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# Improving Corrosion Resistance of MRI 230D Mg Alloy by Hybrid Coating of Laser Surface Alloying and Plasma Electrolytic Oxidation

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**Abstract.** A permanent mould cast creep resistant MRI 230D Mg alloy was laser surface alloyed (LSA) with Al and Al<sub>2</sub>O<sub>3</sub> in order to improve its wear and corrosion resistance. However, this treatment was successful only in improving wear resistance but not corrosion resistance due to the presence of micro–cracks in the coated layer, which has been discussed in an earlier paper. The LSA coated Mg alloy has been further subjected to plasma electrolytic oxidation (PEO) treatment in alkaline silicate electrolyte in order to cover those micro–cracks and improve corrosion resistance, which is discussed in the present manuscript. For comparison, the PEO coating has also been applied on the as–cast MRI 230D Mg alloy. The microstructural characterization of coatings and corroded surfaces was carried out by scanning electron microscope and X–ray diffraction. Electrochemical corrosion tests were conducted in 3.5 wt% NaCl solution having neutral pH to investigate the corrosion behavior. The LSA coatings consisted mainly of  $\beta$  (Mg<sub>17</sub>Al<sub>12</sub>) phase, the coatings produced by PEO treatment on MRI 230D Mg alloy consisted mainly of Mg<sub>2</sub>SiO<sub>4</sub> phase, and hybrid coatings of PEO on LSA consisted of Mg<sub>2</sub>SiO<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> phases in the PEO layer. Scanning electron micrographs of the cross–section revealed that the PEO treatment covered the micro–cracks present in the LSA and corrosion tests revealed that it improved the corrosion resistance, though not to the extent of the corrosion resistance of the PEO coated MRI 230D Mg alloy. All the samples exhibited localized form of corrosion.

## Introduction

Mg alloys are potential candidates for aerospace and automotive applications due to their excellent combination of properties, viz., high specific strength, excellent die–castability, machinability, vibration damping, electromagnetic interference shielding properties and recyclability [1,2]. During the last decade a vast deal of research have been done for developing and optimizing new Mg alloys with improved creep resistance. MRI 230D is a newly developed creep resistant alloy by Magnesium Research Institute for automotive powertrain applications with a service temperature capability up to 190°C [3,4]. Despite these developments, a relatively poor corrosion and wear resistance of Mg alloys imposes severe limitations for its wider applications. Therefore, protective surface coatings are essential for the successful application of Mg alloys. Laser, due to its low energy–high power density beam, can be effectively used for surface coatings [5,6]. Recently, surface coatings based on plasma electrolytic oxidation (PEO) have gained wide research attention due to its characteristic properties, such as, increased coating thickness, good adhesion to the substrate, superior corrosion resistance, high hardness, crystalline nature of coatings and lower environmental impact due to dilute electrolytes employed [7,8].

In the present investigation, surface coatings were prepared on a permanent mould cast creep resistant MRI 230D Mg alloy by laser surface alloying (LSA) with Al and by a dual process of Al followed by Al+Al<sub>2</sub>O<sub>3</sub>. These coatings improved the wear resistance but not the corrosion resistance due to the presence of micro-cracks present in the coatings [9]. Therefore, the LSA coated specimens were subjected to PEO treatment. The effectiveness of the PEO coating in sealing the cracks present in the LSA coatings and improving the corrosion resistance by applying this hybrid (LSA+PEO) coating is investigated in the present manuscript.

## Experimental procedure

A permanent mould cast Mg alloy ingot having a composition (in wt.%) 6.45% Al, 2.25% Ca, 0.25% Sr, 0.84% Sn, 0.27% Mn, <0.1% Zn, balance Mg, was sliced into plates of dimension 45mm\*45mm\*5mm and was used as the substrate for the coatings. Two sets of LSA coated specimens were prepared. In the first set, the precursor of Al powder was spray deposited and subjected to laser irradiation (hereafter designated as Al-LSA) and in the second set, a dual LSA treatment consisting of initial LSA with Al followed by a subsequent LSA treatment with the precursor powder consisting of 50 wt% Al and 50 wt% Al<sub>2</sub>O<sub>3</sub> (hereafter designated as [Al+(Al+Al<sub>2</sub>O<sub>3</sub>)]-LSA) was imparted. The LSA was carried out at the scan speeds of 21, 42, 63 and 84 mm/s with a constant pulse width of 0.5 ms, repetition rate of 30 Hz and pulse energy of 5 J using argon as cover gas at a pressure of 5.5 bar. Several laser tracks were laid with minimal overlap (< 5%) to cover the entire surface area.

