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The wear characteristics of CeO$_2$ containing nanocomposite coating made by aluminate-based PEO on AM 50 magnesium alloy

M. Atapour$^{a1}$, C. Blawert$^b$, M.L. Zheludkevich$^{b,c}$

$^a$ Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

$^b$ MagIC – Magnesium Innovation Centre, Institute of Materials Research, Helmholtz Zentrum Geesthacht, Max-Plank-Str. 1, 21502 Geesthacht, Germany

$^c$ Faculty of Engineering, University of Kiel, Kaiserstrasse 2, 24143 Kiel, Germany

Abstract

This study examined the influence of CeO$_2$ nanoparticles on the wear characteristics of aluminate-based PEO coatings formed on the AM50 magnesium alloy, which was developed for the automotive industry. Sliding wear assessments were conducted on a ball-on-disk tribometer at 2N, 5N and 10N loads (against an AISI 52100 steel ball). It was found that the wear characteristics were greatly affected by the addition of CeO$_2$ nanoparticles, especially under intermediate and high loads. The coatings with and without CeO$_2$ remained intact during the sliding test at 2N. Under an intermediate load of 5 N, the coating treated in the absence of CeO$_2$ failed, while the one made in the presence of CeO$_2$ offered superior wear resistance without any signs of wear failure. Under the 10 N load, the CeO$_2$-free coating was completely removed and the substrate emerged, which was mainly due to a combined adhesive–abrasive wear damage mechanism; in contrast, the CeO$_2$-containing coating (PEO-CeO$_2$) offered much superior wear resistance to the Mg alloy, which was consistent with the friction coefficient data. SEM-EDS analysis of the worn surface of the steel balls also indicated that the transfer of the coating fragments to the ball surface was more intensive for the nanoparticle-free coating, as

$^1$ Corresponding author. Tel: +983113915735, Fax: +98 311 3912752
E-mail address: m.atapour@cc.iut.ac.ir (M. Atapour)
compared to that observed for the PEO-CeO$_2$ coating. Also, the appearance of some deep scoring in the worn surface of the balls could be considered as a result of the three-body abrasive wear. The superior wear resistance of the CeO$_2$ embedded nanocomposite coating could be mainly attributed to its lower porosity, lower roughness, and higher hardness.

**Keywords:** Plasma electrolytic oxidation; Wear; Nanocomposite; Mg alloy; CeO$_2$; Friction coefficient

**1- Introduction**

Magnesium alloys have attracted much attention in automotive, aerospace and biomedical applications due to their high specific strength, excellent castability, good machinability, recyclability, and biocompatibility [1]. However, poor wear resistance and low corrosion resistance are two major obstacles hindering the wide usage of Mg alloys for structural applications. In recent years, considerable effort has been made to improve the performance of magnesium alloys using surface treatments and coatings [2]. A prominent approach is the plasma electrolytic oxidation (PEO) process, which is emerging as a green surface treatment due to its environmental friendliness. PEO, which is evolved from the anodizing process, is a promising candidate to improve the wear and corrosion resistance. As compared to the anodizing process,
PEO is carried out at high voltages, giving rise to the generation of short-lived micro-discharges [3]. This process is accompanied by the increased pressure and temperature at the location of discharges, and a stable ceramic coating is formed due to the activation of chemical, electrochemical and plasma reactions [4]. The properties of the resulting coatings are influenced by the substrate, electrolyte, treatment time, and current regime (AC, DC or bipolar) [5]. Among these factors, the electrolyte exerts a strong effect on the coating properties [6].

With a particular focus on the effect of the PEO coatings on Mg alloys, this study developed three main electrolyte classes including silicates, phosphates and aluminates to form the proper phases for different applications. Many investigations have been previously carried out to determine the relationship between the structure and properties of the PEO coatings on Mg alloys fabricated in these electrolytes.
Recently, various investigations have been carried out to improve the composition and optimization of the microstructure of the PEO coatings, aiming to promote industrial applications. The addition of particles to the electrolytes is considered as a new strategy to obtain new functionalities for PEO coatings. It has been reported that the size, concentration, melting point and the zeta potential of the particles are the main factors affecting the coating properties [7]. Recent advances in PEO coatings with particles have been overviewed by Lu et al. [6], concluding that the introduction of particles could be an important approach to improve the coatings properties.

