Original Article

Erosion and corrosion resistance of plasma electrolytic oxidized 6082 aluminum alloy surface at low and high temperatures

Ali Algahtani\textsuperscript{a, b}, Essam R.I. Mahmoud\textsuperscript{c, d, *}

\textsuperscript{a} Department of Mechanical Engineering, King Khalid University, Abha, Saudi Arabia
\textsuperscript{b} Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha, Saudi Arabia
\textsuperscript{c} Department of Mechanical Engineering, Islamic University of Madinah, Madinah, Saudi Arabia
\textsuperscript{d} Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt

\begin{abstract}
This paper embodies the findings of a study on improving the surface tribology of Al alloy 6082-T6 through plasma electrolytic oxidation (PEO) process. The surface macro/microstructure and composition were investigated. Electrochemical measurements were performed at temperatures of 20 and 80 °C using an inductively coupled plasma and open circuit potential tests after immersion in 3.5%NaCl solution. The erosion tests were performed with water carrying sand particles at different sand loadings (200 and 1000 mg/l) and temperatures (20 and 80 °C). After erosion experiments, the weight loss measurements were recorded, and the worn surfaces were assessed through SEM study and profilometry analysis. The micro-hardness of the coated layer and the substrate were measured before and after the erosion test. The formed PEO layer of 40 \( \mu \)m thick was almost sound, uniform, well adhered to the substrate and consisted mainly of alumina phases (\( \alpha-Al_2O_3 \), \( \gamma-Al_2O_3 \)). The relative proportions of \( \alpha-Al_2O_3 \) to \( \gamma-Al_2O_3 \) were 31: 79%. The PEO coating shows much better corrosion and erosion resistance and less surface damage compared to the aluminum substrate, especially at elevated temperature and high sand loading. The PEO hardness increases as the distance from the substrate increases until near the middle of the coating.
\end{abstract}

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Aluminium and its alloys have been widely used in various industries because of their properties, such as lightness, high specific strength, high strength-to-weight ratio, high thermal and electrical conductivities, good formability and excellent machinability \cite{1,2}. Also, Al is a passive metal which can naturally form an oxide dense layer to give corrosion protection \cite{3}. However, under aggressive environments, such as petroleum environments, Al surfaces can be subjected to many types of failure due to wear and erosion \cite{4}. One of the most considerations to minimise the cost in industry is to minimise the equipment downtime. So, the surface treatment should achieve this objective in the long-term project regardless the cost of each technology individually \cite{5}. Several surface modification techniques have been developed in recent years to
enhance corrosion and wear resistance, and consequently, increase the lifetime of the components [6–9]. Moreover, the cost of each technique will consider different requirements such as surface conditions and component’s geometry [10].

