Laser Melting Effects on Microstructure and Corrosion Behavior of Plasma Electrolytic Oxidation Nanocomposite Coatings on Pure Titanium

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Abstract

In this study, pure titanium was treated using hybrid techniques of plasma electrolytic oxidation (PEO) in phosphate-based electrolyte including alumina nanoparticles and laser surface treatment (LST) process. The aim is to control laser parameters, such that heat input is adjusted to only melt PEO coating and to preserve the interface between the coating and substrate in order to create a dense layer across the thickness of PEO coating. To accomplish this purpose, after the PEO process, surface of samples was exposed to LST by an 80 W pulsed laser using the voltage of 230 V with the pulse durations of 4, 6 and 8 ms. X-ray diffraction was used to study the composition of phases and Scanning Electron Microscope (SEM) was used to study the morphology and porosity of surface and cross-sectional area and also the distribution of elements in both coating and substrate. The corrosion behaviour of coatings was examined by cyclic potentiodynamic polarization test. Results showed that in all samples, in the range of selected laser parameters, the interface between coating and substrate remains after the LST. The density of porosity on surface and cross-sectional area is reduced by about 75% in hybrid coatings of laser treated PEO (L-PEO) compared to PEO coatings. By an increase in pulse duration, deep cracks appear and transport electrolytes to substrates; therefore, the corrosion resistance of coatings are decreased.

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Keywords: Plasma Electrolytic Oxidation (PEO); Laser Surface Treatment (LST); Porosity; Corrosion; Conversion Coating; Hybrid Coating.
1. Introduction

Efforts in recent decades are directed to build and develop hybrid coating systems in order to achieve optimum surface properties by combining two or more coating processes and producing multi-layer coatings. In the meantime, the laser surface treatment (LST) due to its characteristics in terms of surface modification and ease of combination with other processes are highly regarded. The combination of anodizing with LST, Yusof et al. (2012), Yavari et al. (2014), thermal spraying with LST, Khanna et al. (2003), Antou et al. (2003), Voisey et al. (2006), and cold spray with LST, Sova et al. (2013), Poza et al. (2012), Rolland et al. (2011), Poza et al. (2011) are examples of laser treated coatings. The combination of laser with plasma electrolytic oxidation (PEO) has recently been introduced in this area, Wang et al. (2012), Rapheala et al. (2011), Rapheala et al. (2012); however, very few studies have been conducted on hybrid coatings of laser treated PEO (L-PEO). Studies in this area show that by conducting LST before PEO, as a result of radiation, surface grains are reformed and rearranged, and some phase are redistributed in a homogenous manner, Wang et al. (2012). By redistribution of phases and other reasons, such as the surface evaporation, the amount of some elements are decreased or increased. As a result of surface modifications, porosity and cracks are reduced. In other words the laser pre-treated PEO coating becomes denser than the PEO one. This process improves wear and corrosion behavior of PEO coatings, Wang et al. (2012). In the only study in which the laser were applied to the surface after PEO, results show a reduction in corrosion and abrasion resistance of L-PEO coatings, Rapheala et al. (2011). In fact, it seems that post laser treatment eliminates the interface between coating and substrate, so that corrosion and wear properties of coatings are degraded. The aim of this study is to conduct L-PEO hybrid coatings, such that by controlling the laser parameters, the extent of heat input to the surface are to be limited; thereby maintaining the interface layer and improving the behavior of hybrid coatings.

2. Materials and experimental procedures

Samples used in this study are pure titanium in the form of sheets. Chemical compositions (wt.%) of sheets are listed in table 1. These sheets were cut into 5 × 5 cm pieces with the thickness of 1 mm and then polished with 2500 emery paper. The polished samples were degreased in white acetone and then pickled in acid solutions. For conducting PEO process, a phosphate based electrolyte composition as specified in table 2 was used. The total volume of electrolyte used in the process was 500 cc. In order to form a nanocomposite coating for decreasing the percentage of voids and porosities in PEO coatings, alumina nanoparticles were used. In fact, such nanoparticles are used that have different peaks in elemental analysis from coating and substrate, so that mixing between coating and substrate at the interface layer can be studied. Transmission electron microscopy (TEM) (model Philips CM120) image of alumina nanoparticles used in this study has been illustrated in Fig. 1.
Table 1. Chemical compositions of pure titanium sheets (wt.%).

| Element | Ti  | Si  | V   | Cr  | Cu  | Fe  | Mn  | Mo  | Nb  | Sn  | Zr  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Based  | 0.01| 0.05| 0.01| 0.02| 0.05| 0.01| 0.03| 0.01| 0.05| 0.01| 0.01|

Table 2. Composition of phosphate based electrolyte.

| Composition         | Sodium phosphate (gr/lit) | Sodium hydroxide(gr/lit) | Alumina nanoparticles (gr/lit) |
|---------------------|---------------------------|--------------------------|-------------------------------|
| Density             |                           |                          |                               |
|                     | 20                        | 1                        | 6                             |

The appropriate time, the required current density and also the optimum concentration of alumina nanoparticles were selected such that PEO coatings with the thickness of about 12 μm were produced. Current density and time were respectively selected to be 156 mA/cm² and 17 minutes for all specimens. Magnetic stirrer with 250 rpm was used. This optimum stirring velocity prevents deposition and agglomeration of nanoparticles in electrolyte without creating disturbances. The temperature of coating process was set at 250°C by using continuous passage of water through the cathode. After the PEO process, the specimens were washed by water and dried in warm air.