The effects of the tribological properties of PEO coatings on the magnesium alloys have been the subject of several studies [2, 8], revealing that the PEO coatings are not capable of offering long-term wear resistance. However, the incorporation of various particles has been used to enhance the wear performance of PEO coatings applied on the Mg alloys. For instance, Yang et al.
[9] reported that the addition of SiC nanoparticles to the PEO coatings on the AZ91D magnesium alloy resulted in the higher hardness, which could be attributed to a remarkable enhancement in wear resistance. In another attempt, Zhang et al. [10] demonstrated that the incorporation of Al₂O₃ nanoparticles into PEO coatings which are on AZ31 alloy could significantly improve the wear resistance. They explained that the higher hardness and the denser microstructure associated with composite coatings were the main factors enhancing the wear performance. AZ31 magnesium alloy was coated with PEO coatings containing SiC nanoparticles by Vatan et al. [11], indicating that SiC-reinforced coatings exhibited a lower wear rate in comparison to those without SiC due to the rolling effect of SiC during sliding. More recently, Mingo et al. [4] fabricated AZ91/SiC composites by applying the PEO method. The results indicated that the introduction of SiC particles to the electrolyte deteriorated the wear resistance. The negative effect of the reinforcement was attributed to the relatively large particles used in their investigation.
and the activation of the third-body wear mechanism due to particles removal.

Recently, rare earth compounds have received considerable attention for the surface modification of Mg alloys due to their special physical and chemical characteristics as well as their environmentally friendly nature [5]. Fabrication of composite coatings containing rare earth oxides is mostly carried out with the aim of improving corrosion resistance and mechanical properties. Ceria, CeO$_2$, is one of the most important rare earth oxides incorporated into PEO coatings which are on different substrates [5, 12, 13]. A considerable enhancement in the corrosion resistance was reported after PEO treatment in the silicate electrolytes containing CeO$_2$ particles for AZ31 [13] and AM50 [5] magnesium alloys. The incorporation of CeO$_2$ was found to reduce the transmission pathways for corrosive ions such as Cl$^-$. Since the introduction of CeO$_2$ particles can effectively alter the microstructure of PEO coatings, the wear characteristics can also
be expected to change. Nevertheless, it is useful to investigate the wear performance of PEO coatings with CeO$_2$ on the Mg alloy substrates. However, the effect of the tribological characteristics of PEO coatings on Mg alloys fabricated in the electrolytes containing CeO$_2$ have not been studied in detail yet.

The aim of this study was, therefore, to develop an aluminate-based PEO coating with CeO$_2$ nanoparticles on the AM50 magnesium alloy in order to conduct a systematic assessment and to understand the effects of CeO$_2$ incorporation on the tribological performance of coatings. The wear mechanisms were discussed based on the microstructural changes resulting from the presence of CeO$_2$ nanoparticles. This work can provide an opportunity to produce coatings that can offer superior wear protection to Mg alloys.

2- Experimental

2.1. Material
An AM50 Mg alloy (4.74 wt% Al, 0.383 wt% Mn, 0.063 wt% Si, 0.065 wt% Zn, 0.002 wt% Fe, 0.002 wt% Cu and Mg balance) was used in this investigation and machined to produce the 25 × 25 × 4 mm substrates. Before PEO processing, the specimens were progressively ground with emery papers to 1200 grit and degreased with acetone, rinsed with distilled water, and then dried.

2.2. PEO processing

The PEO electrolyte was prepared using NaAlO$_2$ (12 g/l), Na$_3$PO$_4$ (8 g/l) and KOH (1 g/l) dissolved in distilled water. To study the role of nanoparticles, the specimens were coated in electrolytes with and without CeO$_2$ (5 g/L) nanoparticles (size < 5 nm, 99.95 % purity, Sigma-Aldrich). The XRD spectrum of as-received CeO$_2$ nanoparticles is presented in Fig. 1. PEO treatment was accomplished by applying a pulsed DC power source at a constant current density of 65 mA/cm$^2$ for the treatment time of 10
min. The pulse ratio was $t_{\text{on}}:t_{\text{off}} = 2 \text{ ms} : 18 \text{ ms}$. The specimens and a stainless steel tube were applied as the anode and cathode, respectively. The details of the electrolytes used for the PEO processing are presented in Table 1. To provide a uniform dispersion of nanoparticles, a magnetic stirrer and a bubbling generator were applied. The temperature was held at 20 ± 2 °C by applying a cooling system. The conductivity and pH of the electrolytes were recorded using a Mettler Toledo Inlab 730 probe and a Metrohm 691 pH meter. Based on the coating electrolytes, two names including PEO and PEO-CeO$_2$ were used for the coatings made in the absence and presence of CeO$_2$, respectively.