The PEO coating on as-cast and LSA coated specimens was carried out in an alkaline silicate based electrolyte at a constant current density of 50 mA/cm<sup>2</sup> for 15 minutes. The electrolyte was prepared by adding 10 g Na<sub>2</sub>SiO<sub>3</sub> and 1 g KOH in 1 liter of distilled water. 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 preparation of coatings with specimen serving as anode. Duty cycle of the pulse employed for the coatings was 10% with t<sub>on</sub> = 2 ms and t<sub>off</sub> = 18 ms. Hybrid coatings are henceforth designated as Al-LSA+PEO and [Al+(Al+Al<sub>2</sub>O<sub>3</sub>)]-LSA+PEO, as the case may be.

Electrochemical corrosion tests were carried out in 3.5 wt% NaCl neutral pH solution with an exposed area of 0.5 cm<sup>2</sup> using a computer controlled GillAC<sup>TM</sup> potentiostat/ galvanostat. A standard three electrode corrosion cell, with the sample as the working electrode, a saturated Ag/AgCl electrode as reference electrode and a platinum mesh as counter electrode, was used. Free corrosion potential was monitored for 5 minutes immediately after the commencement of the test. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the free corrosion potential over the frequency range of 10 kHz to 0.01 Hz using sinusoidal signal of amplitude ±10 mV. The EIS scans were conducted at the intervals of 5 minutes, 1 h, 3 h, 6 h, 12 h and 18 h of immersion. Subsequently, potentiodynamic polarization scan was carried out starting from -150 mV relative to free corrosion potential with a scan rate of 0.2 mV/s to a terminal current density of 0.1 mA/cm<sup>2</sup>.

A FEI Quanta 200<sup>TM</sup> scanning electron microscope (SEM) equipped with Oxford Instruments<sup>TM</sup> energy dispersive X-ray spectroscopy (EDS) analysis was used for microstructural characterization. The phase composition of the coatings was determined by X-ray diffraction (XRD) with Cu-K $\alpha$  radiation ( $\lambda=0.154060$  nm) using PANalytical X'Pert Pro<sup>TM</sup> diffractometer. Standard techniques were employed for metallographic specimen preparation. Etching reagent employed was a solution of 100 ml ethanol, 10 ml acetic acid, 6 ml picric acid and 20 ml distilled water.

## Results and discussion

**Microstructural characterization.** Fig. 1 shows the microstructure and elemental profile obtained by EDS line scan along the cross-section of the LSA coated specimens. Both the LSA coatings exhibit good interfacial bonding with a negligible heat affected zone. A few micro-cracks due to

thermal stresses are observed in the coatings. The  $\text{Al}_2\text{O}_3$  precursor powder in  $[\text{Al}+(\text{Al}+\text{Al}_2\text{O}_3)]$ -LSA specimens got completely melted/decomposed by laser irradiation and reconstituted in different sizes and shapes. A distinct interface is not observed between 1<sup>st</sup> and 2<sup>nd</sup> LSA coatings in the case of  $[\text{Al}+(\text{Al}+\text{Al}_2\text{O}_3)]$ -LSA specimens. Thus, the primary LSA coating got melted and homogenized along with the precursor powder of the second LSA treatment. Al-LSA specimens exhibit about 60 at.% Mg and 40 at.% Al at the surface, which gradually approaches the substrate composition at the interface. On the other hand  $[\text{Al}+(\text{Al}+\text{Al}_2\text{O}_3)]$ -LSA coatings exhibit a more or less uniform profile of about 60 at.% Mg and 40 at.% throughout the thickness, which corresponds to the composition of  $\beta$  ( $\text{Mg}_{17}\text{Al}_{12}$ ) phase, corroborated by XRD patterns of the two coatings (not shown here). The microstructure and phases were found to be essentially the same at all the scan speeds.

