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Wear behavior of plasma electrolytic oxidation (PEO) and hybrid coatings of PEO and laser on MRI 230D magnesium alloy

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Abstract

Wear resistant coatings were produced on a permanent mould cast MRI 230D Mg alloy by (a) PEO in silicate based electrolyte, (b) PEO in phosphate based electrolyte, (c) hybrid coatings of silicate PEO followed by laser surface alloying (LSA) with Al and Al₂O₃, and (d) hybrid coatings of phosphate PEO followed by LSA with Al and Al₂O₃. Microstructural characterization of the coatings was carried out by scanning electron microscopy (SEM) and X-ray diffraction. The tribological behavior of the coatings was investigated under dry sliding condition using linearly reciprocating ball-on-flat wear test. Both the PEO coatings exhibited a friction coefficient of about 0.8 and hybrid coatings exhibited a value of about 0.5 against the AISI 52100 steel ball as the friction partner, which were slightly reduced with the increase in applied load. The PEO coatings sustained the test without failure at 2 N load but failed at 5 N load due to micro-fracture caused by high contact stresses. The hybrid coatings did not get completely worn off at 2 N load but were completely removed exposing the substrate at 5 N load. The PEO coatings exhibited better wear resistance than the hybrid coatings and silicate PEO coatings exhibited better wear resistance than the hybrid coatings and silicate PEO coating or laser irradiation and all the hybrid coatings exhibited similar microstructure and wear behavior irrespective of the nature of the primary PEO coating or laser energies. SEM examination of worn surfaces indicated abrasive wear combined with adhesive wear for all the specimens. The surface of the ball exhibited a discontinuous transfer layer after the wear test.

Keywords: Plasma electrolytic oxidation, Laser surface alloying, Wear, Microstructure

1. Introduction

Mg alloys are finding increasing applications due to their attractive combination of properties, such as, high specific strength, excellent die-castability, good machinability, vibration damping, electromagnetic interference shielding properties and recyclability [1]. Today, Mg alloys are widely used as die castings in automotive,

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aerospace and Information and Communication Technology sectors. During the last decade a great deal of research has been done on developing and optimizing new Mg alloys with improved properties, which are considered to be a direct replacement for Al alloys and ferrous materials. The weight reduction achieved as a result of direct replacement of parts with Mg alloys in automotive and aerospace sectors reflects in increased efficiency and lower green house gas emissions. However, a serious impediment in the successful application of Mg alloys is its low wear resistance [2].

A wide variety of surface coatings, viz., organic, conversion, CVD, PVD, plasma electrolytic oxidation (PEO), laser surface alloying (LSA) etc. have emerged as effective means to improve the wear resistance of Mg alloys [3–7]. Amongst these coating processes, LSA and PEO have gained attention during recent years due to the exhibited increased wear resistance [8–17]. PEO coatings are basically conversion coatings performed at high voltages in an aqueous electrolyte, which rely on repetitive local dielectric breakdown and formation of plasma modifying the coating with the incorporation of species from the electrolyte [18]. Coatings produced by PEO treatment consist of hard crystalline ceramic phases, which have good adherence to the substrate. However, they are porous and rough and exhibit high coefficient of friction under dry sliding conditions. The open and interconnected pore structure, in fact, makes them vulnerable to fracture failure under load and reduced corrosion resistance, especially in the long run. Amongst PEO coatings on light metals, two widely studied types are based on silicate and phosphate electrolytes. Lasers, due to their inherent property of yielding high power density, low total energy beams are particularly suitable for surface modifications processes, viz., melting, alloying, cladding etc [19].

In the present investigation, a permanent mould cast MRI 230D Mg alloy has been subjected to silicate and phosphate based PEO treatments as well as to hybrid treatments consisting of PEO and LSA with Al and Al_2O_3 in order to improve the wear resistance of the alloy. MRI 230D is a creep resistant Mg alloy developed for automotive power train applications by Magnesium Research Institute, a joint venture between Dead Sea Magnesium and Volkswagen AG [20–21].