2.2. Characterization

The surface and cross section morphology of the coatings were assessed using a scanning electron microscope (Tescan Vega3) equipped with an energy dispersive spectrometer (EDS). Before
performing the SEM analysis, the coated specimens were embedded into resin, ground successively with 800, 1200 and 2500 grit emery papers, and then polished using the diamond paste (1 μm). X-ray diffraction technique (GIXRD, D8 Advanced Bruker AXS with the Cu Ka wavelength of 1.54056A) was applied to identify the phases present in the coatings.

In order to obtain the hardness of coatings, nano-indentation experiments were carried out on four different locations of coatings cross section. Before hardness examinations, the samples were cut, mounted and mechanically polished. Nano-indentation tests were performed using a diamond berkovich indenter. The speed of indenter during test was 1.5 μm min⁻¹ at 30 mN maximum load. Also, the rates of loading and unloading were controlled to be 60 mN min⁻¹.

2.3. Wear tests
The friction and wear behavior of the coatings were evaluated using a ball on disc tribotester (TRIBOtechnic company - France), which was operating at the ambient conditions (25 ± 2 °C and 30% r.H.) with an AISI 52100 steel ball of 6 mm diameter as the static sliding counterpart.

The wear tests were implemented at three loads of 2N, 5N and 10N, with the oscillating amplitude of 10 mm and the sliding velocity of 5 mm/s for 60 minutes. These parameters were selected on the basis of the previous works of the members of our group [7, 8, 14]. The wear tracks and the worn ball surfaces were studied using SEM and EDS. All tests were repeated three times to verify their reproducibility.

2.4. Corrosion tests

The corrosion behavior of the coatings in 0.5 wt% NaCl solution was examined using a computer controlled potentiostat system (Gamry interface 1000) at room temperature. A three-electrode cell consisting of a coated specimen (as working electrode with an
exposure area of 0.5 cm²), counter electrode (a platinum mesh wire) and reference electrode (saturated Ag/AgCl) was used. Potentiodynamic polarization tests were carried out at a potential scanning rate of 0.5 mV/s started from −250 mV below the open circuit potential (OCP). The corrosion parameters were extracted by Tafel extrapolation method. Also, surface morphologies of the coated specimens after potentiodynamic polarization tests were examined using optical microscopy.

3. Results and discussion

3.1. Voltage-time characteristics

The voltage-time responses of the coatings formed in the presence and absence of CeO₂ nanoparticles were recorded and presented in Fig. 2. As seen, the voltage-time response curves indicate an almost constant potential (around 400 V) after a rapid rise in the initial stages. Very similar behavior was observed for both coatings.
3.2. Microstructure

Fig. 3 presents the SEM micrographs of PEO coatings made in the presence and absence of CeO$_2$ particles. A porous morphology was formed for both coatings due to the generation of discharge channels and plasma bubbles implosion during the PEO treatment. Clear differences were observed in the pore size and coating roughness of PEO and PEO-CeO$_2$ specimens. PEO-CeO$_2$ coating revealed the mean surface roughness ($R_a$) of 0.91 ± 0.02 μm, while the coating without CeO$_2$ was relatively rough with the $R_a$ value of 1.4 ± 0.1 μm. The addition of CeO$_2$ nanoparticles reduced the porosity and roughness of coating, confirming the results of the previous studies [12, 15]. The pores inside PEO-CeO$_2$ coating were partially filled by nanoparticles. However, contrary to our finding, M. Mohedano et al. [5] reported that the roughness of the coatings was increased for the specimen with CeO$_2$ micro-particles. This can be explained based
on the relatively larger size (size < 5 μm) of the reinforcement particles used in that work. It can be concluded that the size of particles is the main factor controlling the roughness of the coatings. It seems that CeO₂ nanoparticles were entered into the discharge channels during PEO as a result of the forces which originated from electrical field and mechanical stirring. Di et al. [15] reported that the fused CeO₂ particles obstructed the discharge channels, consequently reducing the number of pores.

