Journal of Physical Chemistry and Functional Materials

Home Page of Journal: https://dergipark.org.tr/jphcfum

Microstructure and Wear Behavior of Cr2O3-40% TiO2 Coating on Magnesium Alloy via Plasma Spraying

Cihan Özel[a,*] and Abdulkadir Zirek[a]

[a]*Department of Mechanical Engineering, Faculty of Engineering, Firat University, 23119, Elazig, Turkey*
** Corresponding author: E-mail:* cozel@firat.edu.tr

ABSTRACT

In this study, the surface of the magnesium alloy was coated with Cr_2O_3-40% TiO_2 by plasma spray coating method. The surface coating process was carried out at two different current (580 and 500 A) and two different spray distances (110 and 130 mm), and the effects of these parameters on microstructure and mechanical properties were examined. Characterization of the coated surface layers was analyzed by optical microscope (OM), scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersed X-rays (EDS). Tribological properties of coatings were determined in disc-on-disc type wear test device at 3 different loads (2.5, 5 and 7.5 N) and 150 m sliding distance. Cr_2O_3, TiO_2 and TiO were detected in the coating layers of samples coated with Cr_2O_3-40% TiO_2. The hardness and wear resistance of the coatings are quite high compared to the magnesium alloy. Hardness and abrasion resistance decreased with decreasing current and increasing spray distance. The friction coefficient of the magnesium alloy is lower than the coated samples.

ARTICLE INFO

Keywords:
Surface coating;
Plasma spray;
Magnesium alloys;
Ceramics;
Wear; Friction

Received: 14-May-2020,
Accepted: 03-June-2020
ISSN: 2651-3080

1. Introduction

Interest in magnesium alloys is increasing day by day in industries such as automotive, aerospace and biomedical. This is due to the properties of magnesium alloys such as high specific strength, excellent castability, recyclability, lightness, biocompatibility, good machinability, good electrical and thermal conductivities. However, the low corrosion and abrasion resistance of magnesium alloys is a limiting factor in their use in the industry. Therefore, in order to improve the surface properties of magnesium alloys, studies with surface heat treatment and surface coating have gained speed in recent years [1-3]. The most effective method used to increase the corrosion and wear resistance of magnesium alloys is by coating the surface to prevent its interaction with the environment [4].

The surfaces of magnesium alloys are made resistant to wear with different spray coating methods such as high velocity oxy-fuel [5], plasma spray [6], cold spray [7] and flame spray [8]. Plasma spray method is frequently preferred in coating industry due to its advantages such as high spraying temperature, small heat effect on substrate, fast deposition rate and large variety of materials [9]. With the plasma spray method, material surfaces can be successfully coated with various materials such as ceramics, carbides, cermets, metals and intermetallics, due to high flame temperature [10].

Material surfaces are successfully modified with Al_2O_3, TiO_2, Cr_2O_3 etc. and their mixtures in different proportions. The wear resistance of ceramic coatings is quite high due to their high hardness [11-15]. Due to its high hardness, the wear resistance of Cr_2O_3 is higher compared to other ceramics. In addition, the friction, oxidation and corrosion resistance of Cr_2O_3 is good compared to other ceramics. The most important disadvantage of Cr_2O_3 is its low fracture toughness. Coatings made by adding TiO_2 to Cr_2O_3 have higher coating density. Thus, fracture toughness and wear resistance are improved [16]. Some previous researches on coating magnesium alloys by plasma spray method are given in Table 1.

Table 1. Literature research.

Processes and f examined properties	Thirumalaikumarasamy et et al. [17]	Gao et al. [18]	Kubatik et al. [19]	Kubatík et al. [20]	Ge et al. [21]	Xu et al. [22]	Zou et al. [23]	Çelik [24]
Mg alloy	AZ31	AZ91	AZ91	AZ91	AZ31	MB26	MB26	AZ31
Coating powder	Al_2O_3	Al_2O_3	Al and AlCr6Fe2 (Mn, Si, Ti)	NiAl10 and NiAl40	Al–Si + nano Si_3N_4	ZrC–ZrB_2/Ni	TiC–TiB_2	Al_2O_3–13 ağ.% TiO_2 and Al_2O_3–40 ağ. % TiO_2
Plasma spray coating	+	+	+	+	+	+	+	+
Current change	+	-	-	-	-	-	-	-
Spray distance change	+	-	+	-	-	-	-	-
Powder feed rate change	+	-	-	-	-	-	-	-
Microstructure investigation	+	+	+	+	+	+	+	+
Microhardness investigation	+	+	-	-	+	+	+	+
Wear investigation	-	+	-	-	-	+	+	+
Friction investigation	-	-	-	-	-	-	-	-

In this study, the surface of AZ91D magnesium alloy was coated with Cr_2O_3-40% TiO_2 powder via plasma spray coating method. The microstructure of coating layers was examined by using OM, SEM, XRD and EDS. The hardness, wear and friction behavior of samples were investigated. Finally, worn surfaces were examined by SEM.