2. Experimental procedure

Permanent mould cast MRI 230D alloy ingot of nominal composition (in wt. %) 6.45% Al, 2.25% Ca, 0.25% Sr, 0.84% Sn, 0.27% Mn, <0.1% Zn, bal. Mg, was sliced into plates of size 50*50*5 mm³ and used as substrate for coatings. Specimens were ground successively with emery papers of 500, 800 and 1000 grit size, cleaned with ethyl alcohol followed by distilled water prior to PEO treatment. PEO coating was carried out in alkaline silicate and phosphate based electrolytes at a constant current density of 15 mA/cm² for 30 minutes with the specimen serving as anode. Electrolytes were prepared using analytical grade reagents in double distilled water with a composition of 10 g/l Na₂SiO₃ + 1 g/l KOH for silicate and 10 g/l Na₃PO₄ + 1 g/l KOH for phosphate PEO coatings.

The temperature of the electrolyte bath was maintained constant at 10 ± 2 °C by water circulation through a dedicated chiller unit. A custom built, variable duty cycle pulsed DC power supply capable of delivering 5A at

600V was used for the coatings. Duty cycle of the pulse employed for the coatings was 10% with $t_{on} = 2$ ms and $t_{off} = 18$ ms. Specimens were thoroughly rinsed in water immediately after the PEO treatment and dried in ambient conditions. Silicate and phosphate PEO coatings are henceforth designated as Si-PEO and P-PEO coatings.

For the preparation of hybrid coatings by LSA of PEO treated specimens, pre-placed precursor method was adopted. First, precursor powder of Al (99.5% purity, 10 μ m particle size) was mixed with a previously prepared 95 vol% water and 5 vol% proprietary water-based organic solvent 'LISI W 15853' (Warren Paint and Color Company, Nashville, TN, USA) and was spray deposited on the PEO treated plates to a thickness of 80 μ m and subjected to laser irradiation. Subsequently, the precursor powder consisting of Al₂O₃ (99.0% purity, 10 μ m particle size) was spray deposited to a thickness of 80 μ m and laser irradiated. Hybrid coatings are designated as (Si, P)–PEO + LSA (5, 5.5, 6, 6.5)J in the text, as the case may be. For laser irradiation, a 400W mean power LumonicsTM JK701 pulsed Nd:YAG laser equipped with fiber–optic beam delivery system was used. Laser beam was delivered with uniform energy distribution, both in spatial and temporal coherence, employing a 120 mm focal length convex lens, which provided a defocused spot diameter of 800 μ m on the specimen surface. Laser surface treatment was carried out at a scan speed of 42 mm/s with a pulse width of 0.5 ms, repetition rate of 20 Hz using argon as cover gas at a pressure of 5.5 bar. Laser pulse energies of 5, 5.5, 6 and 6.5J, which correspond to beam energies 90, 100, 110, 120 and 130W, were employed for the coating process. Several laser tracks were laid with minimal overlap (< 5%) to cover the entire surface area.

Surface roughness of PEO coatings was measured by HommelwerkeTM T1000 surface profile roughness gage and hardness was measured by CSMTM instrumented indentation test set–up using a load of 0.1 N. Friction and wear behavior of the coatings were analyzed by a Tribotec ball on disc oscillating tribometer (TribotechnicTM, 92110, Clichy, France) conforming to ASTM G–133 standard. AISI 52100 steel ball of diameter 6 mm was employed as the friction partner. Tests were conducted at a sliding speed of 5 mm/s for a total sliding distance of 100 m at normal loads of 2 N and 5 N with oscillating amplitude of 10 mm.

Microstructural characterization of the surface and cross-section of the coatings were carried out on FEI QuantaTM 200 scanning electron microscope (SEM) equipped with Oxford InstrumentsTM energy dispersive X-ray spectroscopy (EDS) analysis. Standard metallographic techniques were employed for specimen preparation. Etching reagent employed was a solution comprising of 100 ml ethanol, 10 ml acetic acid, 6 ml picric acid and 20 ml distilled water. The phase composition of the coatings were determined by X-ray diffraction with Cu-K α radiation ($\lambda = 0.154060$ nm) using PANlytical X'Pert ProTM diffractometer.