The effect of the particle size on the roughness of the PEO coatings was also reported by others. Lu et al. [7] reported that under the same condition, the roughness of the PEO coating with nano-sized SiO₂ particles (12 nm) decreased compared with the coating containing micro-sized particles (1-5 μm) on magnesium alloy. In another attempt, three different sizes of Si₃N₄ particles were in-situ incorporated into alkaline- based coatings on AM50 [16]. It was found that the microstructure of the PEO coatings was not affected by Si₃N₄ addition with different sizes due to inert
incorporation of particles. It was also reported that the incorporation of some nanoparticles such as CNT [17] and SiC nanoparticles [9] decreased the roughness of PEO coatings.

According to the EDS results of the top surface of coatings (Table 2), the presence of O, Na, Mg, Al and P was confirmed for both coatings. The detection of cerium in the case of PEO-CeO$_2$ coating showed that CeO$_2$ nanoparticles had been successfully introduced into the coating, because the electrolyte was the only source for Ce.

The addition of CeO$_2$ nanoparticles did not reveal a pronounced effect on the average coating thickness, as evidenced in Fig. 4. The average coating thicknesses were 14 ± 3 μm and 11 ± 4 μm for the PEO and PEO-CeO$_2$ specimens, respectively. Meanwhile, both coatings exhibited a porous outer layer and a compact inner one, as illustrated in Fig. 4. The presence of O, Na, Mg, Al and P was confirmed for both coatings based on the EDS results of the top surface of the coatings (Table. 2). Furthermore, the detection
of cerium on the surface of PEO-CeO$_2$ coating indicated that CeO$_2$ nanoparticles had been successfully embedded into the coating.

In order to determine the distribution of nanoparticles in the coating, a cross-section elemental map of the PEO-CeO$_2$ specimen was obtained. As shown in Fig. 5, a uniform distribution of Ce was recorded over the whole cross-section of PEO-CeO$_2$ coating. A relatively even distribution of nanoparticles has also been observed by others [7, 18]. Based on the findings of Lim et al. [13], CeO$_2$ particles migrated toward the anode due to their negative zeta potential; then they were deposited on the surface. A similar incorporation mechanism was reported for ZrO$_2$ nanoparticles [19]. Apart from the zeta potential, the particle size and their melting temperature are other important factors influencing the incorporation of particles [6]. Owing to the pore size distribution of the coating, it was expected that the CeO$_2$ nanoparticles could be deposited into the coating via discharge
channels. The high temperature and pressure associated with spark discharges facilitated the fusion of the coating material, which was coincident with the entry of nanoparticles.

Further, it was expected that the melting of particles would not be a prevailing phenomenon during PEO because the melting temperature of CeO2 (2750 °C [5]) was higher than that of the PEO process temperature (1843–2370 °C) [20]. However, according to the binary phase diagram of the MgO-CeO2 system [21], the formation of a mixture of MgO-CeO2 phases could decrease the melting temperature.

For a comparative purpose, the EDS mapping analysis was employed for elemental distributions of O, Mg, Al and P on the cross section of coating made without CeO2. As can be seen in Fig. 6, a relatively uniform distribution of elements was observed in most coating regions. By comparing Fig. 6 with Fig. 5, a similar distribution of phosphorous was displayed in the coatings with
and without CeO2. It can be deduced that the addition of CeO2 nanoparticles did not influence the distribution of phosphorous.

X-ray diffraction patterns of the coated specimens are illustrated in Fig. 7. The XRD results revealed that both coatings were composed predominantly of MgAl$_2$O$_4$. Also, the diffraction peaks of Mg were detected in the coatings. The presence of Mg peaks in the diffraction patterns of the coatings could be due to the lower thickness of the coatings, as compared to the X-ray theoretical depth, or the easy penetration of the X-ray through the porosity networks created [22] in the coatings. The formation of MgAl$_2$O$_4$ has been reported to be due to the reactions between Al$_2$O$_3$ and MgO during the high temperature sparking [23].