After drying and measuring the thickness, surface of samples are melted by pulsed Nd:YAG laser with the maximum power of 80 W. LST are conducted at the voltage of 230 V, the laser spot diameter of 1.47 mm, the laser beam travel speed of 0.66 mm per second, the frequency of 6 Hz, the pulse longitudinal overlap of 92% and the transverse overlapping of 30% for laser lines. Three samples with different pulse durations (Tp) of 4, 6 and 8 ms are laser treated according to Table 3. It should be noted that in sample code of Table 3, the subscript numbers of 4, 6 and 8 indicate laser pulse durations. The mean power of laser device was measured using the power meter and then, as indicated in Table 3, the amount of energy, heat input and the percentage of longitudinal overlapping were calculated using formulations in, Tzeng (2000). Due to the nature and formation conditions of ceramic coatings in PEO process, applying inert gas protection during LST was not reasonable.

Table 3. LST variables for titanium samples.

| Sample code | Voltage (V) | mean power (j/s) | mean power density (j/mm².s) | Pulse energy (j) | Heat input (j/mm) |
|-------------|-------------|------------------|------------------------------|------------------|-------------------|
| T4          | 230         | 4.7              | 2.73                         | 0.78             | 7.12              |
| T6          | 230         | 6.4              | 3.72                         | 1.10             | 9.70              |
| T8          | 230         | 7.7              | 4.48                         | 1.28             | 11.67             |

3. Result and discussion

Figure 2 shows SEM micrographs of free surface of coatings after LST (L-PEO coatings) together with that of untreated PEO sample. The effects of increased heat input on gradual reduction of porosities are visible. As shown in Fig. 2a, untreated PEO coating has a spongy surface microstructure. Its surface is porous, uneven and bumpy. Fig. 3 shows elemental analysis of white particles accumulated on the surface (see Fig. 2) and demonstrates these particles are the accumulated primary alumina nanoparticles previously presented in the electrolyte. These nanoparticles probably during the eruption of molten oxide in PEO process are absorbed to it and then during its solidification are sintered on the free surface, Montazeri (2011), Venkateswarlu (2012).

Free surfaces of L-PEO coatings which are shown in Figs. 2 (b) to (d) obviously illustrate completely different morphology compared with that of PEO coating in Fig. 2(a). These results illustrate that by conducting LST, cauliflower-like structure of PEO coatings and their valleys and peaks are vanished, the surface of specimen becomes smooth at microscopic scale. This is due to surface melting or producing metallic mushy surface oxide as a result of
LST. In fact, melted or mushy surface oxide produced by LST flows and fills surrounding porosities and then solidifies as a dense and smooth surface layer. Fig. 2 also shows that cracks appear and fracture occurs in L-PEO coatings. Thermal shocks caused by rapid heating and cooling of surface may cause cracks and fractures in hard and brittle ceramic oxide during LST. Surface porosity fraction of each specimen calculated by ImageJ software are listed in table 4. As per Table 4, surface porosity fraction is reduced by an average of 75% in L-PEO coatings compared with PEO one.

Results of elemental analysis using energy-dispersive X-ray spectroscopy (EDS) for L-PEO coatings are compared with that of PEO coating in table 5. As per this table, by conducting LST, the aluminum content at the surface is reduced. A reason for this reduction is the decomposition of primary alumina nanoparticles where aluminum egresses from alumina compound and forms new phases such as titanium aluminide intermetallic as shown in X-ray diffraction analysis of Fig. 4. X-ray diffraction of Fig. 4 demonstrates that by conducting LST, aluminum based phases vanish and intermetallic compound is formed. Another possible reason for this reduction is the effect of laser beam interaction with the surface. Here, laser can be seen as a tool for further mixing the available elements. This means that aluminum oxide can move from surface toward the sublayers as compared with titanium oxide which may move from sublayers to the surface, thereby replacing each other. This phenomena has been observed in other studies as well, Kurtovic (2014), Hazra et al. (2015), Houdková (2014). The higher laser heat input, the further mixing and element migration occur.

Fig. 2. Free surface SEM micrographs of coatings in (a) TPEO; (b) T4; (c) T6; and (d) T8.

Fig. 3. Elemental analysis of the white particles accumulations on the surface (see Fig. 2).
Fig. 4. XRD diagram of PEO and L-PEO coatings.