3. Results and discussion

3.1 Microstructural characterization

Fig. 1(a) shows the average surface roughness of the PEO coatings. Si-PEO coating was relatively smooth with a R_a value of 1.7±0.2 µm, while P-PEO coating had a R_a value of 4.3±0.4 µm. The Si-PEO coating exhibited

a much higher hardness of 1660 ± 367 Hv, almost three times the hardness of the P-PEO coating, i.e, 560 ± 153 Hv, as shown in Fig 1(b). The ultra high hardness is due to the ceramic nature of these coatings.

Fig. 2(a & b) shows the SEM image of the surface morphology of Si-PEO and P-PEO coatings. Both the coatings exhibited the characteristic porous feature of the PEO coatings. The Si-PEO specimen exhibited a large number of pores while the P-PEO specimen exhibited lesser number of pores, though they were larger in size. The larger size of pores on the surface of the coating may be the reason for the higher surface roughness of the P-PEO coatings observed in Fig. 1(a). Micro-cracks were also observed in the coatings, which can be attributed to thermal stresses generated by rapid solidification and cooling of ceramics produced by plasma discharges. EDS spectrum of Si-PEO and P-PEO coatings, as shown in Fig. 2(c & d), revealed the presence of Si and P respectively in the coatings. The incorporation of species from the electrolyte in the coating takes place by plasma-chemical reactions due to high energy release accompanying localized plasma discharges [15].

Fig. 3(a & b) shows the SEM images of cross-section of the Si-PEO and P-PEO coatings. The thickness of the Si-PEO coating was $11.5\pm1.6 \mu m$ while the thickness of the P-PEO coating was $17.3\pm2.1 \mu m$. A few isolated pores were observed along the cross-section of the coatings as well, and they were found to be lesser in Si-PEO coating, which might also be responsible for their higher hardness than the P-PEO coating observed in Fig. 1(b). The interface of the coatings with substrate exhibited a wavy profile. The EDS line scan demonstrated that the elemental composition remained, in general, constant throughout the cross-section of the coating, as shown in Fig. 4.

X-ray diffraction pattern of the PEO coatings is shown in Fig. 5. The Si-PEO coating essentially consisted of Mg_2SiO_4 with small proportions of MgO, Al_2O_3 and Ca_2SiO_4 . The P-PEO coating mainly consisted of $Mg_3(PO4)_2$ with small proportions of MgO. The difference in the composition of the two PEO coatings will contribute to the difference in hardness values observed in Fig. 1(b). Diffraction peaks corresponding to Mg were detected in both the PEO specimens and this may be due to the penetration of X-ray through the porous coating and subsequent diffraction from the substrate.

SEM images of the cross-section of the hybrid coatings indicate good interfacial bonding with minimal heat affected zone (Fig. 6). A distinct layered structure of the hybrid coatings was not present in the coatings despite the dual coating process involved. This suggests that the primary PEO coatings along with the applied precursor and a part of the substrate melted/decomposed, mixed together and solidified on LSA treatment. A few solidification micro-cracks were visible in the hybrid coatings. A fine cellular microstructure was observed at higher magnification, as shown in the inset of Fig. 6(b). Alumina particles of different shapes and sizes were also observed in the coating. EDS line scan results on the cross-section of hybrid coatings are shown in Fig. 7. Mg concentration in hybrid coatings (Si-PEO + LSA 5.5J) gradually increased from ~75 at.% and reached the substrate value. Similarly, the concentration of Al gradually decreased from ~20 at.% and reached the substrate value. Si and P content were low in the hybrid coatings and appeared to be uniformly distributed throughout the cross-section of the coatings. As the scan traversed the grain boundary region, a dip in the concentration of Mg with simultaneous increase of Al and Ca was observed. This is due to the presence of the Laves phase C-36 [(Mg, Al)₂Ca] at the grain boundary of the MRI 230D alloy [22-25]. Similar trends were observed in other hybrid

coatings (both Si-PEO and P-PEO) processed with different laser energy; therefore, the microstructure and elemental composition profile did not vary with the change in laser beam energy in the range of 5J to 6.5J.

X-ray diffraction pattern of hybrid coatings is shown in Fig. 8. Both the silicate and phosphate based hybrid coatings consist of same phases, viz., α -Mg, β (Mg₁₇Al₁₂), Al₂O₃ and MgO. Peaks corresponding to Mg₂SiO₄ and Mg₃(PO4)₂ are absent in both the diffraction patterns, which confirms that the PEO coatings are completely melted/decomposed by laser beam. Similar diffraction patterns were obtained for specimens processed at other laser energies.