2. Material and method

One of the magnesium alloy commercially AZ91D was used as substrate and its chemical composition is given in Table 2. The substrate to be used in the surface coating process are 20 mm in diameter and 50 mm in length. The substrates were first cleaned with ethanol in the ultrasonic bath for 15 minutes and then rinsed in the ultrasonic bath with distilled water for 15 minutes. Moisture on the samples was removed with hot air and surfaces are sandblasted with 5 bar pressure of Al_2O_3 sand. Thus, the surfaces are roughened for better adhesion. The surfaces are coated with GTV brand -45 and +20 μm size Cr_2O_3-40% TiO_2 coating powder using the plasma spray method in the parameters given in Table 3. The surface roughness values of the coating surfaces were determined using the Mitutoyo SJ-201 profilometer. Measurements were carried out from 10 different points of the coating surface and the surface roughness values were calculated by calculating the average. Coated samples were divided into 10 mm pieces for use in microstructural analysis and wear tests by wire electro discharge machining. The pieces were cleaned with ethanol in the ultrasonic bath for 15 minutes, then rinsed with pure water in the ultrasonic bath and the moisture on it was removed with hot air. Samples required for microstructure investigations were polished metallographically after being bakelite. The coating layers of the polished samples were examined with Nikon Eclipse NA200 brand OM. SEM images of the phases forming the structure were obtained using the ZEISS EVO-MA10 brand SEM device. The chemical composition of the compounds forming the coated surfaces was measured using the Bruker brand EDS detector connected to the ZEISS EVO-MA10 SEM device. The phases formed on the coated surfaces was determined in the BRUKER AXS D8 ADVANCE brand XRD device with copper α-ray tube using Cu-Kα radiation at 1.5406 Å wavelength at 2θ = 20 - 80 degrees, 40 kV and 40 mA. The hardness of the coating layers was found by taking the average of the values measured from 5 different points. Each measurement was made by applying 100 g mass for 10 seconds. Abrasion tests were carried out on disc-on-disc type wear test device at room temperature. AISI 52100 bearing steel with a diameter of 40 mm was used as abrasive and the wear test was carried out at 150 m sliding distance, 100 mm/s sliding speed and 2.5, 5, 7.5 N normal force, respectively. Wear losses were measured with a precision scale with a precision of 10-5 (g). Each test was repeated three times and averaged. The friction coefficients were calculated during the experiment by measuring the friction forces with the load cell and recording them with the data logger. Finally, wear surfaces were examined by SEM.

Table 2. The chemical composition of AZ91D magnesium alloy (wt%).

Mg	**Cu**	**Si**	**Al**	**Zn**	**Mn**	**Other**
88-90.50	0.025 max.	0.050 max.	8.5-9.5	0.45-0.9	0.17-0.4	Rest.

Table 3. Plasma spray coating parameters.

Sample	**Current (A)**	**Spray distance (mm)**	**Shielding gas flow rate (l/min)**	**Powder feed rate (g/min)**	**Plasma gas flow (l/min)**	**Voltage (V)**
Sample1	580	110	38 (Ar)	30	13 (H)	150
Sample2	580	130				
Sample3	500	110				
Sample4	500	130				

The hardness of the coating layers was found by taking the average of the values measured from 5 different points. Each measurement was made by applying 100 g mass for 10 seconds. Abrasion tests were carried out on disc-on-disc type wear test device at room temperature. AISI 52100 bearing steel with a diameter of 40 mm was used as abrasive and the wear test was carried out at 150 m sliding distance, 100 mm/s sliding speed and 2.5, 5, 7.5 N normal force, respectively. Wear losses were measured with a precision scale with a precision of 10-5 (g). Each test was repeated three times and averaged. The friction coefficients were calculated during the experiment by measuring the friction forces with the load cell and recording them with the data logger. Finally, wear surfaces were examined by SEM.

2. Results and discussion

2.1. Microstructure, surface roughness and hardness

As seen in Figure 1, the magnesium alloy surface was successfully coated with Cr_2O_3-40% TiO_2 by plasma spraying. No visible cracks and porosities were found on the surfaces. The surface roughness and hardness values of the coating layers are given in Table 4. The surface roughness of the coated samples is higher than the surface roughness value (0.298 µm) of AZ91D. The high surface roughness is by the nature of the plasma spray coating method [24]. The surface roughness values of the coatings increase with decreasing energy input and increasing spray distance. The reason for this may be that the non-molten particles increase with decreasing energy input and increasing spray distance. As the current increases, the plasma temperature rises, so more particles will melt and accumulate on the surface to be coated. Also, increasing the spray distance causes some small particles to pass from the plasma region to neighboring orbits and absorb some heat. This is thought to lead to an increase in the number of non-melting particles [25]. When the average hardness values of the coating layers are examined, the hardness ranges between 656-730 $HV_{0.1}$ and is considerably higher than the hardness value of the substrate (70 $HV_{0.1}$). Hardness values increased with increasing current and decreased with increasing spray distance.

