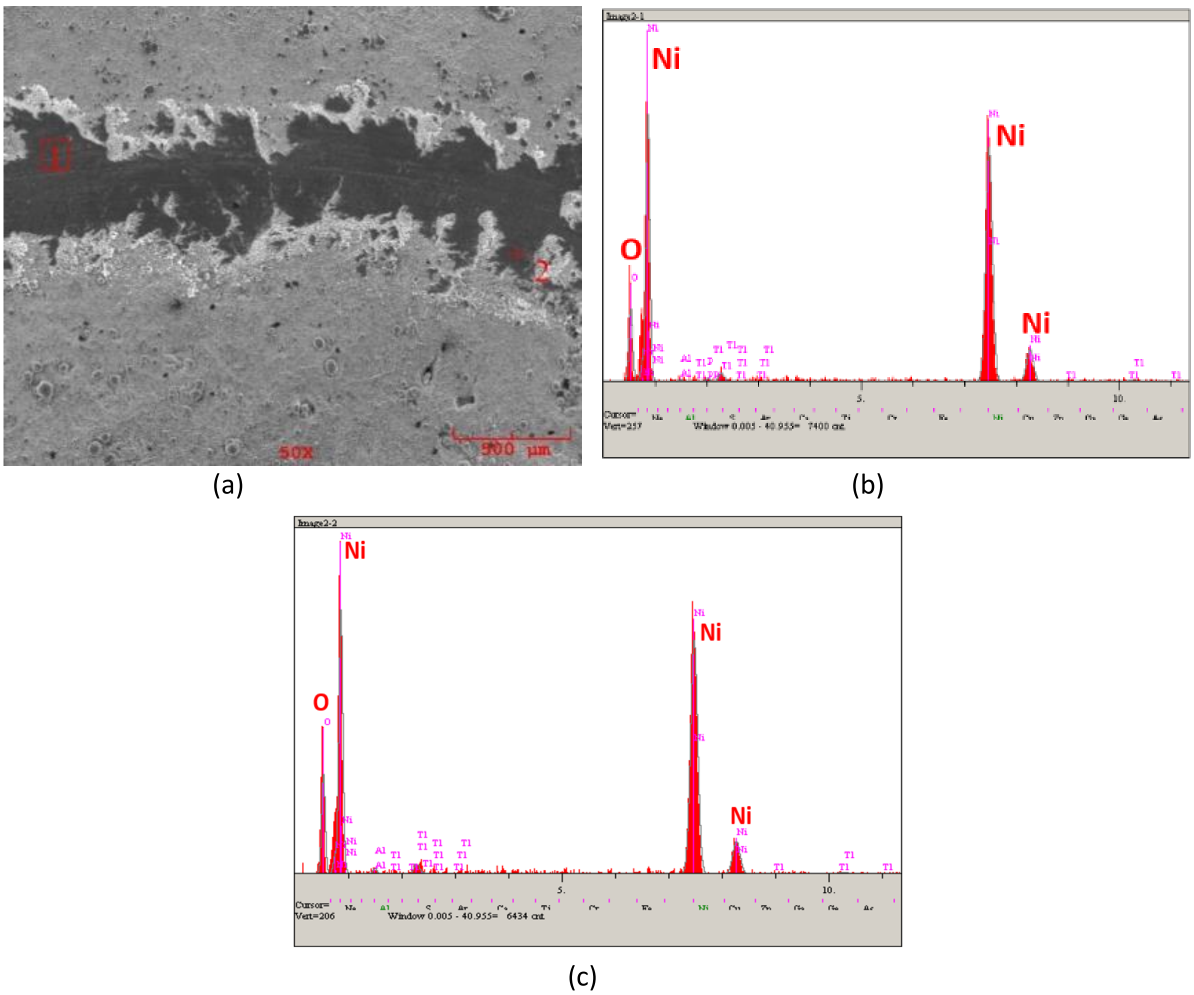


Fig. 5. (a) Scanning electron micrograph and (b-c) EDS analysis of the wear track of the NiP/NiB coating **(**Applied load: 10 N; Sliding distance: 250 m)

XRD patterns of electroless Ni-B coatings post-crystallization heat treated for 1 h in 350°C, confirms the formation of Ni_3B precipitate phase together with Ni matrix, see Figure 4.