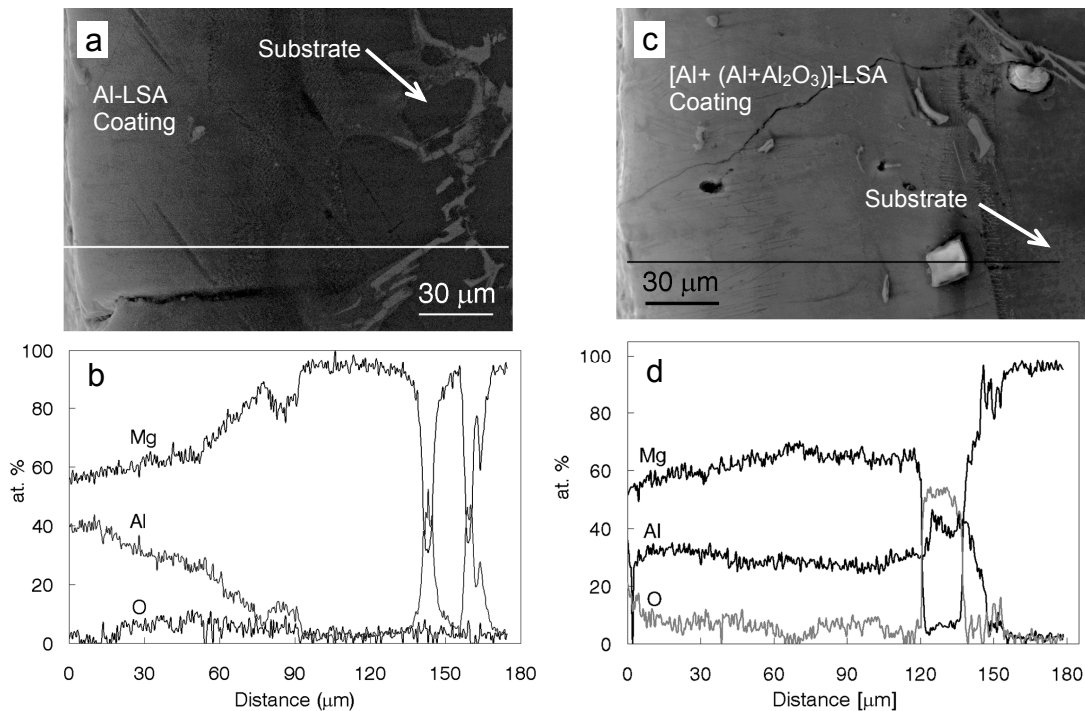


Fig. 1: SE micrographs and EDS line scan of cross-section of LSA coated specimens (a) Al-LSA 63mm/s, (b) elemental profile of (a), (c)  $[\text{Al}+(\text{Al}+\text{Al}_2\text{O}_3)]$ -LSA 63mm/s, (d) elemental profile of (c)

Fig. 2 shows the microstructure and EDS line scan along the cross-section of the PEO coated specimen. The PEO coating exhibits good interfacial bonding with the substrate and a few pores are observed in the cross-section of the coating. The elemental profile remains more or less constant throughout the thickness of the coating and then jumps to the substrate composition at the interface. The elemental composition suggests that the PEO coating essentially consists of  $\text{Mg}_2\text{SiO}_4$ , which was indeed confirmed by the XRD pattern (not shown here).

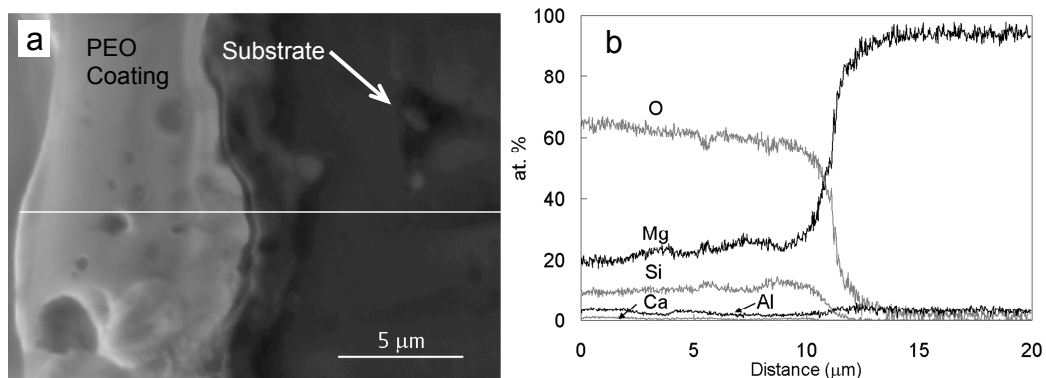


Fig. 2: (a) SE micrographs of cross-section of PEO coated specimen and (b) elemental profile of (a)



Hybrid coatings exhibit a two-layer coating structure consisting of PEO and LSA coatings, as shown in Fig. 3. The elemental composition suggests that the  $MgAl_2O_4$  phase is also present along with  $Mg_2SiO_4$  in the PEO coating, which was confirmed by the XRD pattern (not shown here). The LSA portions of the hybrid coatings exhibit the same composition as the LSA coatings alone shown in Fig. 1.