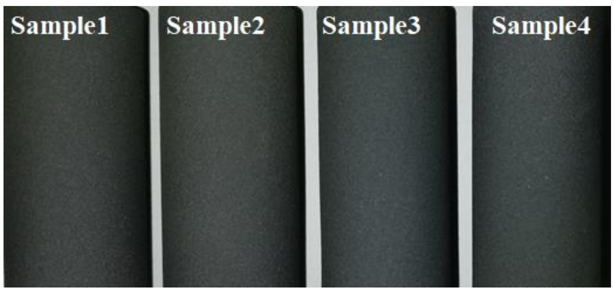


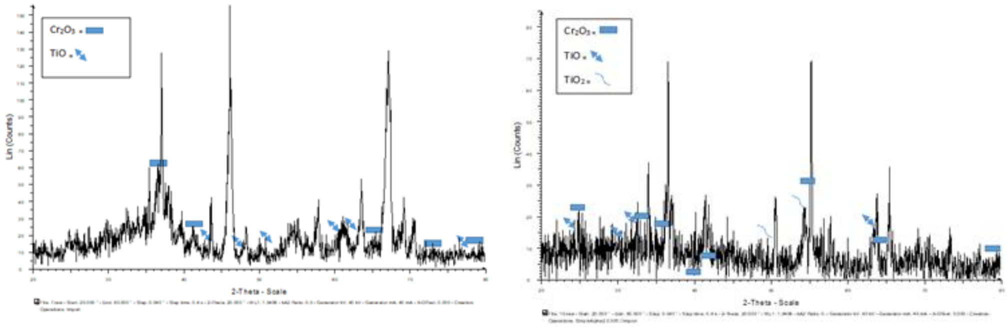
Figure 1. Macro images of coated samples.

Figure 2 shows the results of XRD analysis of samples (Sample1 and Sample4). Coating layers consist of Cr_2O_3, TiO_2 and TiO. This shows that coating powders have been successfully deposited on the surfaces.

Figure 3 shows OM images of Cr_2O_3-40% TiO_2 coated samples by plasma spray method. As can be seen, the coating powders are melted and deposited on the substrate surface and metallurgically bonded to the surface of the AZ91D. It can be seen from the OM images that the coating layers are generally composed of some micro pores, oxides and lamellar structures which are generally formed in plasma spray coatings. Plasma spray coatings mainly consist of flat splashes and when they hit the surface, these splashes accumulate on each other in the molten coating layers and form the lamellar structure [25].

Table 4. The surface roughness and hardness values of the coating layers**.**

Sample	Current (A)	Sprey distance (mm)	Surface roughness (R_a=µm)	Hardness ($HV_{0.1}$)
Sample1	580	110	5.306	730
Sample2	580	130	5.500	701
Sample3	500	110	5.626	689
Sample4	500	130	5.720	656



a) b)

Figure 2. XRD analysis results of samples a) Sample1 and b) Sample4.

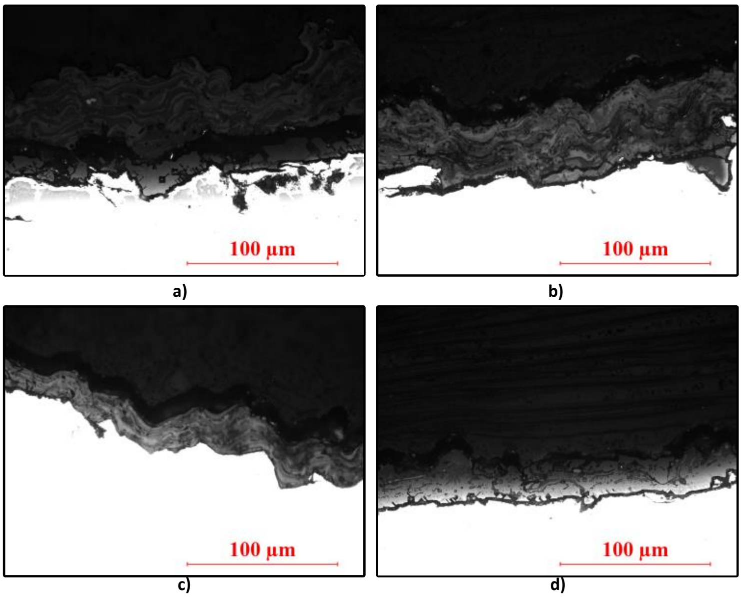


Figure 3. OM images of samples cross-sections a) Sample1, b) Sample2, c) Sample3 and d) Sample4.