3.2 Wear mechanism of the coatings

In the Fig. 5 (a), SEM image of the Ni-P/Ni-B coating showed that wear track showed a adhesive wear with micro-abrasive scratch. Wear mod was micro abrasive adhesive coating. As seen from the Figure 5 (b-d), EDS analysis of the worn surface include oxygen besides the Ni and B elements. Wear mod of the coting was oxidative adhesive and micro-abrasive.

No significant adhesion is observed on the counter alumina ball during the along the wear, as can be seen in Figure 6. During the wear test, at the initial period of the test, top surface of the coating layer was polished and rough surface was getting smooth layer on the wear track. The Ni-P/Ni-B coating with a smooth surface breaks into the rough top regions during wear test in the running in 50 m sliding distance.

Fig 6. Optical microscope surface of testing alumina ball after dry sliding

As defined in the EDS analysis, there are partially covered oxide particles in some areas on the wear surface of the duplex coating.

The presence of oxygen on the wear track is probably due to the oxidation of the Ni-B based coating during the wear test. The friction coefficient of the T6 heat treated AZ91D alloy and Ni-P/Ni-B dublex coatings realized on the T6 heat treated samples were measured under the dry sliding conditions. As shown from Figure 7 that T6 heat treated samples was getting steady-state behavior in the running in period of 10m. Whereas, Ni-P/Ni-B coated samples friction coefficient was getting increase slightly during the wear test. Friction behaviour of the coated samples increases sharply up to 20m sliding distance and then was getting increase slightly during the all wear test. Friction coefficient of T6 heat treated samples and the coated samples were getting increase up to 0.33µm and 0.57µm, respectively. E. Correa et.al was studied about the NiB electroless coatings' versus Al_2O_3 ball for 50m sliding distance [5]. As shown from Figure 7 in the present study, friction coefficient values were similar and increase in sliding distance caused to increase during the wear test. In addition, in the present study, wear test was applied for 250 m sliding distance and friction coefficient value increased during the wear test up to 0.57µm value.

It was seen from the Figures 8 and 9 that the optical 3D profiles and cross-sectional view of the wear tracks of the T6 heat treated AZ91D alloy and T6 heat treated and Ni-P/Ni-B dublex coated samples, respectively. Wear volume of the worn samples were calculated from the cross-sectional area of the worn samples wear tracks using the formula o f Eq. 1. As shown from the Figure 10 that the wear rates of the dublex coating was 97.74 % lower than that of the T6 heat treated AZ91D alloy. E. Correa et.al. study showed that the wear rate of the dublex NiP/Ni-B coatings was 98,67 % lower than that of the AZ91D alloy [5].