Table 4. Surface porosity fraction of PEO and L-PEO coatings

| Sample code | $T_{PEO}$ | $T_4$ | $T_6$ | $T_8$ |
|-------------|-----------|-------|-------|-------|
| Surface porosity fraction (%) | 11.46 | 3.55 | 3.44 | 1.82 |

Table 5. Elemental analysis of PEO and L-PEO coatings

| Sample code | O   | Al  | P   | Ti   |
|-------------|-----|-----|-----|------|
| $T_{PEO}$   | 50.6| 30.6| 1.9 | 16.9 |
| $T_4$       | 49.8| 19.7| 6.4 | 24.1 |
| $T_6$       | 48.2| 21.9| 4.7 | 25.2 |
| $T_8$       | 47.1| 17.7| 5.4 | 29.8 |

3.1. Morphology and elemental map of cross-sections

Figure 5 shows the SEM micrographs of cross-sectional area of PEO and L-PEO coatings together with related elemental maps. In Fig 5, the pink line indicates the interface layer between coating at the top and substrate at the bottom. By an increase in the heat input of LST, morphology of cross sectional area alters significantly, such that cross-sectional porosity fraction decreases and the coating becomes denser gradually throughout its thickness. Elemental distribution map in Fig. 5 shows that in the range of studied parameters for LST, the interface between coating and substrate remains after the LST. The reason for this claim can be clearly associated with the presence of sharp interface between coating and substrate for elements that are expected to exist in only one of those layers such as oxygen and aluminum which are supposed to only be identified in coating due to the oxidation process or resulting from the electrolyte used in PEO. As can be seen in Fig.5, even in L-PEO samples with high value of heat input, these two elements exist in more quantities in the coating compared to the substrate. Fig. 5 also illustrates that elemental distribution in cross-sectional area of L-PEO coating is much more homogeneous than the one of PEO one.

Figure 6 shows cyclic potentiodynamic polarization curve of specimens. The corrosion potential, the corrosion current density, Tafel slope of the anodic and cathodic polarization curve and corrosion resistance of specimens derived from polarization curves are listed in table 6. The curves in Fig. 6 show negative hysteresis which demonstrates the capability of pitting recovery in reversal potential scan. The hysteresis loops are approximately equal in all samples; however, corrosion current value in reverse scan in $T_8$ sample is about 8 times higher than other L-PEO
coatings; therefore, T4 and T6 represents much more capability for pitting recovery. This result is consistent with the measure \( i_{corr} \) value in Table 6.

Since the SEM image of free surfaces (Figs. 2b, 2c and 2d) and cross-sections (Fig. 5) of L-PEO coatings shows no significant differences, probably it can be concluded that those minor differences are due to connections between porosities and cracks in the coating. Actually specimens of T4 and T6 have ability to prevent diffusion of electrolyte to interface of substrate and coating, but in T8, it seems that this ability is reduced and the electrolyte has more interactions with metallic substrate. As previously mentioned, with laser surface treatment and increasing heat input due to gradual increasing pulse duration of laser beam, cracks and fractures appear on the surface of L-PEO coating (see Figs. 2b to 2d). It is possible that in T8, with the highest heat input in Table 3, cracks join together and produce deeper cracks, thereby allowing transportation of electrolyte to sublayers and reducing the corrosion resistance.

Table 6. Calculated parameters extracted from cyclic potentiodynamic polarization of L-PEO coatings

| Sample code | \( E_{corr} \) (mV vs. SCE) | \( I_{corr} \) (nA/cm²) | \( \beta_a \) (V/decade) | \( \beta_c \) (V/decade) | \( E_b \) (mV vs. SCE) | \( \times 10^4 R_p \) (Ω·cm²) |
|-------------|--------------------------|---------------------|-----------------|-----------------|----------------|----------------------|
| T4          | -200                     | 79.43               | 0.12            | 0.07            | -160           | 24.16                |
| T6          | -250                     | 83.18               | 0.05            | 0.04            | -180           | 11.60                |
| T8          | -280                     | 138.04              | 0.06            | 0.05            | -240           | 8.58                 |

Fig. 5. Elemental distribution map of PEO and L-PEO coatings.

Fig. 6. Cycle potentiodynamic polarization diagram of PEO coating after laser surface treatment in voltage of 230.
4. Conclusion

- Interface layer of L-PEO coatings can be preserved by controlling the pulsed laser parameters.
- Microstructure and morphology of both free surface and cross-sectional area of L-PEO coatings alter significantly compared with that of PEO coatings. Surface porosity fractions are reduced by about 75% and the free surface becomes level or even at microscopic scale. Moreover, microstructure of coatings shows more homogeneity after remelting.
- By an increase in heat input of LST, cracks and fractures appear in both free surfaces and cross-sectional areas. These cracks and fracture gradually becomes deeper and more connected, thereby transporting electrolyte to sublayers which in turn decreases the corrosion resistance of L-PEO coatings at high laser heat input.

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