Hardness profiles of the hybrid coatings exhibited similar trend (Fig. 9). An average value of 55 Hv was observed in the substrate region and hardness values were found to be gradually increasing towards the edge. Vickers hardness values of 273 Hv and 230 Hv were observed for (Si-PEO + LSA 5J) and (P-PEO + LSA 5J) hybrid coatings respectively at a distance of 25 μ m from the edge. The increased hardness appears to be due to the presence of hard β -phase, solid solution strengthening, finer microstructure and the dispersion of alumina particles, as also reported by Hazra et al. [13].

3.2 Wear behavior

The plot of coefficient of friction against sliding distance for tests conducted at 2 N load for as-cast and PEO coated specimens is shown in Fig. 10(a). The as-cast material exhibited a steady state coefficient of friction of 0.37 ± 0.03 after an initial 16 m of sliding. The fluctuations in the coefficient of friction is due to periodic material transfer by adhesive wear from the specimen to the ball leading to the formation of transfer layer and subsequent formation of wear debris by fracture of this transfer layer. The PEO coatings started with a coefficient of friction of ~0.4 but soon rose to much higher steady state values, i.e., 0.82±0.01 after 13 m of sliding for the Si-PEO and 0.85±0.01 after 44 m sliding distance for the P-PEO coating. The friction of ceramics against metallic materials, such as PEO coatings against steel in the present case, is accompanied by the continual renovation of the friction contact area. Owing to this, the chemical interaction is accelerated in the contacting area, resulting in a rise in coefficient of friction [18, 26-28]. These steady state values are maintained till the end of the test, which implies that these coatings survived the test without failure at 2 N load. The plot of coefficient of friction against sliding distance for tests conducted at 5 N load is shown in Fig. 10(b). The as-cast material exhibited a slightly lower steady state friction coefficient of 0.29±0.02 at 5 N as compared to 2 N load. This is due to the relative ease in the establishment of adhesive transfer layer at higher loads, modifying the surfaces in contact and reducing the coefficient of friction. The PEO coatings again exhibited a much higher initial coefficient of friction than the substrate. However, these values soon dropped to the level of as-cast material, which indicates the abrupt failure of these coatings at 5 N load. In case of P-PEO coatings the drop takes place immediately after the commencement of the test, whereas the Si-PEO coatings survive up to about 20 m of sliding distance due to the higher strength of these coatings.

SEM images of worn surface of as-cast material exhibited abrasive wear combined with severe plastic deformation characterized by the formation of ridged grooves at both the loads of 2 N and 5 N, as shown in Fig. 11. EDS analysis of the worn surface exhibited the presence of all the alloying elements in the MRI 230D alloy along with oxygen. SEM images of the worn surface of the PEO coatings at 2 N load are shown in Fig. 12. The Si-PEO coating exhibited a few parallel grooves and the coating survived the entire duration of the test. For P-PEO coating, local failure of coatings was observed at few places, but it did not lead to the lowering of the coefficient of friction. The EDS analysis of the worn surfaces of both the Si-PEO and P-PEO coatings revealed the presence of Fe and O. Thus, the hard PEO coatings caused the abrasive wear of steel ball and the formation of oxide tribo-layer, which supports the argument put forth for the high steady state coefficient of friction in the previous paragraph. Srinivasan et al. have also reported abrasive wear of steel ball under dry sliding conditions for both Si-PEO and P-PEO coatings [17, 29]. SEM images of the worn surface of the PEO coatings tested at 5 N load are shown in Fig. 13. A complete failure of coatings was observed in the micrographs. Micro-fracture of the coating due to high contact stresses is evident in the narrow band of partial coating failure between exposed substrate and the coating, as also observed by Srinivasan et al. [17, 29]. The porous nature of the coatings, even though provides a great degree of compliance [30], is detrimental to wear resistance. The EDS analysis of the worn surfaces of both the PEO coatings did not indicate any presence of Fe, and the Al content was close to that of the substrate, indicating the complete early failure of the coatings at 5 N load.