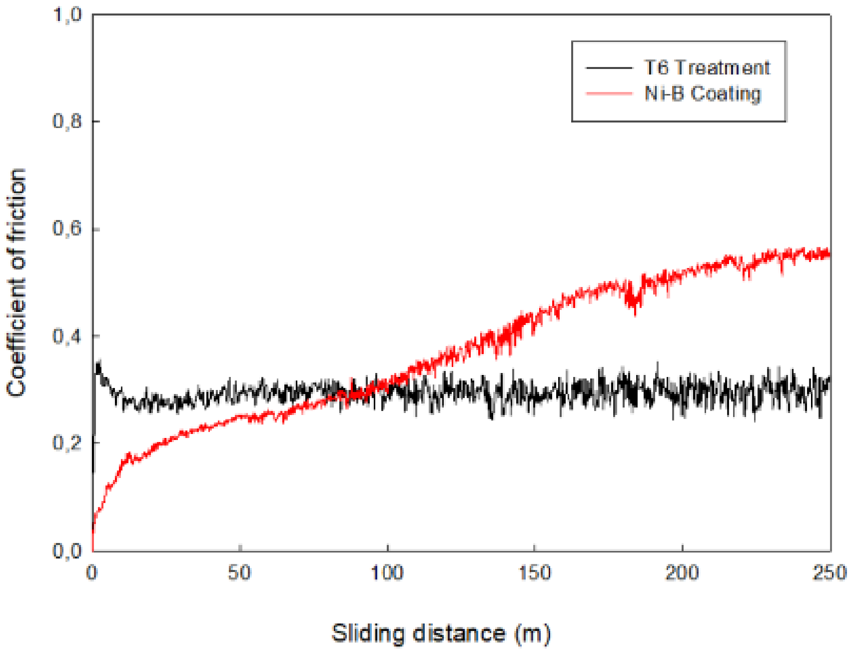


Fig. 7. Evolution of Coefficient of friction with sliding duration

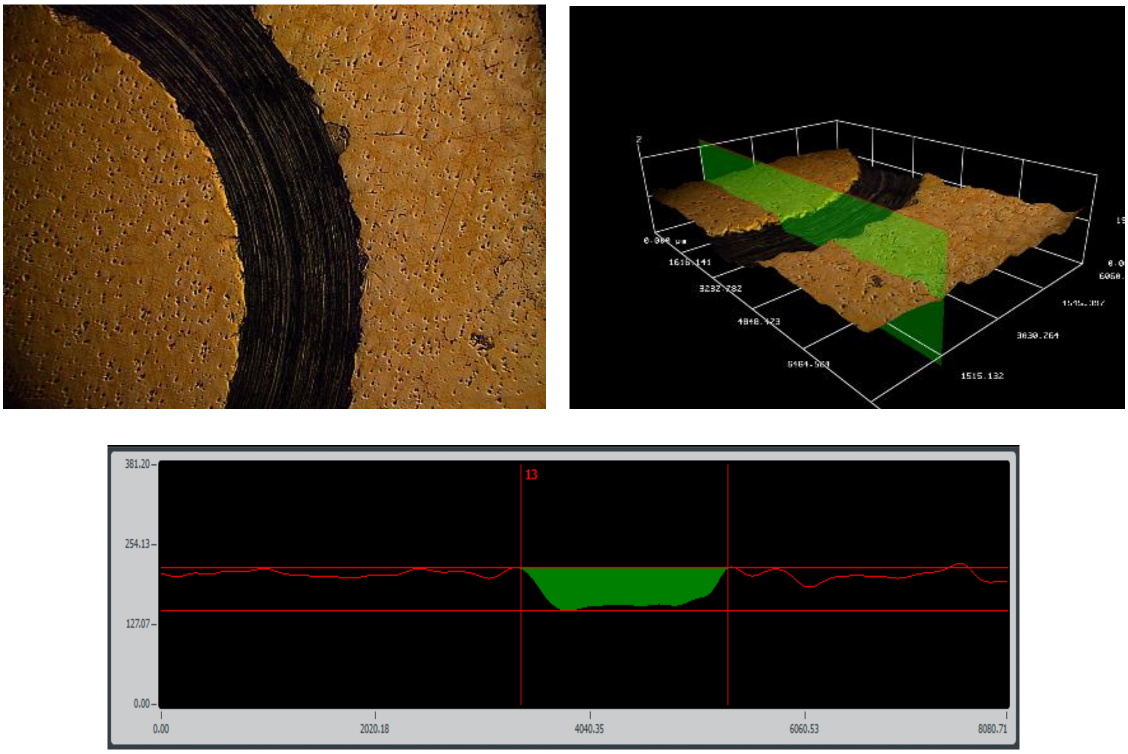


Fig 8. 3D optical profilometer image and crossectional area of the worn track of T6 heat treated AZ91D alloy