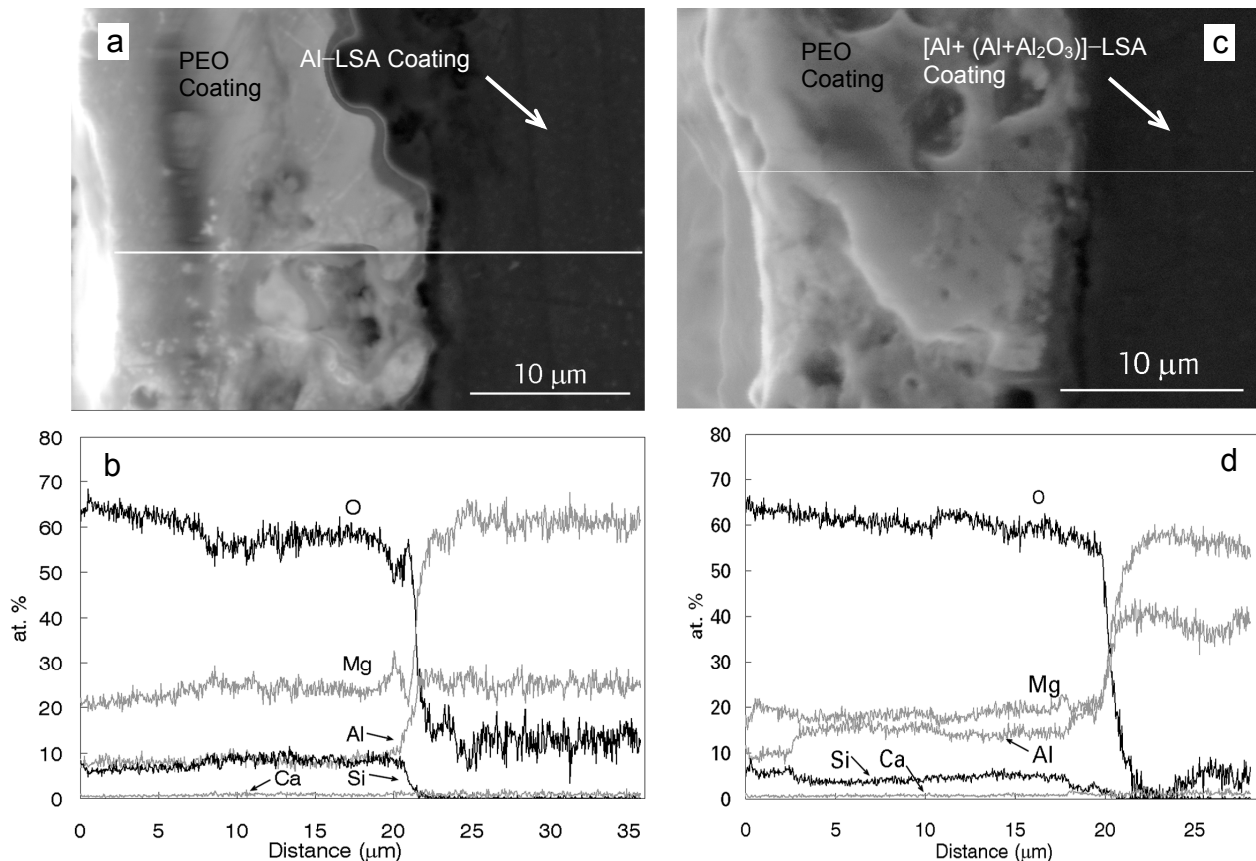


Fig. 3: SE micrographs and EDS line scan of cross-section of hybrid coatings (a) Al-LSA 63 mm/s + PEO, (b) elemental profile of (a), (c) [Al+(Al+Al<sub>2</sub>O<sub>3</sub>)]-LSA 63 mm/s + PEO and (d) elemental profile of (c)