Additionally, the peaks of CeO$_2$ were identified in the XRD pattern of PEO-CeO$_2$ coating, which is in agreement with the SEM results. It confirmed the successful incorporation of CeO$_2$ nanoparticles in the PEO-CeO$_2$ coating.
3.3. Wear performance

The wear behavior of the coatings was assessed by sliding against an AISI 52100 steel ball. The coefficient of friction (COF) of coatings versus distance was recorded for different loads of 2N, 5N and 10N, as illustrated in Fig. 8. As can be seen, both coatings revealed the same curve shapes for the loads of 2N and 5N, where COF was raised considerably in the first 10m of testing; then, it reached a steady state condition. The steady state values of COF recorded for both coatings are summarized in Table. 3. Based on the previous works [1], the increase in the abrasive component of friction is responsible of an increase of COF in the first steps.

In the wear examinations at 10N, a distinct difference was observed between the COF curves of the coatings fabricated with and without particles. The COF of the specimen without CeO$_2$ particles revealed large fluctuations after about 20 minutes of sliding; this was followed by a noticeable drop to around 0.35,
which was the COF of the untreated specimen. The observation of fluctuations and a sudden drop in the COF of the PEO coating with no CeO$_2$ particles could be correlated to the failure and the lower load bearing capacity of this coating. As depicted in Fig. 8a, the specimen produced without CeO$_2$ addition revealed the lowest COF of 0.35 (approximately equal to the COF of the base metal), indicating the complete removal of the layer. The appearance of severe oscillation in the friction coefficient confirmed that the Mg alloy substrate underwent adhesive wear and stick–slip phenomena. In contrast, PEO-CeO$_2$ coating decreased the dynamic COF fluctuations.

Probably, filling the pores with the wear debris during the test and therefore, increasing the contact area between the wear couples could be responsible for the rise of COF at the higher loads [24]. Surface appearance of the worn surfaces depicted in Fig. 9 demonstrated that the coating without CeO$_2$ suffered more severe wear, as compared to the coating containing CeO$_2$, revealing an
increase in the wear depth with load. As can be seen, the coating incorporated with CeO₂ remained intact during the wear tests for all loads.

In order to examine the wear quantitative, the wear resistance and the average wear rate of the coatings were calculated for different loads, as reported in Fig. 10. The wear rates of the coatings containing CeO₂ (PEO-CeO₂) were lower than those for the coatings with no CeO₂ at all loads. A more pronounced difference between the wear rates was registered for the 10N load. It demonstrated that the existence of reinforcing CeO₂ nanoparticles could significantly improve the wear resistance of PEO coatings.

Fig. 11 reveals the worn tracks of PEO and PEO-CeO₂ coatings at the higher magnification. As can be seen, the extent of damage was increased with load for both coatings. While both coatings remained intact at 2N, the worn surfaces obtained at 5N and 10N were distinctly different. It seemed that both coatings offered more
resistance to the AM50 alloy against abrasive and adhesive mechanisms at the load of 2N. It should be noted that the wear resistance is a characteristic that can be controlled by the roughness and hardness of PEO coatings. The fragile nature and the low plastic flowability of PEO coatings could facilitate the occurrence of the abrasive wear [24].

Under an intermediate load of 5 N, the removal of the exterior (porous) layer of the coating without CeO$_2$ was observed and no catastrophic wear damage occurred. Some loose debris was observed along the edges of the wear track of this coating (Fig. 11b). However, the PEO-CEO$_2$ coating seemed to be more or less intact after sliding against the steel ball at 5N. PEO-CeO$_2$ coating did not show any considerable failure, reflecting the ability of this coating to retain wear during the test at 5N.