The variation of coefficient of friction of hybrid coatings wear tested at 2 N load is shown in Fig. 14(a). The values of coefficient of friction $(0.48\pm0.08 \text{ for Si}-\text{PEO} + \text{LSA} 5\text{J} \text{ and } 0.51\pm0.03 \text{ for P}-\text{PEO} + \text{LSA} 5\text{J})$ were well below those of the PEO coated samples tested at the same load but above the value of the as-cast material. This is expected in this case, since the coatings are metallic and consist mainly of solid solution of Mg with few other phases present in it. The plot of coefficient of friction against sliding distance for hybrid coatings tested at 5 N load is shown in Fig. 14(b). Both the hybrid coatings exhibited a steady state coefficient of friction 0.36 ± 0.03 , which was again slightly greater than that of the as cast material at the same load.

Fig. 15(a) shows the SEM image of worn surface of hybrid coating Si-PEO + LSA 5J wear tested at 2 N load. Long parallel grooves with severe plastic deformation, especially at the ridges of wear tracks were noticed in the SEM images. Therefore, the wear mechanism operating at 2 N load is a combination of abrasive wear and adhesive wear. Wear debris appeared scantly dispersed on the wear tracks. No peaks corresponding to Fe were observed in the EDS spectrum and Al content was close to that in the coating (Fig. 15b). This shows that the coating does not completely wear off at 2 N load. SEM images of the worn surface at 5 N load revealed extensive severe plastic deformation on the wear tracks along with abrasive wear (Fig. 16a). EDS analysis of the worn surface revealed 6.41 at.% Al (Fig. 16b), which is close to that of the substrate composition. This implies that the coatings have been completely removed at 5 N load. Similar wear behavior was observed for both the hybrid coatings at all the laser energies employed.

Fig. 17(a) shows the SEM image of the ball surface of (P-PEO + LSA 5J) after the wear test at 5 N load. The region with dark contrast corresponds to material transfer by adhesive wear, which is labeled by arrows. The results of EDS analysis from one such boxed region is shown in Fig. 17(b). It revealed the presence of Mg, Al and

Ca transferred from the test specimen along with Fe and Cr from the steel ball. The presence of oxygen is also detected due to the oxidation of the surfaces. Similar results were obtained for other specimens.

An assessment of wear resistance was made by measuring the maximum wear track depth for all the specimens. For this, the specimens were cut cross the wear-tracks, polished, etched and examined under SEM. The representative depth profiles are shown for (P-PEO + LSA 5J) hybrid coating wear tested at 2N and 5N load in Fig. 18(a & b). The SEM images revealed that the maximum wear track depth was contained within the coatings for both the PEO and hybrid coatings at 2 N load but reached the substrate for both of them at 5 N load. These observations corroborate the inferences based on the measurements of coefficient of friction and the analyses of worn surfaces presented earlier in the manuscript. Therefore, the true wear resistance of the coatings can be inferred from the results obtained at 2 N load. As shown in Fig. 19, all the coatings exhibited greater wear resistance (lower maximum wear track depth) than the substrate and the PEO coatings exhibited greater wear resistance than the hybrid coatings at 2 N load, as expected from the higher hardness of the PEO coatings than the hybrid coatings shown in Figs. 1 & 9. Among the PEO coatings, the Si-PEO exhibited better wear resistance than the P-PEO coating, since the former had greater hardness than the later. Similarly, both the hybrid coatings exhibited similar wear resistance, since both of them had similar composition and hardness.

The maximum wear track depth at 5 N load is not only governed by the wear of the coatings but also of the substrate after the coatings have been removed. All the coatings exhibited greater wear track depth than the ascast material (Fig. 19), since the substrate is subjected to three-body wear mechanism after the coatings have been removed. Hard abrasive wear debris of the coatings and steel ball formed at the initial stages of wear gets entrapped in the wear tracks causing an accelerated abrasive wear of the substrate, so that the wear track depth at the end of the test for the coated materials becomes more than the as-cast material. The P-PEO coating failed earlier than the Si-PEO coating, as inferred from coefficient of friction measurements in Fig. 10(b), resulting in greater duration of the three-body wear of the substrate and hence greater wear track depth. Both the hybrid coatings were much thicker than the PEO coatings and were completely removed after a much longer duration resulting in lower wear track depth than the PEO coatings at the end of the wear test.