The plasma electrolytic oxidation (PEO) process is an electrochemical surface conversion process that produces an oxide coating on light metals and their alloys [11,12]. PEO is considered to be a complex process for the following reasons. Firstly, there are many process parameters, such as electrical parameters, temperature, and electrolyte types that affect the final coating product of the PEO process [13,14]. Secondly, in the discharge channel of PEO process, two processes are happening simultaneously to generate the oxide layers. These are the electrochemical process and plasma chemical process [15]. The coating, which is ceramic, is produced by passing a modulated electrical current through an aqueous solution (usually alkaline) where plasma discharge is formed around the component generating an oxide film with relatively high thickness [16,17]. The resulting coating is well adhered to the substrate and is characterised by high wear and corrosion resistance and good thermal conductivity [18]. PEO can be done on a larger batch in a bath and requires post-treatment steps [20]. Many authors have evaluated the wear behaviour of PEO coatings and concluded that the formed thick oxide coating can improve the wear resistance of an Al substrate by 150–200% [17–20]. The oxide film coating can be affected by changing treatment parameters depending on the purpose of the coating [15]. Gnedenkov et al. [21] reported that parameters of the polarizing signal have a significant effect on formation conditions and the quality of resulting coatings. Egorkin et al. [22] studied effect of duty cycle and oxidation time during the PEO in the thickness and quality of the coating produced on 5754 Al alloy. Their results showed that increasing the duty cycle leads to an increase of the PEO-layers thickness and, in the same time, decrease the porosity, which leads to improving the barrier properties against wear and microhardness of the coating [22]. Gu et al. [23] showed that the average coating thickness is highly dependent on the times of treatment for different current densities. The average coatings thickness increases linearly with the increase in the applied current density, while it decreases and becomes non-linear in the last stages [23]. Most of previous research works agreed that these coating materials increased the wear and corrosion resistance more than the uncoated ones. Qiu et al. [24] showed that the corrosion performance of PEO coating on ZK60 Mg alloy can be improved by increasing the current density in the PEO process. For example, using a current density of 3 A/dm² in the PEO process will decrease the corrosion current density of the Mg substrate from 1.05 × 10⁻⁴ to 8.7 × 10⁻⁶ A/cm² while a current density of 3 A/dm² will decrease the corrosion current density to 4.43 × 10⁻⁷ A/cm² with an enhancement factor of 240 times better than the Mg substrate. Hussein et al. [25] showed that eliminating the strongest discharges during PEO process, by controlling the ratio of the positive to negative pulse currents, would significantly increase coatings quality and consequently improve the PEO coating for industrial applications generally [25]. In particular, the enhancements of PEO coating in improving the erosion and corrosion resistances compared to the Al substrate under oil and gas environments expands its applications in this sector [26]. Also, it was found that as the thickness of the PEO coating increased, the corrosion resistance increased [27]. In another study, Mistry et al. [28] found that PEO coating has enhanced the tribological performance of a cylinder wall made of eutectic Al–Si alloy for a top piston ring better than conventional nickel–ceramic (Ni–SiC) coating since PEO has greater durability and lower wear. This implies that PEO coating gives better wear resistance and, consequently, increases the life service of the components [28]. Regarding the erosion performance of PEO coatings, Barik et al. [29] has studied their response under different kinetic energy conditions and found that PEO provides superior protection to the Al substrate at low energies but not enough resistance at high energy levels, due to the removal of the top layer of the coating. However, their study requires further research, taking into consideration different factors, such as high temperature, different sand concentrations and different impact angles [29]. One of the disadvantages of the PEO coating microstructure is the porous layer at the top surface of PEO [30,31]. A new approach was introduced by Gnedenkov et al. [32] for the formation of composite polymer-containing coatings by plasma electrolytic oxidation using superdispersed polytetrafluoroethylene (SPTFE) at the surface of Mg alloy MA8. Significant improvement in the corrosion and wear resistance of the polymer-containing coating was recorded. This can be attributed to the morphology and insulating properties of surface layers and solid lubrication effect of SPTFE particles [32].

This work has investigated the enhancements of Plasma Electrolytic Oxidation (PEO) coatings on the performance of 6082 Al alloy surface against erosion and corrosion environments. The microstructure of the coating layer was detailed investigated. The hardness, erosion resistance, and corrosion behavior of the coating layer were detailed evaluated at ambient (20 °C) and higher (80 °C) temperatures.

2. Experimental work

The substrate used for plasma electrolytic oxidation (PEO) coating was 6082-T6 Al alloy with chemical composition listed in Table 1. T6 refers to the temper number, which means solution heat-treated and artificially aged. Coatings were prepared using a 100 kW Keromite™ processing rig and an electrolyte consisting primarily of a dilute aqueous solution of potassium hydroxide and sodium silicate. AC power was applied with a 50 Hz modulation, applying both positive and negative potential pulses to the substrates, immersed in commercially

| Table 1 – Chemical compositions of the 6082-T6 aluminum alloy, wt%.
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
</tr>
<tr>
<td>0.957</td>
</tr>
</tbody>
</table>
available electrolytes. The counter electrode was a cylinder of stainless steel. Stirring and cooling systems maintained the temperature of the electrolyte at 25 °C during the process. The plasma electrolytic oxidized specimens and the Al substrate were cut into discs of 25.40 mm diameter and a thickness of 10 mm ± 0.01 mm to be fitted in the holder for erosion and electrochemistry experiments suitable for the rig available in the lab.