**Electrochemical corrosion behavior.** Charge transfer resistance,  $R_{ct}$  values estimated by Nyquist plot obtained from the EIS scan after 18 h of immersion for all the specimens are shown in Fig. 4(a). The EIS scans reveal comparable  $R_{ct}$  values for the as-cast material and LSA coated specimens. Hybrid coatings exhibit higher  $R_{ct}$  values than the LSA coating and as-cast material, but lower than the PEO coatings in majority of the cases corresponding to different laser scan speeds. A similar trend is exhibited by the corrosion rate estimated by Tafel plots obtained from potentiodynamic polarization scan after 18 h of immersion, as shown in Fig. 4(b). The corrosion rate of the LSA specimens is comparable to the as-cast material. Hybrid coatings exhibit a lower corrosion rate than the as-cast material and LSA coated specimens, though it is higher than the corrosion rate exhibited by the PEO specimen in most of the cases. A higher  $R_{ct}$  value and a lower corrosion rate imply a better corrosion resistance. The LSA coatings, which consist of  $\beta$ -phase, appear to be corrosion resistant by virtue of a thin passivating film on its surface. However, the micro-cracks present in the coating make the substrate vulnerable to direct attack by electrolyte. There is no definite trend of corrosion resistance with respect to laser scan speed. The PEO coating on top of LSA coating partially covers these cracks and the hybrid coatings exhibit a better corrosion resistance than the as-cast and LSA coated specimens, though not as good as the PEO coating on the substrate in most of the cases.

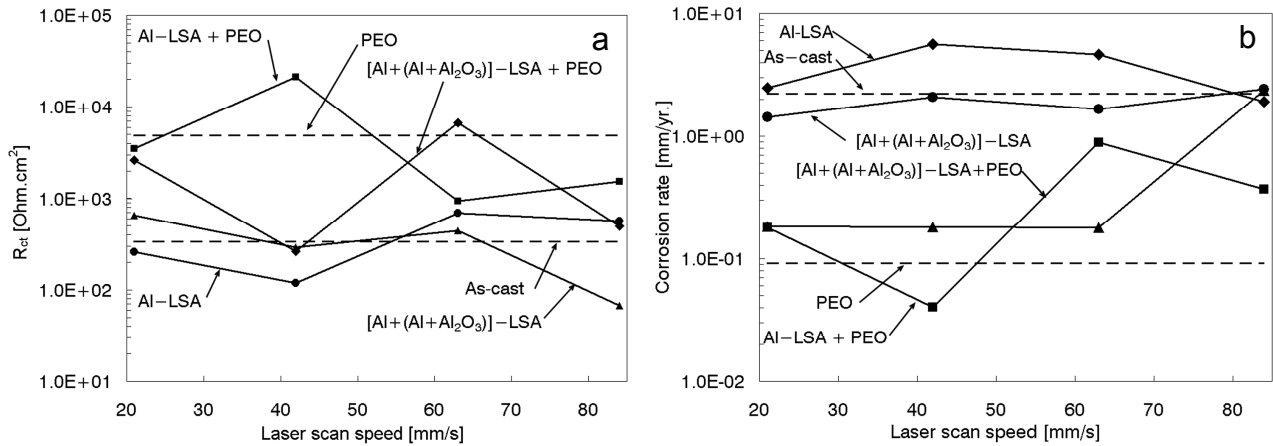


Fig. 4: (a) Charge transfer resistance ( $R_{ct}$ ) and (b) Corrosion rate of as-cast, LSA, PEO and hybrid coatings after 18 h of immersion in 3.5 wt% NaCl solution

Corroded surface morphology of as-cast, LSA, PEO and hybrid coated specimens are shown in Fig. 5. A highly localized form of corrosion is exhibited in all the cases, as indicated by arrows. However, the size and number of pits formed after corrosion test are lowest for the PEO specimen, followed by the hybrid coatings, LSA coatings and as-cast material, i.e. in the same order as the decreasing order of corrosion resistance.