4. Conclusions

Wear resistant surface coatings were produced on permanent mould cast MRI 230D Mg alloy by PEO treatment in alkaline silicate and phosphate based electrolytes, and by hybrid treatment of PEO and LSA with Al and Al₂O₃. The coatings were characterized for microstructure and its effect on dry sliding wear behavior using reciprocating steel ball-on-flat wear test was studied. The following conclusions can be drawn from the present investigation:

1. A characteristic porous coating was obtained by PEO treatment. A few micro-cracks due to thermal stresses were also observed on the surface of the coatings. The Si-PEO coating mainly consisted of Mg₂SiO₄ together with small amount of MgO, Al₂O₃ and Ca₂SiO₄, whereas the P-PEO coating mainly consisted of Mg₃(PO4)₂ together

with small amount of MgO. Both the PEO coatings exhibited high hardness values, 1660±367 for Si-PEO and 560±153 Hv for P-PEO due to ceramic nature of the coatings.

2. A distinct layered coating was not observed in the hybrid coatings. The primary PEO coating was completely melted/ decomposed along with applied precursor and substrate material, mixed together and re-solidified on LSA treatment with Al and Al₂O₃. A few micro-cracks due to thermal stresses were observed in the hybrid coatings. Both the hybrid coatings exhibited similar composition and hardness at all the laser energies employed. The hybrid coatings consisted of α -Mg, β (Mg₁₇Al₁₂), Al₂O₃, and MgO phases. The hybrid coatings exhibited hardness values of about 250 Hv and the increase in hardness is due to the presence of β -phase, solid solution strengthening, microstructural refinement and dispersion of Al₂O₃ particles.

3. The coefficient of friction was highest for the PEO coatings (~0.8) followed by hybrid coatings (~0.5) and substrate (0.37) at 2 N load, which slightly decreased at 5 N load. The Si-PEO coating sustained the wear test at 2 N load, while the P-PEO coating exhibited local failure in some regions. At 5 N load, both the PEO coatings failed due to micro-fracture caused by high contact stresses. However, the P-PEO coating failed immediately upon the commencement of test, whereas the Si-PEO coating failed after a sliding distance of 20 m. Hybrid coatings did not get completely worn off at 2 N load but were completely removed exposing the substrate at 5 N load.

4. Wear track depth measurements revealed improved wear resistance for both the PEO and hybrid coatings as compared to the as-cast material at 2 N load. PEO coatings exhibited better wear resistance than the hybrid coatings and Si-PEO exhibited better wear resistance than the P-PEO coatings. The better wear resistance is directly correlated to the higher hardness values of the respective specimens. At 5 N load, wear track depth of all the coatings were higher than the substrate. This is due to the abrasive three-body wear by hard ceramic wear debris entrapped in wear tracks in case of coated specimens. Laser energies employed in the present investigation did not have any effect on the wear behavior of the hybrid coatings.

5. The test specimens exhibited a combination of abrasive and adhesive wear. The friction partner (ball) showed the formation of a discontinuous transfer layer.

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References

[1] B.L. Mordike, T. Ebert, Magnesium: properties-applications-potential, Mater. Sci. Engg A, 302 (2001)37-45.

[2] P.J. Blau, M. Walukas, Sliding friction and wear of magnesium alloy AZ91D produced by two different methods, Tribol. Int. 33 (2000) 573–579.

[3] J.E. Gray, B. Luan, Protective coatings on magnesium and its alloys–a critical review, J. Alloys Compd. 336 (2002) 88–113.

[4] K.T. Rie, J. Whole, Plasma–CVD of TiCN and ZrCN films on light metals, Surf. Coat. Technol. 112 (1999) 226–229.

[5] K. Brunelli, M. Dabala, I. Calliari, M. Magrini, Effect of HCl pre-treatment on corrosion resistance of cerium-based conversion coatings on magnesium and magnesium alloys, Corros. Sci. 47 (2005) 989–1000.

[6] C. Blawert, D. Manova, M. Stormer, J.W. Gerlach, W. Dietzel, S. Mandl, Correlation between texture and corrosion properties of magnesium coatings produced by PVD, Surf. Coat. Technol. 202 (2008) 2236–2240.