The microstructures of the coated layer and substrates were investigated using optical microscope and Scanning Electron Microscope (Philips XL30 ESEM environmental SEM) equipped Oxford Instruments INCA 250 EDX system analyzer after standard methods of metallography and immersing the samples in an etchant of 4% NaOH. The substrate and the PEO coated layer were analyzed by X-ray diffractometer (XRD, D8 Discover with GADDS system, 35 kV, 80 mA, MoKα radiation), to identify, experimentally, the existent phases that were originally found or newly formed ones during the coating process and erosion tests.

A series of electrochemistry experiments was used to evaluate the corrosion performances of PEO coating together with the Al substrate in the electrolyte of 3.5% NaCl solution. The reference electrode is Ag/AgCl. The first experiment was open circuit potential (OCP) test where the potential (in Volts) was recorded against time (in seconds) for 24 h. The second experiment was DC anodic polarization measurements, which involves changing the electrode potential from its OCP in a certain direction and a given scan rate. Anodic Polarization (AP) tests were involved in measuring the scan from OCP to more positive voltages (up to 1 V from OCP) to reveal more information about the kinetics of the corrosion and its type. The third experiment was the AC impedance test which was applied to the materials using an electrochemical measurement unit called Solarton (SI 1280B). The amplitude of the sinusoidal voltage was 10 mV, which was selected to keep the system linear. The measurements were performed at frequencies ranging from the high value of 20 kHz to low-frequency value of 0.1 kHz to minimize the sample perturbation.

The erosion tests were performed using a recirculation jet impinging rig. The rig was equipped with a thermostat to monitor the water temperature by controlling heating coils immersed in the water. The water carrying sand particles was impinging the sample surface through two 4 mm nozzles. Each sample was f1RX406146821CNxed at a distance of 20 mm from the nozzle where the water was ejected at a speed of 10 m/s. Two sand loadings (200 and 1000 mg/l) and two temperatures (20 and 80 °C) were selected as the main experimental variables to go from medium to highly severe erosion conditions. After completing the erosion experiments, the weight loss measurements were recorded after 2, 5, 8 and 10 h respectively. The surfaces of the coated samples were analyzed after the erosion experiments using “Form Talysurf 120L” equipment in order to measure the surface shape, texture, profile of volumetric damage and to identify the depth of the attack and the zones that suffer the greatest degradation. The microhardness of the coated layer and the substrate were measured (before and after the erosion test) using Knoop indenter. The shape of this type of indenter is an elongated diamond pyramid and it is more sensitive to surface conditions than Vickers test which is more suitable for thin coatings [33].

3. Results and discussions

3.1. Macro/microstructure analysis

Fig. 1 shows the microstructure of the substrate 6082-T6 Al alloy in both polished and etched conditions. The micrographs reveal particles with different sizes distributed within the Al matrix. These particles may be the well-known intermetallics (β-Al₃FeSi, Mg₄Si, Al₃Mn₃Si, Mg₄Si, α-Al(FeMn)Si) shown in this type of Al alloy [34,35].

The SEM surface morphologies for PEO sample in Fig. 2 shows high numbers of particle-like structures in the oxide layer that have lamellar, spherical and irregular shapes. These surface morphologies are characterised by macro-particles similar to volcano-like eruptions that resulted from the spark discharges during the layer growth [6]. The cross-sectional microstructure, shown in Fig. 3(a), reveals that the PEO coating consisted of two main distinct layers of total thickness of about 90 μm. Firstly, the inner interface layer, which was dense and well adhered to the substrate. This layer composes the major part of the coatings and it has a thickness of approximately 40 μm. This interface coating layer has a uniform distribution with the substrate, as shown in the cross-sectional image in Fig. 3(a). Also, micro-scale porosity can be observed in PEO surface (arrowed with circle in Fig. 3(b)) which could be due to the spark discharges during the layer growth. The second layer is the outer porous layer, which is not uniform compared to the inner one. In addition, the material becomes rougher as

---

**Fig. 1** – Microstructure of the substrate 6082-T6 Al alloy in (a) polished and (b) etched conditions.
the distance from the substrate increases. According to Curran and Clyne [6], this outer layer has a higher amount of $\gamma\text{-Al}_2\text{O}_3$ phase than the inner layer because of the final stage of discharges taking place during the PEO process.