The SEM images taken from the surfaces of the samples coated with Cr_2O_3-40% TiO_2 via the plasma spray coating method is seen in Figure 4. As can be seen, the coating surfaces have a rough structure formed by the overlapping of the molten particles. In addition, micro pores are seen in places on the surfaces. According to the results of EDS analysis taken from the surfaces of the samples, Sample1 consists of (wt%) 18.61Cr-47.80Ti-34.04O, Sample2 consists of (wt%) 20.81Cr-44.68Ti-34.51O, Sample3 consists of (wt%) 23.67Cr-26.06Ti-36.72O and Sample4 consists of (wt%) 37.39Cr-32.44Ti-30.17O. These results show that the coating powders melt together and successfully accumulate on the surface.

2.2. Wear and friction

In Figure 5, the wear loss (mg) of the coated samples and the substrate material with different loads at a sliding distance of 150 m are shown. Wear loss of coated samples are lower than AZ91D at all load values. The reason for this may be that the hardness values of the coated samples are much higher than the substrate material. Also hardness has a positive effect on wear resistance [26]. As the hardness value of the coatings decreases, their wear resistance decreases. Again, as the load increases, the wear loss of the substrate and coated samples have increased. In coated samples, the wear loss increases with the decrease of the current value and the increase of the spray distance. The reason for this may be the decrease in hardness by changing the coating densities [25]. Figure 6 shows the friction coefficients of samples and AZ91D according to normal load. The friction coefficient (μ) of AZ91D is lower than the coated samples at all force values and is 0.278 at 2.5 N load, 0.464 at 5 N load and 0.507 at 7.5 N load. This situation is thought to be due to less surface roughness and to be more homogeneous in its structure. Friction coefficient values of AZ91D and coated samples increased with increasing load. This is thought to be due to the fact that the particles breaking off from the material surfaces with the increase of load and therefore the contact area is reduced. Again, μ values of coated samples increase with decreasing current and increasing spray distance.

Worn surface SEM images of samples and AZ91D at high load (7.5 N) are seen in Figure 7. As can be seen, a significant amount of particle loss has occurred from the surface of the AZ91D. In addition, deep grooves have formed on the wear surfaces substrate (Figure 6a). The wear of the coated samples generally occurred as a rupture of particles from the surface and the particles that were broken off from the surface generally were plastered to the surface.

3. Conclusions

The surface of the magnesium alloy was successfully modified with Cr_2O_3-40% TiO_2 by plasma spray method. Coating layers consist of Cr_2O_3, TiO_2 and TiO. The highest surface roughness value was measured as 5.306 μm in the sample coated with low heat input and high spray distance. The hardness and wear resistance of the coatings are quite high compared to AZ91D. The highest hardness and wear resistance values were obtained in coating with high heat input and low spray distance. The hardness and wear resistance of the coated samples decrease with decreasing heat input and increasing spray distance. The wear resistance of the coated samples at all normal load values is higher than the AZ91D. The friction coefficient of the AZ91D is lower than the coated samples at all load values.

Acknowledgements

The authors thank the Firat University Research Fund (FUBAP-MF.18.13) for their financial contribution to this research.