In the tests conducted under 10 N load, the coating prepared in the absence of CeO$_2$ was completely removed (Fig. 11c). After the removal of coating, the bare metal surface experienced
extensive ploughing and adhesive wear mechanisms.
Furthermore, a three-body abrasive wear was also activated due to the generation of the debris which originated from the collapse of the coating during wear testing. This was corroborated by the higher wear rate of this coating. In contrast, PEO-CeO$_2$ coating exhibited excellent resistance against the steel ball. The formation of some ridges in the wear track of the PEO-CeO$_2$ coating could be attributed to the three-body-abrasive wear. This improvement could be explained according to the hardness and microstructure of the coatings. The formation of MgAl$_2$O$_4$ phase with high hardness in the coatings offered a higher load bearing capacity. It should be noted that the hardness of the studied coatings was measured using the nano-indentation method. For this purpose, the hardness of the dense materials was provided, whereas the studied coatings were highly porous. The hardness of the PEO coating was 329 ± 76 HV and that of the untreated substrate was about 58 HV. The hardness of the PEO-CeO$_2$ coating was 456 ± 48 HV too.
Higher magnification SEM studies combined with EDS analysis revealed more details about the wear features of the coatings. As shown in Fig 12, the presence of all coating elements in the worn surface of the PEO-CeO₂ coating after sliding at 10N demonstrated that the coating was still present on the surface and not removed. Fe and O were also detected, probably due to the occurrence of the abrasive wear of the steel ball and the creation of the oxide tribo-layer. This conclusion could be verified by considering the high steady state friction coefficients registered for the PEO-CeO₂ coating. Similar SEM-EDS results (not presented here) were observed for the wear tracks of PEO and PEO-CeO₂ coatings after testing at 2N and 5N loads.

In order to obtain more information regarding the wear mechanisms, the worn surface of the corresponding counterparts (steel balls) was also examined using SEM, as presented in Fig. 13. All balls exhibited a flattened surface after sliding against PEO coatings, confirming the occurrence of the abrasive mechanism
during the test. Also, the formation of some deep scoring in the worn surface of balls could be as a result of the entrapment of debris between the damaged coating and the ball surface. It should be noted that the hardness of steel balls used in this work was around 900 HV.

In comparison to the PEO coating counterpart, a completely different wear mechanism was found to occur based on the appearance of the ball surface after wear testing against the PEO-CeO$_2$ specimen at the 10N load. As shown in Fig. 13c, extensive ploughing and detachment of debris from the nanoparticle-free coating occurred on the surface of the ball under 10N load. However, by comparing the worn surfaces of the balls in terms of their appearance, it became evident that the balls sliding against the PEO-CeO$_2$ coating exhibited fewer and shallower scores under all loads. These observations were consistent with the results obtained for the wear rates. Also, the detachment of flakes from the worn surface of the coating to the
steel ball was decreased for the PEO-CeO$_2$ specimen, as compared to the CeO$_2$-free coating. This could be attributed to the fact that abrasive wear prevailed over the adhesive mechanism in the case of the PEO-CeO$_2$ specimen.

A close view of the surface of the steel ball tested against the coatings (Fig. 14) indicated that the extent of damage due to the three-body abrasive wear was increased for the corresponding counterpart of CeO$_2$-free coating. EDS results of the worn surfaces of the balls (Fig. 14b and d) demonstrated that the white wear debris observed on the ball surfaces comprised the elements from the coatings (Mg, Al, P, Na), thereby confirming the occurrence of the adhesive wear mode. Clearly, the transfer of the coating fragments was more intensive for the nanoparticles-free coating (Fig. 14a), as compared to that observed for the coating containing CeO$_2$ nanoparticles (Fig. 14c). The adhesively transferred materials from PEO coatings to the steel counterpart has also been reported by others [25]. It should be noted that the
roughness of PEO coatings could be of great importance for wear resistance [12]. Integration of CeO$_2$ nanoparticles into the coating led to the decrease of the cracks and micro-pores; also, the consequent decrease of roughness might be responsible for the wear behavior improvement.

3.4. Corrosion studies

The corrosion behavior of the coatings was assessed by potentiodynamic polarization technique in a 0.5 wt% NaCl solution after 30 min immersion in OCP condition. The corrosion plots are depicted in Fig. 15. The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) were extracted from the plots and listed in Table 4. Based on these results, the corrosion current density ($i_{corr}$) was decreased by CeO$_2$ addition. The incorporation of CeO$_2$ nanoparticles into the coating has led to a significant improvement in corrosion resistance as compared with corresponding PEO coating without particles. The superior corrosion resistance of the
PEO-CeO$_2$ coating attributed to its high compactness and the presence of small amount of ionic conducting pathways. The corroded surfaces after polarization tests demonstrated further the different corrosion aspects between the PEO and PEO-CeO$_2$ specimens as presented in Fig. 16. This surface appearances revealed that the PEO coating suffered from severe localized corrosion attack. This is in accordance with previous findings in the case of PEO coatings on Mg [5], Ti [12] and AL [26] alloys.