For the XRD analysis, the main phases detected in PEO coatings are alumina phases ($\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$) beside the Al element of the substrate as shown in Fig. 4. This result is consistent with the literature where $\alpha\text{-Al}_2\text{O}_3$ was formed in the PEO coating applied on Al alloy on the inner coating layer due to the high temperature during the discharge stage of the PEO process. Also, the amorphous $\gamma\text{-Al}_2\text{O}_3$ alumina is abundant in the outer layer, which is formed during the cooling stages because of the contact between the molten alumina and the electrolyte. The relative proportions of alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) phases can be estimated from the intensity (area) of the peaks in the XRD plots for the material. Conventionally, this is achieved using the most intense peaks for each phase and using an reference intensity ratio (RIR) for each phase. RIR values are normalised against corundum (alpha alumina, which has a value of 1.0). Due to peak overlap and strong scattering from the substrate, it was not possible to use the most intense peaks. Therefore, to gauge the relative proportions, less intense, but unobstructed peaks were used at 25.578° for alpha and 19.318° for gamma. The area of the peaks was then divided by the product of the RIR and the relative intensity of the peak (from the database). The database (ICDD, International Centre for Diffraction Data) entries used were 00-046-1212 and 01-074-4629 for alpha and gamma respectively. The area of the peaks was determined using the software XPerf Highscore Plus. The amount of alumina phases ($\alpha\text{-Al}_2\text{O}_3$) available in PEO coating was found to be 31%.
3.2. **Electrochemistry experimental results**

3.2.1. **Inductively coupled plasma (ICP) test results**

No aluminium ions (Al\(^{3+}\)) were detected from the 3.5% NaCl solutions using ICP technique after each test condition for the coated sample at low (20 °C) or high (80 °C) temperatures. After the 80 °C free corrosion tests, the samples were immersed in the solution for another 24 h and, also, no ions of Al\(^{3+}\) were released.

3.2.2. **Mass loss (Al\(^{3+}\)) from polarization test**

Fig. 5 shows the potential current versus time plot to calculate the charge transfer at 400 mV for a PEO coated sample. The PEO coating showed a gradual increase of the current density throughout the test period without any sudden increase of the current, which indicates a low rate of ion transfer through the coating. In addition, the current values were an order of magnitude lower. The amount of aluminium ions (Al\(^{3+}\)) released from the substrate through the coating samples after immersion in 3.5% NaCl solution for 24 h was 1 mg. Fig. 6 shows the results of the anodic polarization measurements for PEO layer together with Al substrate. The breakdown voltages for both materials can be determined from the anodic polarization curves at the potential value where the current increased rapidly and deviated from the initial growing rate. The value of the breakdown potentials of the PEO coated material was about 1.1 V and 0.3 V for Al substrate.

3.2.3. **Open circuit potential (OCP) measurements results**

The open circuit potential (OCP) experiments were applied for 30 s to find the starting OCP values for PEO coating and Al substrate. Many measurements were made, and the average values were presented in Fig. 7(a). This figure represents the initial OCP measurements when the samples were immersed in 3.5% NaCl without applying any potential. Firstly, it can be seen that the Al sample has the most negative OCP value of −0.69 V. It is expected that Al has a low negative value of \(E_{corr}\) since it can release three electrons per atom and, consequently, makes the Al to be used as an anode in power sources applications. Moreover, it has been reported that in chloride solutions it has an \(E_{corr}\) value of −0.75 V/SCE [35]. However, PEO coating has the higher starting OCP value with −0.048 V. According to Wang et al. [36], high open circuit potentials give better corrosion protection, which indicates the enhancements of the coating in the corrosion performance. The OCP measurements have been extended for five thousand seconds, as shown in Fig. 7(b), and it has been observed that the OCP value for the PEO sample dropped to the OCP value for the Al substrate after about 650 s. This sudden change in the OCP curve can indicate a rapid movement of ions through the coating part (insulator). In general, anodic areas are, at least in the early stages, much smaller than cathodic areas. Therefore, in the early stages, the corrosion potential is more...
positive. However, with an increase in anodic sites during immersion, the corrosion potential becomes more negative.