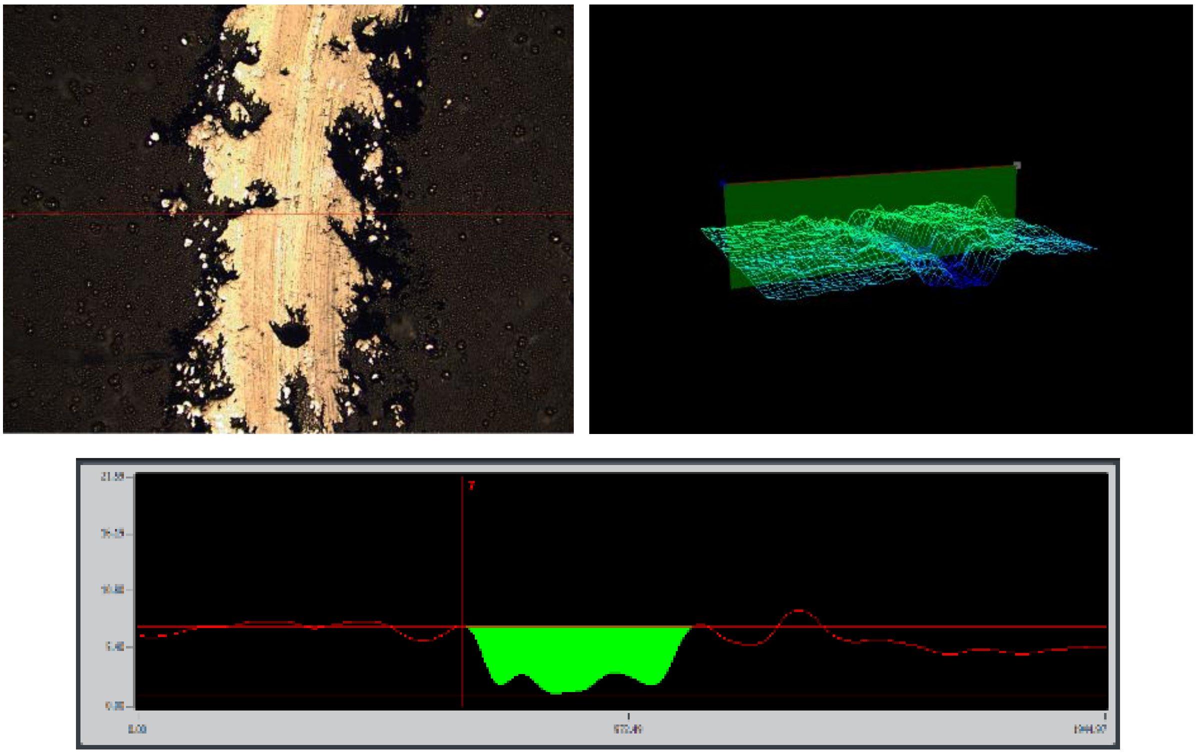


Fig 9. 3D optical profilometer image and crossectional area of the worn track of T6 heat treated and Ni-P/Ni-B dublex coatings of AZ91D alloy.

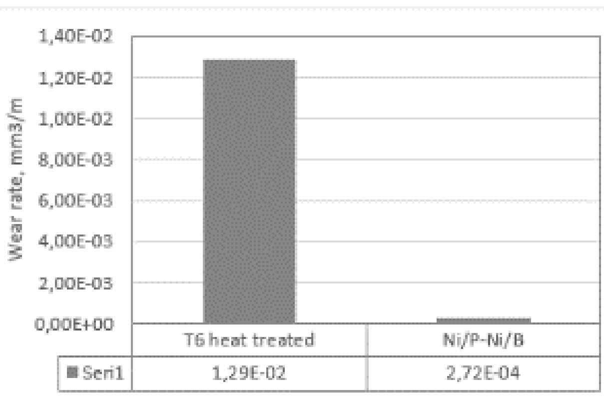


Fig 10. Wear rate values of surfaces uncoated and Ni-P / Ni-B coated.

4. Conclusions

It is observed that the Ni-P / Ni-B coating has a favourable as tribological effect on the T6 heat treated specimen. General results obtained without work;

1. The sample which is Ni-P/Ni-B coated exposed to the wear test, has been subjected to the certain load but no coating is completely removed from the surface.
2. Ni-P / Ni-B coating layer is located on the entire surface of the AZ91D magnesium alloy substrate, exhibiting a partially smooth, pore-free, nodular structure.
3. The presence of abrasion residues in the undercoating conditions, confirms the adhesive wear mechanism.
4. Duplex Ni-P / Ni-B coating with the lowest wear rate increases wear resistance of T6 heat treated AZ91D alloy.
5. The wear rate of the Ni-P / Ni-B duplex coatings is lower than that from the T6 heat treated sample and not observed significant changes in the friction coefficients.
6. As wear testing results show of the Ni-B coating is well adhered to the Ni-P layer coating and both of them exhibit coherent to each other.

References

[1] N.N. Aung, W. Zhou, 'Effect of heat treatment on corrosion and electrochemical behavior of AZ91D magnesium alloy' journal of Applied Electrochemistry, 2002, 32: 1397–1401.