It is well known that CeO$_2$ has a high chemical stability. Tae Seop Lim et al. [13] studied the corrosion properties of PEO coatings obtained in a CeO$_2$ particle-containing Na$_2$SiO$_3$-based electrolyte. They have stated that the addition of CeO$_2$ led to corrosion inhibition due to the formation of a barrier-type interface between coating/substrate.

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Conclusions

The influence of CeO$_2$ nanoparticles on the wear characteristics (against AISI 52100 steel) of aluminate-based PEO coatings formed on the AM50 magnesium alloy was investigated. The following conclusions could be drawn from this work:

1- CeO$_2$ nanoparticles were distributed over the whole cross section of the coating. Also, the incorporation of ceria nanoparticles reduced the porosity and roughness of the coating, resulting in the higher hardness.

2- The PEO coatings, with and without CeO$_2$, revealed a steady state friction coefficient throughout the whole sliding test against steel ball at small (2N) and intermediate (5N) loads. However, at
the higher test load of 10N, a sharp friction transition was recorded for the CeO$_2$-free coating, while the CeO$_2$ containing the coating exhibited a steady state regime during the whole test.

3- The coatings, in the absence and presence of nanoparticles, increased the wear resistance of the AM50 alloy at the load of 2N. At the intermediate load of 5N, while the coating without CeO$_2$ revealed some local damages, the PEO-CeO$_2$ specimen sustained the wear test. At a load of 10N, the coating prepared without CeO$_2$ was completely removed and the substrate emerged. However, PEO-CeO$_2$ coating appeared to be more or less intact after sliding against the steel ball at 10N.

5- SEM-EDS analysis of the wear tracks and the worn ball surfaces revealed that the abrasive wear mode due to the entrapment of debris between the sliding couples complete wore off CeO$_2$-free coating during the wear test at 10N. Furthermore, the transfer of the coating fragments was more intensive for the
nanoparticle-free coating, as compared to that observed for the coating containing CeO$_2$ nanoparticles.

6- PEO-CeO$_2$ composite coating revealed superior corrosion resistance compared to the PEO coating without CeO$_2$, mostly due to decrease in the amount of pores and microcracks in CeO$_2$-containing coating.

Consequently, the results implied that the addition of CeO$_2$ could enhance wear resistance due to the increased hardness of PEO coatings.

References


Table Captions

Table 1. Characteristics of the PEO electrolytes used in this investigation.
Table 2. EDS results of the top surface of coatings (wt%)
Table 3. Steady state values of COF recorded for both coatings
Table 4. The extracted corrosion parameters from the polarization curves using Tafel extrapolation method.

Figure Captions

Fig. 1. X-ray diffraction pattern of CeO2 powders used in this work.

Fig. 2. Voltage vs. Time plots during the PEO treatment in the presence and absence of CeO2.

Fig. 3. SEM micrographs of PEO coatings made in the presence and absence of CeO2 particles. (a) PEO and (c) PEO-CeO2; Higher magnification image of (b) PEO and (d) PEO- CeO2.
Fig. 4. SEM images of the cross section of PEO coatings (a) PEO, (b) PEO-CeO$_2$.

Fig. 5. Elemental map of PEO-CeO$_2$ specimen.

Fig. 6. Cross-section elemental map of the PEO coating without CeO2 nanoparticles obtained by EDS.

Fig. 7. X-ray diffraction patterns of the coated specimens

Fig. 8. Variation of friction coefficient with sliding distance for (a) PEO and (b) PEO-CeO2 coatings under 2N, 5N and 10 N loads.

Fig. 9. SEM image showing the appearance of the worn surfaces: (a) PEO and (b) PEO-CeO$_2$

Fig. 10. Wear rate of both specimens under different loads.

Fig. 11. SEM micrographs of the wear track of coatings after sliding against steel ball under different loads.