### 3.3. Erosion test results

This part presents the results of erosion experiments performed on the samples of the Al substrate and the PEO coating. Fig. 8 shows the weight loss measurements of the materials for ten-hour experiments under low (200 mg/l) and high (1000 mg/l) sand loadings at temperatures of 20 and 80°C. The data points have been fitted with either linear regression line or polynomial curve according to the weight loss trend for each material. A consistent increase in the wear losses has been observed with increasing both time and sand loading. At low temperature of 20°C and low sand loading of 200 mg/l (Fig. 8(a)), the weight loss was very close to that of the Al substrate. On the other hand, the PEO coating has a lower erosion rate and its weight loss is less than the Al substrate at high sand loading of 1000 mg/l, as shown in Fig. 8(b). At elevated temperature (80°C), the erosion rates are higher than at room temperature tests for the coated sample and Al substrate as illustrated in Fig. 8(c) and (d); however, it is shown that PEO coating has better erosion performance. The increase of the weight loss at 80°C test of PEO coated samples can be explained by the viscosity effect of the fluid at high temperature, where the fluid velocity increases and the kinetic energy of the impacting particles will, consequently, increase resulting in higher erosion rates. However, good erosion resistance of PEO coating under all test conditions can be explained by coating uniformity, good adhesion to the substrate (Fig. 3) and low porosity level. It has been reported that PEO coating exhibits excellent adhesion since it is a conversion coating process [36], and its adhesion is not directly proportional to the coating thickness [13]. In addition, the existence of the dense aluminium oxide (α-Al2O3) improves the material mechanical properties by giving it a high hardness, which increases the level of protection against erosion. Also, the wear loss rate increases gradually.

Fig. 9 illustrates the effect of PEO surfaces in terms of surface condition at two sand loadings (200 and 1000 mg/l) over ten-hour tests. It can be seen that the polished surfaces of PEO coating have better erosion resistance than the unpolished ones by about 150% at low sand loading (Fig. 9(a)). At high impact sand loading, as shown in Fig. 9(b), this percentage
has decreased to 105%. The hypothesis is that the rougher surface will have lower surface integrity because of more valleys and higher number of peaks, which could be easily removed due to the impact of sand particles, and, as a result, the erosion rate will increase. In average, the enhancement factor for the polished/unpolished surface is doubled at both 200 and 1000 mg/l sand loadings. There is a direct relationship between surface condition and weight loss in erosion experiments: rougher material is more easily removed because of the surface integrity. However, this does not apply to the very high sand loading (2000 mg/l) as clearly shown in Fig. 10. This is due to the high amount of material loss at this condition and the difference in weight loss between rough and soft surfaces is lower at high loading conditions.

Optical and SEM images were taken for the eroded surface after erosion test conditions (Figs. 11 and 12). The surface macrostructure of PEO samples shows some small pits (or perforation sites) (dark areas in Fig. 11(a)) at low temperature (20 °C) and sand loading (200 mg/l). Although there is no indication of the high material loss since the wear propagations did not reach the substrate. The number of these perforation sites is increased at high sand loading condition as shown in Fig. 12.

**Fig. 10** – Effect of PEO surface conditions on weight loss measurements for duration of two-hours at higher sand loading (2000 mg/l); impingement angle of 90°; and temperature of 20 °C.

**Fig. 11** – Optical micrographs of damaged surfaces after erosion test for; (a) sand loading of 200 mg/l and (b) 1000 mg/l, for test duration of ten-hours at temperatures of 20 °C.

**Fig. 12** – SEM images of PEO coating surface after erosion test at temperature of 80 °C for different sand loadings of; (a) 200 mg/l and (b) 1000 mg/l.
3.4. Hardness measurements

Fig. 13 shows the micro-hardness values on the top and cross-sectional surfaces of the tested materials. The hardness measurements of the eroded regions of the coatings were compared with the un-eroded surfaces after the test and it is obvious that the hardness for the eroded surface are higher for all materials. The increase of the material’s hardness after the erosion tests is expected since there is a work hardening undergone on the surface due to the effect of the impact sand particles loading. The PEO coating is much harder than the Al substrate at both eroded and un-eroded conditions. Regarding the hardness distributions through the thickness, Fig. 14 shows that the material’s hardness increases as the distance from the substrate increases until near the middle of the coating. The highest hardness value across the PEO coating is about 17 μm. It was reported by [37] that the maximum hardness value for PEO coating occurs at 10–30 μm from the interface and this change of hardness is due to the phase transformation from α-Al₂O₃ to γ-Al₂O₃ near the outer layer [38].