[2] Fatemeh Madah, Ahmad Ali Amade, Changiz Dehghanian, 'Investigation on the phase transformation of electroless Ni -B coating after dry sliding against alumina ball' Journal of Alloys and Compounds, 2015, 15: 31412-2.

[3] E. Correa, A.A. Zuleta, L. Guerra, M.A. Gómez, J.G. Castaño, F. Echeverría, H. Liu, A. Baron-Wieche, T. Hashimoto, P. Skeldon, G.E. Thompson, Coating development during electroless Ni –B plating on magnesium and AZ91D alloy' Surface & Coatings Technology, 2013, 232: 784-794.

[4] Prasanta Sahoo, Suman Kalyan Das, 'Tribology of electroless nickel coatings – A review', Materials and Design, 2011, 32: 1760-1775.

[5] E. Correa, A.A. Zuleta, L. Guerra, M.A. Gómez, J.G. Castaño, F. Echeverrí, H. Liu, P. Skeldon, G.E. Thompson 'Tribological behavior of electroless Ni-B coatings on magnesium and az91d alloy', Wear, 2013, 305: 115-123.
[6] Z.C. Wang, F. Jia, L. Yu, Z.B. Qi, Y. Tang, G.-L. Song 'Direct electroless nickel boron plating on AZ91D magnesium alloy', Surface & Coatings Technology, 2012, 206: 3676-3685.
[7] Zhou-Cheng Wang, Lu Yu, Fei Jia, and Guang-Ling Song 'Effect of Additives and Heat Treatment on the Formation and Performance of Electroless Nickel-Boron Plating on AZ91D Mg Alloy', Journal of The Electrochemical Society, 2012, 159 (7): D406-D412.
[8] Fatemeh Madah, Changiz Dehghanian, Ahmad Ali Amadeh,'Investigations on the wear mechanisms of electroless Ni–B coating during dry sliding and endurance life of the worn surfaces' Surface&Coatings Technology, 2015, 282: 6-15.
[9] Zeng, Shiwei Yang, Wei Zhang, Yahuan Guo, Chuanwei Yan, 'Preparation and characterization of a double-layer coating on magnesium alloy AZ91D' Electrochemica Acta, 2010, 55: 3376–3383.
[10] J.E. Gray, B. Luan, 'Protective coatings on magnesium and its alloys a critical review', journal of Alloys and Compounds, 2002, 336: 88–113.
[11] Arkadeb Mukhopadhyay, Tapan Kumar Barman, Prasanta Sahoo, 'Tribological behavior of sodium borohydride reduced electroless nickel alloy coatings at room and elevated temperatures', Surface&Coatings Technology, 2017, 321: 464-476.
[12] A.-F. Kanta, M. Poelman V. Vitry, F. Delaunois, 'Nickel–boron electrochemical properties investigations' Journal of Alloys and Compounds, 2010, 505:151–156.
[13] C. Subramanian, K. Palaniradja,'Effect of Surfactant on the Electroless Ni-P/Ni-B Duplex Coatings on Aluminium 7075' International Journal of Metallurgical Engineering 2015,4(2): 25-32.
[14] K. Krishnaveni, T.S.N. Sankara Narayanan, S.K. Seshadri 'Electroless Ni–B coatings: preparation and evaluation of hardness and wear resistance', Surface & Coatings Technology, 2005, 190: 115–121.
[15] L. Bonin, V. Vitry 'Mechanical and wear characterization of electroless nickel mono and bilayers and high boron-mid phosphorus electroless nickel duplex coatings' Surface & Coatings Technology, 2016, 307: 957–962.
[16] Y. Y. Lv, Z. Liub, H. Liu, G.E. Thompson, H. Liu, 'Dry sliding wear behavior and structural characteristics of laser-annealed electroless Ni–P/Ni–Mo–P duplex coatings', Tribology International, 2016, 103: 343-351.
[17] W.X. Zhang, N. Huang, J.G. He, Z.H. Jiang, Q. Jiang, J.S. Lian, 'Electroless deposition of Ni–W–P coating on AZ91D magnesium alloy', Applied Surface Science, 2007, 253: 5116–5121.
[18] F. Masoumi, H. R. Ghasemi, A. A. Ziaei, D. Shahriar 'Tribological characterization of electroless Ni–10% P coatings at elevated test temperature under dry conditions' Int J Adv Manuf Technol, 2012 62:1063–1070.