Fig. 12. SEM–EDS analysis of the worn surface of PEO-CeO2 specimen after sliding against steel ball under 10N load.
(a) Micrograph illustrating the zone of EDS analysis. (b) and (c) EDS spectra of box regions in (a).

Fig. 13. Surface morphology of the steel ball counterparts slid against coated specimens under different loads of 2N, 5N and 10N.

Fig. 14. High magnification SEM images and EDS analyses of the steel balls after testing under 10N load. (a) PEO coating, (b) EDS spectrum of the box region in (a), (c) PEO-CeO$_2$ coating, (d) EDS spectrum of the box region in (c).

Fig. 15. Polarization curves of the coated samples after 30 min immersion in 0.5 wt% NaCl.

Fig. 16. Surface morphologies of coated specimen after polarization tests (a) PEO and (b) PEO-CeO$_2$. 
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<th>Na₃PO₄ (g/l)</th>
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<th>P</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>18</td>
<td>0.7</td>
<td>24</td>
<td>46</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>PEO-CeO$_2$</td>
<td>20</td>
<td>0.6</td>
<td>28</td>
<td>32</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 3

<table>
<thead>
<tr>
<th>Coating</th>
<th>2N</th>
<th>5N</th>
<th>10N</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>0.53 ± 0.01</td>
<td>0.6 ± 0.01</td>
<td>0.35 ± 0.05</td>
</tr>
<tr>
<td>PEO-CeO$_2$</td>
<td>0.48 ± 0.02</td>
<td>0.55 ± 0.02</td>
<td>0.63 ± 0.02</td>
</tr>
</tbody>
</table>
### Table 4

<table>
<thead>
<tr>
<th>Coating</th>
<th>$E_{\text{corr}}$ vs Ag/AgCl (mV)</th>
<th>$I_{\text{corr}}$ (nA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>1523 ± 6</td>
<td>541 ± 21</td>
</tr>
<tr>
<td>PEO-CeO$_2$</td>
<td>1522 ± 14</td>
<td>24 ± 5</td>
</tr>
</tbody>
</table>
Figure 1

CeO₂ nanoparticles
Figure 4

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Figure 7a

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Figure 13
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## Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>OKa</td>
<td>23.25</td>
<td>44.22</td>
</tr>
<tr>
<td>NaK</td>
<td>0.46</td>
<td>0.61</td>
</tr>
<tr>
<td>MgKα</td>
<td>10.18</td>
<td>12.74</td>
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<tr>
<td>AlKα</td>
<td>9.28</td>
<td>10.47</td>
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<tr>
<td>Pβα</td>
<td>2.77</td>
<td>2.14</td>
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<tr>
<td>Cr</td>
<td>0.97</td>
<td>0.57</td>
</tr>
<tr>
<td>FeLα</td>
<td>53.09</td>
<td>29.25</td>
</tr>
</tbody>
</table>

Figure 14ab

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Figure 14cd

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<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>OKa</td>
<td>12.98</td>
<td>32.02</td>
</tr>
<tr>
<td>NaK</td>
<td>0.09</td>
<td>0.16</td>
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<tr>
<td>MgKa</td>
<td>3.69</td>
<td>5.99</td>
</tr>
<tr>
<td>AlKa</td>
<td>3.55</td>
<td>5.19</td>
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<tr>
<td>Pka</td>
<td>0.76</td>
<td>0.96</td>
</tr>
<tr>
<td>Cr</td>
<td>1.23</td>
<td>0.95</td>
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<tr>
<td>FeLa</td>
<td>77.15</td>
<td>54.57</td>
</tr>
<tr>
<td>CoLa</td>
<td>0.56</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Figure 16
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Suggested Reviewers

1- Dr. P. Bala Srinivasan,
   SAstra University, GE Global Research, GKSS Forschungszentrum, NIT-Trichy
   pbs@nitt@edu

2- MetinUsta
   ustam@gyte.edu.tr
   Department of Materials Science and Engineering, Gebze Institute of Technology, Gebze, Kocaeli 41400, Turkey

3- Arash Fattah-alhosseini
   Associate Professor of Materials Engineering, Bu-Ali Sina University, Iran
   a.fattah@basu.ac.ir