3.5. Talysurf tests

Figs. 15–18 show the surface textures of the tested samples after 10 h tests for different sand loadings (200 and 1000 mg/l) and different temperatures (20 and 80 °C). The 3-D profile of the sample was captured to show the affected zone of the surface and its type in terms of the deformation conditions such as plastic deformation, cutting chip, etc. Also, the materials’ volume loss due to impact particles was calculated to be compared with the weight loss measurements. There is severe damage on the Al (Figs. 15(a) and 16(a)) more than PEO coating (Figs. 15(b) and 16(b)) for both sand loadings of 200 and 1000 mg/l. Also, it can be seen that the impact loading for PEO sample is concentrated at the impacting area as the sand loading increases (Fig. 16(b)) whereas the affected surface is wider at low sand loading (Fig. 15(b)). Also, the effect of the elevated temperatures (80 °C) is quite limited in case of PEO coatings where there is no considerable increase in depth loss between room temperature tests and temperature of 80 °C tests as shown in Figs. 17 and 18.
Fig. 16 – 3-D Profilometry after erosion test for Al substrate and PEO coating at lower temperature (20 °C) for 1000 mg/l sand loading.

Fig. 17 – 3-D Profilometry after erosion test for Al substrate and PEO coating at higher temperature (80 °C) for 200 mg/l sand loading.

Fig. 18 – 3-D Profilometry after erosion test for Al substrate and PEO coating at higher temperature (80 °C) for 1000 mg/l sand loading.

4. Summary and conclusions

In the present work, an oxide layer was formed on the surface of Al 6082-T6 through plasma electrolytic oxidation process. The coating surface macro/microstructure and composition were investigated using optical, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Electrochemical measurements were performed at temperatures of 20 and 80 °C using inductively coupled plasma and open circuit potential tests after immersion in 3.5%NaCl solution for 24 h. The erosion tests were performed with water carrying sand particles at
different sand loadings (200 and 1000 mg/l) and two temperatures (20 and 80 °C). After erosion experiments, the weight loss measurements were recorded, and the worn surfaces were assessed through SEM study and profilometry analysis. The micro-hardness of the coated layer and the substrate were measured before and after the erosion test. The following conclusions are reported:

- The formed PEO coating consisted of two main layers. The inner layer of 40 μm thick was almost sound, uniform and well adhered to the substrate. The outer layer was porous and not uniform compared to the inner one.
- The PEO coating layer consisted mainly of alumina phases (α-Al₂O₃, γ-Al₂O₃) beside the Al element of the substrate. The relative proportions of alpha alumina (α-Al₂O₃) to gamma alumina (γ-Al₂O₃) phases were 31:79%.
- The anodic polarization tests indicated that PEO coating had a lower corrosion current density than Al substrate, which indicates better corrosion resistance. The PEO coating had the lowest amount of aluminium ions (Al³⁺) released from the coating samples after immersion in 3.5%NaCl solution for 24 h.
- The PEO coating had lower erosion rate and its weight loss was less than that of the Al substrate under all test conditions, especially at elevated temperature and high sand loading.
- The PEO coating was much harder than the Al substrate at both eroded and un-eroded conditions. The PEO hardness increased as the distance from the substrate increased until near the middle of the coating (about 17 μm) and then decreased.
- The Talysurf test showed that the Al substrate eroded surface suffered severe damage more than the PEO coating, especially at elevated temperature and high sand loading.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

Authors thankfully acknowledge the funding and support provided by the Scientific Research Deanship, King Khalid University (KKU), Abha-Asir, Saudi Arabia, with grant number G.R.P.2/6/38 under the research group “Materials & Production” to complete the research work.

REFERENCES