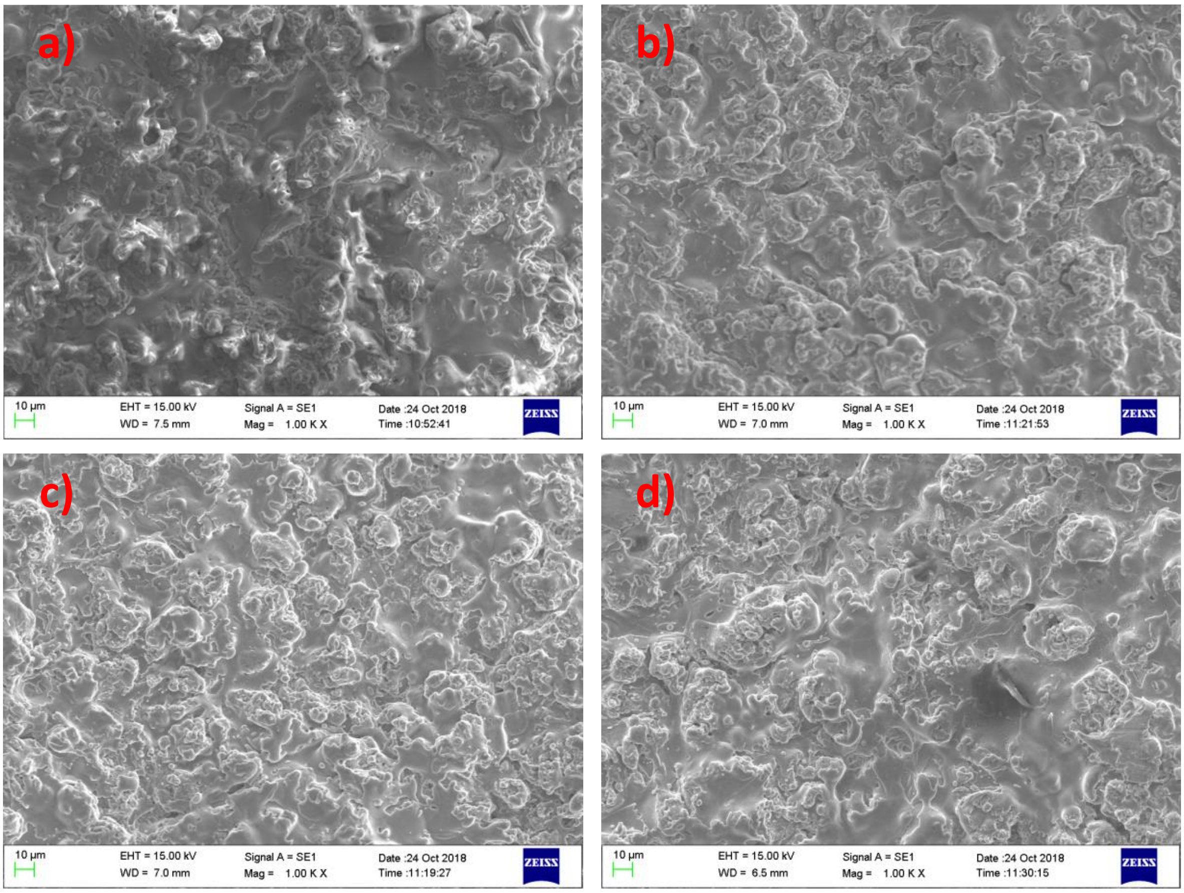


Figure 4. SEM images of coting surfaces a) Sample1, b) Sample2, c) Sample3 and d) Sample4.