[7] C. Blawert, W. Dietzel, E. Ghali, G Song, Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments, Adv. Eng. Mater. 8 (2006) 511–533.

[8] S. Ignat, P. Sallamand, D. Grevey, M. Lambertin, Magnesium alloys laser (Nd:YAG) cladding and alloying with side injection of aluminium powder, Appl. Surf. Sci. 225 (2004) 124–134.

[9] Y. Gao, C. Wang, Q. Lin, H. Liu, M. Yao, Broad-beam laser cladding of Al-Si alloy coating on AZ91HP magnesium alloy, Surf. Coat. Technol. 201 (2006) 2701–2706.

[10] J.D. Majumdar, B.R. Chandra, B.L. Mordike, R. Galun, I. Manna, Laser surface engineering of a magnesium alloy with Al+ Al₂O₃, Surf. Coat. Technol. 179 (2004) 297–305.

[11] Y.H. Liu, Z.X. Guo, Y. Yang, H.Y. Wang, J.D. Hu, Y.X. Li, A.N. Chumakov, N.A. Bosak, Laser (a pulsed Nd:YAG) cladding of AZ91D magnesium alloy with Al and Al₂O₃ powders, Appl. Surf. Sci. 253 (2006) 1722–1728.

[12] Y. Jun, G.P. Sun, C. Liu, S.Q. Jia, S.J. Fang, S. S. Jia, Characterization and wear resistance of laser surface cladding AZ91D alloy with Al + Al₂O₃, J. Mater. Sci. 42 (2007) 3607–3612.

[13] M. Hazra, A.K. Mondal, S. Kumar, C. Blawert, N.B. Dahotre, Laser surface cladding of MRI 153M magnesium alloy with (Al+ Al₂O₃), Surf. Coat. Technol. 203 (2009) 2292–2299.

[14] K.C. Goretta, A.J. Cunningham, N. Chen, D. Singh, J.L. Routbort, R.G. Rateick, Solid–particle erosion of an anodized Mg alloy, Wear 262 (2007) 1056–1060.

[15] J. Liang, L. Hu, J. Hao, Preparation and characterization of oxide films containing crystalline TiO_2 on magnesium alloy by plasma electrolytic oxidation, Electrochim. Acta 52 (2007) 4836–4840.

[16] P.B. Srinivasan, J. Liang, C. Blawert, M. Stormer, W. Dietzel, Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy, Appl. Surf. Sci. 255 (2009) 4212–4218.

[17] P.B. Srinivasan, C. Blawert, W. Dietzel, Dry sliding wear behaviour of plasma electrolytic oxidation coated AZ91 cast magnesium alloy, Wear 266 (2009) 1241–1247.

[18] A.L. Yerokhin, X Nie, A Leyland, A. Matthews, S. J. Dowey, Plasma electrolysis for surface engineering, Surf. Coat. Technol. 122 (1999) 73–93.

[19] E. K-Asibu Jr., Principles of laser materials processing, John Wiley & Sons, New Jersey, 2009, pp 593-609.

[20] B. Bronfin, E. Aghion, S. Schuman, P. Bohling, K.U. Kainer, Magnesium alloys for high temperature applications, US Patent: 6 139 651, 2000.

[21] B. Bronfin, N. Moscovitch, New magnesium alloys for transmission parts, Metal Sci. and heat treatment 48 (2006) 479–486.

[22] A. Suzuki, N.D. Saddock, J.W. Jones, T.M. Pollock, Solidification paths and eutectic intermetallic phases in Mg–Al–Ca ternary alloys, Acta Mater. 53 (2005) 2823–2834.

[23] A. Suzuki, N.D. Saddock, J.R. TerBush, B.R. Powell, J.W. Jones, T.M. Pollock, Precipitation strengthening of a Mg–Al–Ca–based AXJ530 die–cast alloy, Metall. Mater. Trans A 39 (2008) 696–702.

[24] A. Suzuki, N.D. Saddock, J.W. Jones T.M. Pollock, Phase equilibria in the Mg–Al–Ca ternary system at 773 and 673 K, Metall. Mater. Trans A 37 (2006) 975–983.