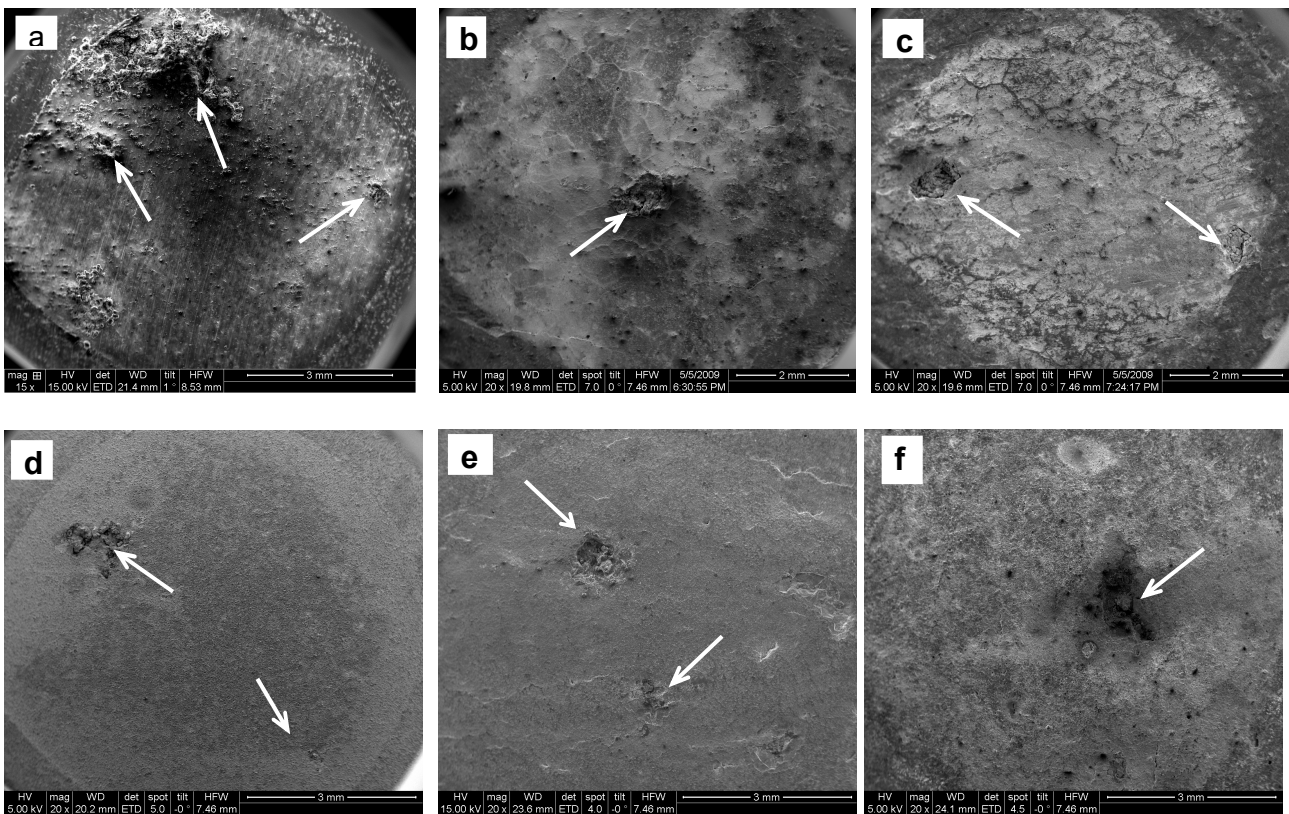


Fig. 5: Corroded surface morphology of (a) as-cast (b) Al-LSA 63 mm/s (c)  $[Al+(Al+Al_2O_3)]$ -LSA 63 mm/s (d) PEO coating (e) Hybrid coating, Al-LSA 63 mm/s + PEO (f) Hybrid coating,  $[Al+(Al+Al_2O_3)]$ -LSA 63 mm/s + PEO

## Conclusions

Surface coatings were produced on a permanent mould cast Mg alloy MRI 230D by LSA, PEO and hybrid process of LSA followed by PEO. The prepared coatings were characterized for microstructure and corrosion. The LSA coatings consisted predominantly of  $\beta$  ( $Mg_{17}Al_{12}$ ) phase and the PEO coating consisted mainly of  $Mg_2SiO_4$  phase. The hybrid coatings consisted of a layer of the LSA coating, which predominantly consisted of  $\beta$  ( $Mg_{17}Al_{12}$ ) phase, and a layer of PEO coating, which consisted of a mixture of  $Mg_2SiO_4$  and  $MgAl_2O_4$  phase. The microstructure and phases of the LSA coatings were found to be the same for all the laser scan speeds ranging from 21 mm/s to 84 mm/s employed in the present investigation. The LSA coated specimens did not exhibit an improvement in corrosion resistance due to the presence of micro-cracks in the coatings. However, the application of the PEO coating on top of LSA coatings improved corrosion resistance by covering the micro-cracks in the hybrid coatings, though the corrosion resistance, in most of the cases, was not as good as in the case of PEO coating on the substrate. Again, the laser scan speed did not exhibit any trend on the corrosion behavior of the LSA coated specimens. All the specimens exhibited a highly localized form of corrosion with the appearance of pits on the corroded surface. The size and number of pits were found to increase with decrease in corrosion resistance.

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