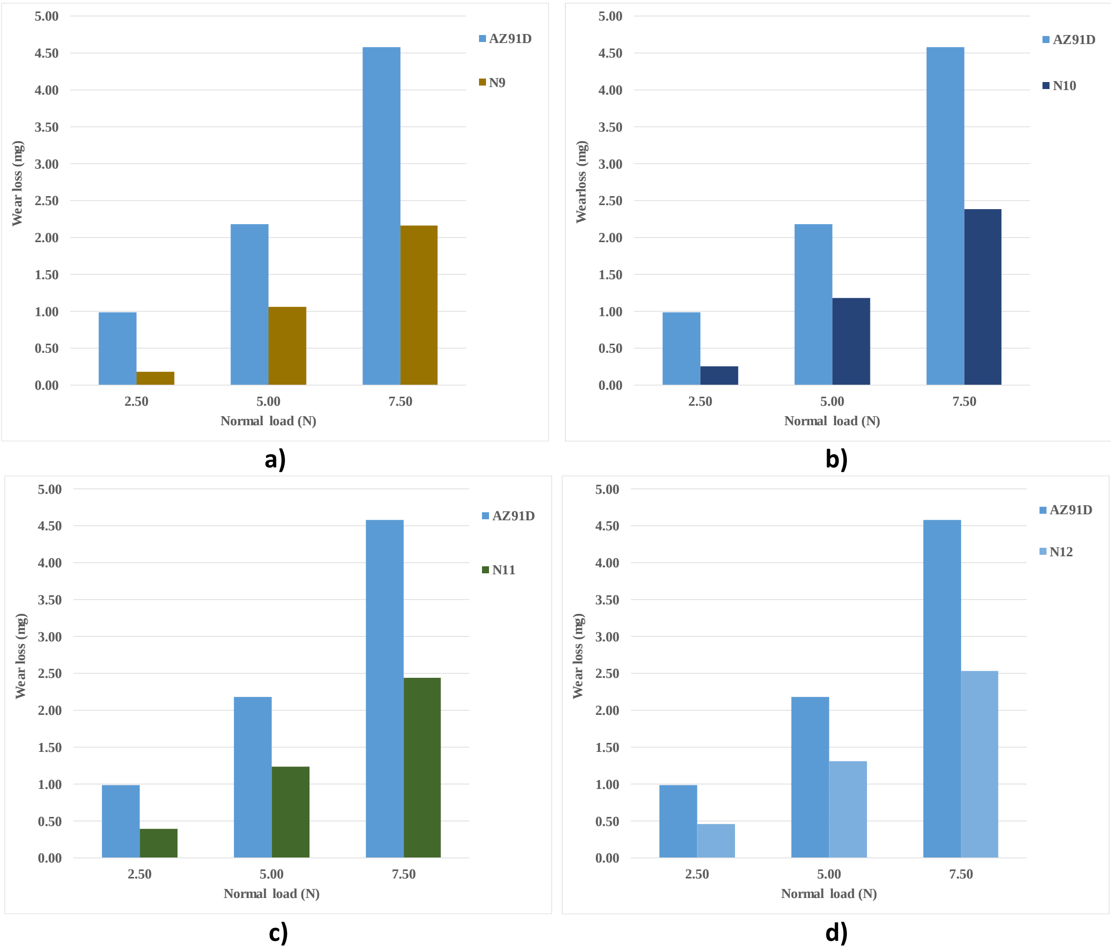


Figure 5. Wear loss of samples and AZ91D according to load a) Sample1, b) Sample2, c) Sample3 and d) Sample4.

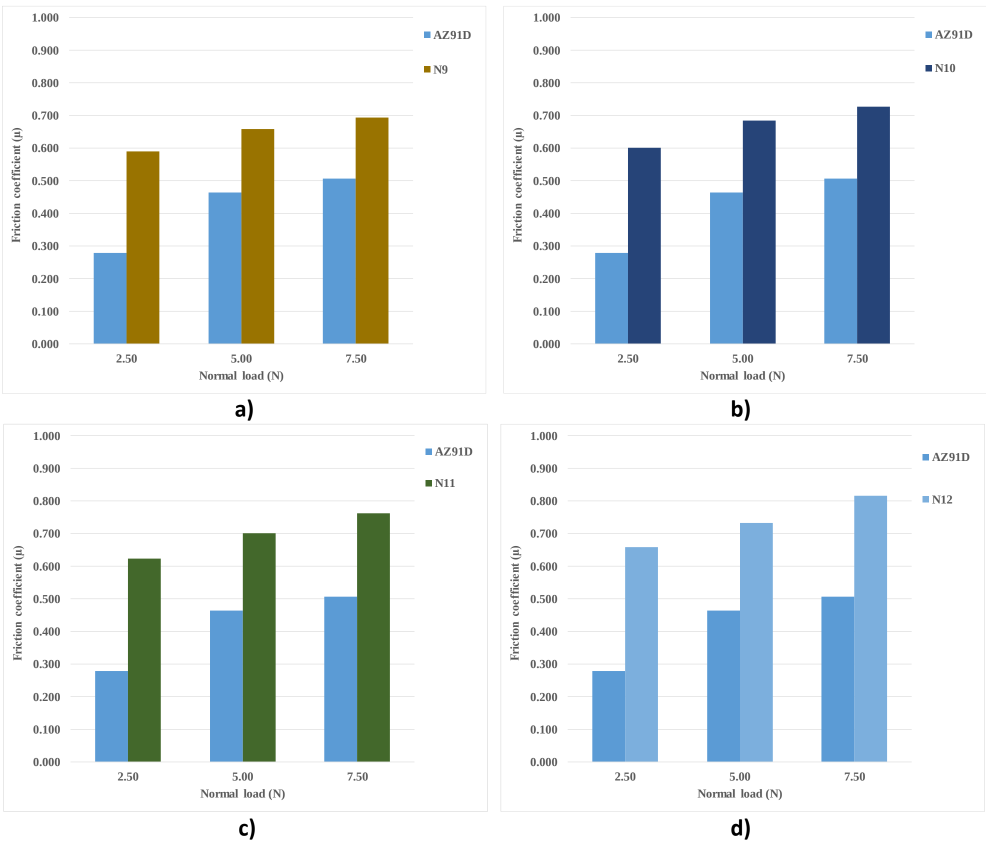


Figure 6. Friction coefficient of samples and AZ91D according to load a) Sample1, b) Sample2, c) Sample3 and d) Sample4.