[25] A. Suzuki, N.D. Saddock, L. Riester, E. Lara–Curzio, J.W. Jones, T.M. Pollock, Effect of Sr additions on the microstructure and strength of a Mg–Al–Ca ternary alloy, Metall. Mater. Trans A 38 (2007) 420–427.

[26] K.H.Z. Gahr, Sliding wear of ceramic-ceramic, ceramic-steel and steel-steel pairs in lubricated and unlubricated contact, Wear 133 (1989) 1-22.

[27] W. Xue, J. Du, X. Wu, Y. Lai, Tribological behavior of microarc oxidation coatings on aluminum alloy, ISIJ Int. 46 (2006) 287-291.

[28] Y.M. Wang, B.L. Jiang, L.X. Guo, T.Q. Lei, Tribological behavior of microarc oxidation coatings formed on titanium alloys against steel in dry and solid lubrication sliding, Appl. Surf. Sci. 252 (2006) 2989–2998.

[29] P.B. Srinivasan, J. Liang, C. Blawert, W. Dietzel, Dry sliding wear behaviour of magnesium oxide and zirconium oxide plasma electrolytic oxidation coated magnesium alloy, Appl. Surf. Sci. 256 (2010) 3265–3273.

[30] J.A. Curran, T.W. Clyne, Thermo–physical properties of plasma electrolytic oxide coatings on aluminium, Surf. Coat. Technol. 199 (2005) 168–176.



Fig. 1 (a) Average surface roughness (b) Vickers hardness of PEO coatings



Fig. 2 SEM images of the top surface of PEO coatings (a) Si–PEO (b) P–PEO (c) EDS spectrum of Si–PEO (d) EDS spectrum of P–PEO



Fig. 3 SEM images of the cross section of PEO coatings (a) Si-PEO (b) P-PEO



Fig. 4 EDS line scan across the cross-section of PEO coatings (a) Si-PEO (b) P-PEO



Fig. 5 X-ray diffraction pattern of Si-PEO and P-PEO coatings using Cu-K α radiation ($\lambda = 0.154060$ nm)



Fig. 6 SEM images of hybrid coatings (a) Si-PEO + LSA 5J (b) P-PEO + LSA 5J



Fig. 7 EDS line scan across the cross–section of hybrid coatings (a) Si–PEO + LSA 5.5J and (b) P–PEO + LSA 5.5J



Fig. 8 X-ray diffraction pattern of hybrid coatings using Cu–K α radiation (λ = 0.154060 nm)



Fig. 9 Hardness profile across the cross-section of hybrid coatings



Fig. 10 Variation of coefficient of friction with sliding distance for as-cast, Si-PEO and P-PEO coatings at (a) 2 N (b) 5 N



Fig. 11 SEM images of as-cast MRI 230D alloy (a) wear tested at 2 N (b) EDS spectrum of worn surface at 2 N (c) wear tested at 5 N (d) EDS spectrum of worn surface at 5 N



Fig. 12 SEM images of wear tested PEO coatings at 2 N (a) Si-PEO (b) EDS spectrum of the worn surface of Si-PEO (c) P-PEO (d) EDS spectrum of the worn surface of P-PEO



Fig. 13 SEM images of wear tested PEO coatings at 5 N (a) Si-PEO (b) EDS spectrum of the worn surface of Si-PEO (c) P-PEO (d) EDS spectrum of the worn surface of P-PEO



Fig. 14 Variation of coefficient of friction with sliding distance for as cast, (Si-PEO + LSA 5J) and (P-PEO + LSA 5J) hybrid coatings at (a) 2 N (b) 5 N



Fig. 15 (a) SEM image of wear tested (Si-PEO + LSA 5J) hybrid coating at 2 N (b) EDS spectrum of the worn surface in (a)



Fig. 16 (a) SEM image of wear tested (Si-PEO + LSA 5J) hybrid coating at 5 N (b) EDS spectrum of the worn surface in (a)



Fig. 17 (a) SEM image of wear tested ball for (P–PEO + LSA 5J) at 5 N and (b) EDS spectrum of box region in (a)



Fig. 19 Maximum wear track depth for as-cast, PEO and hybrid coatings