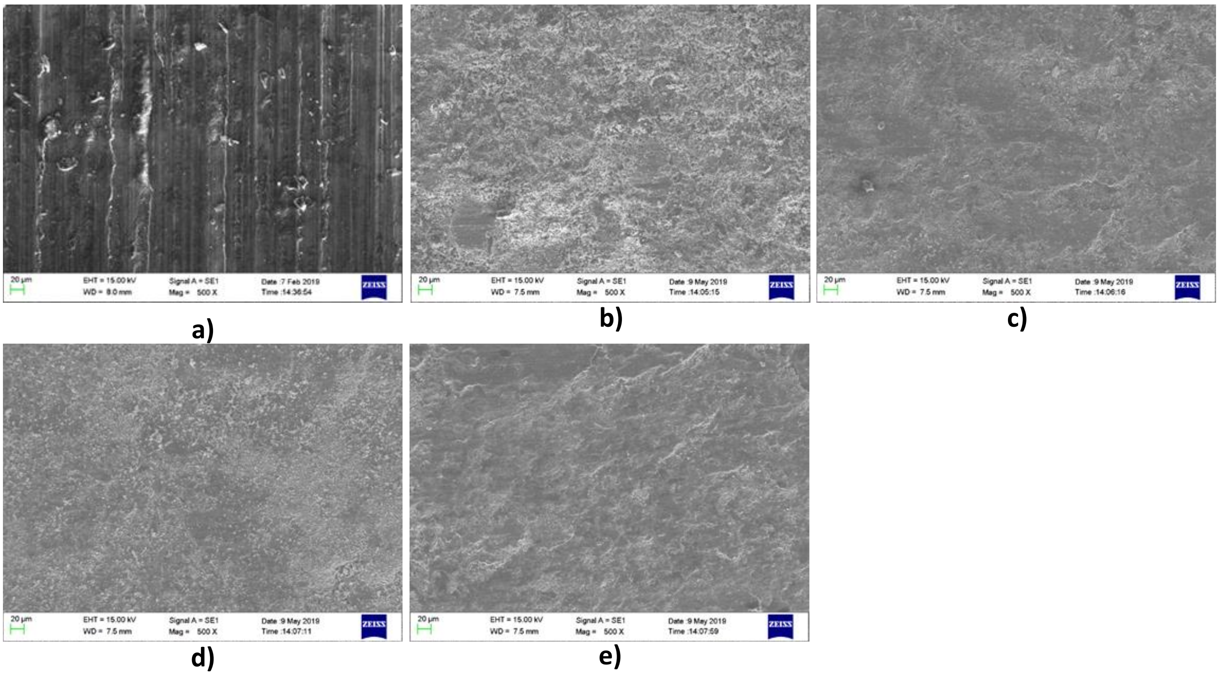


Figure 7. Worn surface SEM images of a) AZ91D, b) Sample1, c) Sample2, d) Sample3 and e) Sample4

REFERENCES

[1] Muhaffel, F., Cimenoglu, H. (2019). Development of corrosion and wear resistant micro-arc oxidation coating on a magnesium alloy. *Surface and Coatings Technology*, 357: 822-832,

[2] Atapour, M., Blawert, C., Zheludkevich, M. (2019). The wear characteristics of CeO2 containing nanocomposite coating made by aluminate-based PEO on AM 50 magnesium alloy. *Surface and Coatings Technology*, 357: 626-637,

[3] Carrillo, D. F., Santa, A. C., Valencia-Escobar, A., Zapata, A., Echeverría, F., Gómez, M. A., Zuleta, A. A., Castaño, J. G. (2019). Tribological behavior of electroless Ni–P/Ni–P–TiO 2 coatings obtained on AZ91D magnesium alloy by a chromium-free process. *The International Journal of Advanced Manufacturing Technology*, 105 (1-4): 1745-1756,

[4] Chen, J., Ma, B., Feng, S., Dai, Y., Liu, G., Song, H., Jia, L. (2019). Preparation and application of 420 martensitic stainless steel wear resistant coating on magnesium alloy by cold spraying. *Surface Engineering*, 35 (4): 351-359,

[5] López, A., Torres, B., Taltavull, C., Rams, J. (2013). Influence of high velocity oxygen-fuel spraying parameters on the wear resistance of Al–SiC composite coatings deposited on ZE41A magnesium alloy. *Materials & Design*, 43: 144-152,

[6] Shen, J., Zou, B., Dong, S., Cai, X., Cao, X. (2019). Fabrication and characterization of TiB2-TiC-Co wear-resistant coatings on AZ91D magnesium alloy. *Surface and Coatings Technology*, 364: 358-368,

[7] Chen, J., Ma, B., Liu, G., Song, H., Wu, J., Cui, L., Zheng, Z. (2017). Wear and corrosion properties of 316L-SiC composite coating deposited by cold spray on magnesium alloy. *Journal of Thermal Spray Technology*, 26 (6): 1381-1392,

[8] Rodrigo, P., Campo, M., Torres, B., Escalera, M., Otero, E., Rams, J. (2009). Microstructure and wear resistance of Al–SiC composites coatings on ZE41 magnesium alloy. *Applied Surface Science*, 255 (22): 9174-9181,

[9] He, L., Tan, Y., Wang, X., Xu, T., Hong, X. (2014). Microstructure and wear properties of Al2O3-CeO2/Ni-base alloy composite coatings on aluminum alloys by plasma spray. *Applied Surface Science*, 314: 760-767,

[10] Goel, S., Björklund, S., Curry, N., Wiklund, U., Joshi, S. V. (2017). Axial suspension plasma spraying of Al2O3 coatings for superior tribological properties. *Surface and Coatings Technology*, 315: 80-87,

[11] Güney, B. r., Mutlu, I. (2019). TRIBOLOGICAL PROPERTIES OF BRAKE DISCS COATED WITH Cr2O3–40% TiO2 BY PLASMA SPRAYING. *Surface Review and Letters*, 26 (10): 1950075,

[12] Güney, B., Mutlu, I. (2019). Wear and corrosion resistance of Cr2O3%-40% TiO2 coating on gray cast-iron by plasma spray technique. *Materials Research Express*, 6 (9): 096577,

[13] Singh, V. P., Sil, A., Jayaganthan, R. (2011). Tribological behavior of plasma sprayed Cr2O3–3% TiO2 coatings. *Wear*, 272 (1): 149-158,

[14] Babu, P. S., Sen, D., Jyothirmayi, A., Krishna, L. R., Rao, D. S. (2018). Influence of microstructure on the wear and corrosion behavior of detonation sprayed Cr2O3-Al2O3 and plasma sprayed Cr2O3 coatings. *Ceramics International*, 44 (2): 2351-2357,

[15] Deng, W., Li, S., Hou, G., Liu, X., Zhao, X., An, Y., Zhou, H., Chen, J. (2017). Comparative study on wear behavior of plasma sprayed Al2O3 coatings sliding against different counterparts. *Ceramics International*, 43 (9): 6976-6986,

[16] Bagde, P., Sapate, S., Khatirkar, R., Vashishtha, N., Tailor, S. (2018). Friction and wear behaviour of plasma sprayed Cr2O3-TiO2 coating. *Materials Research Express*, 5 (2): 026410,

[17] Thirumalaikumarasamy, D., Kamalamoorthy, K. S., Visvalingam, V. B. (2015). Effect of experimental parameters on the micro hardness of plasma sprayed

alumina coatings on AZ31B magnesium alloy. *Journal of Magnesium and Alloys*, 3 (3): 237-246,

[18] Gao, Y., Jie, M., Liu, Y. (2017). Mechanical properties of Al2O3 ceramic coatings prepared by plasma spraying on magnesium alloy. *Surface and Coatings Technology*, 315: 214-219,

[19] Kubatík, T., Pala, Z., Neufuss, K., Vilémová, M., Mušálek, R., Stoulil, J., Slepička, P., Chráska, T. (2015). Metallurgical bond between magnesium AZ91 alloy and aluminium plasma sprayed coatings. *Surface and Coatings Technology*, 282: 163-170,

[20] Kubatík, T., Lukáč, F., Stoulil, J., Ctibor, P., Průša, F., Stehlíková, K. (2017). Preparation and properties of plasma sprayed NiAl10 and NiAl40 coatings on AZ91 substrate. *Surface and Coatings Technology*, 319: 145-154,

[21] Ge, Y., Wang, W., Wang, X., Cui, Z., Xu, B. (2013). Study on laser surface remelting of plasma-sprayed Al–Si/1 wt% nano-Si3N4 coating on AZ31B magnesium alloy. *Applied Surface Science*, 273: 122-127,

[22] Xu, J., Zou, B., Zhao, S., Hui, Y., Huang, W., Zhou, X., Wang, Y., Cai, X., Cao, X. (2014). Fabrication and properties of ZrC–ZrB2/Ni cermet coatings on a magnesium alloy by atmospheric plasma spraying of SHS powders. *Ceramics International*, 40 (10): 15537-15544,

[23] Zou, B., Tao, S., Huang, W., Khan, Z. S., Fan, X., Gu, L., Wang, Y., Xu, J., Cai, X., Ma, H. (2013). Synthesis and characterization of in situ TiC–TiB2 composite coatings by reactive plasma spraying on a magnesium alloy. *Applied Surface Science*, 264: 879-885,

[24] Çelik, İ. (2016). Structure and surface properties of Al2O3–TiO2 ceramic coated AZ31 magnesium alloy. *Ceramics International*, 42 (12): 13659-13663,

[25] Kar, S., Bandyopadhyay, P. P., Paul, S. (2018). Effect of arc–current and spray distance on elastic modulus and fracture toughness of plasma-sprayed chromium oxide coatings. *Friction*, 6 (4): 387-394,

[26] Sun, L., Pan, J., Lin, C. (2003). Wear behavior of TiC–MoSi2 composites. *Materials Letters*, 57 (7): 1239-1243,