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Stress Corrosion Cracking Behaviour of a Surface Modified Magnesium Alloy

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Abstract

The effect of plasma electrolytic oxidation (PEO) treatment on the stress corrosion cracking (SCC) of a cast magnesium alloy was assessed. Even though the PEO coating has offered an improved corrosion resistance, as evidenced in electrochemical tests, its effect in improving the SCC resistance in ASTM D1384 test solution was only marginal. The SCC behaviour of PEO coated specimens was attributed to the development of micro cracks in the coating, leading to cracking of the substrate under slow strain rate test conditions.

Key words

Magnesium alloy; plasma electrolytic oxidation; microstructure; electrochemical behaviour; stress corrosion cracking

In recent times magnesium alloys, owing to their excellent combination of properties, find numerous applications in electronic, automobiles and aerospace industries. However, these alloys suffer heavily on account of their poor corrosion resistance in many environments [1-3] and many of the alloys have been reported to exhibit a high degree of susceptibility to environmentally assisted cracking [4-6]. A good number of surface modification procedures have been developed and contemplated with a reasonable degree of success for different applications [7-9]. The plasma electrolytic oxidation (PEO) treatment has been found to be quite effective in improving the tribological and corrosion properties of magnesium alloys [10-12]. Even though many researchers have assessed the general corrosion behaviour of PEO coated magnesium alloys, there seems to be no published information on the stress corrosion cracking behaviour of magnesium alloys with PEO coating available. This work addresses the electrochemical corrosion and stress corrosion cracking behaviour of a cast magnesium alloy, with and without a silicate based PEO coating.

Magnesium alloy specimens corresponding to the alloy designation AM50 were received in the as-cast condition. Specimens of size 30 mm x 30 mm x 5 mm were ground successively in 320, 500, 800, 1000 and 2500 grit emery sheets for the PEO treatment. The PEO treatment was carried out using a simple DC power supply source of 600V, 4A capacity. The specimens were PEO coated in an electrolyte constituted by 10 g.L⁻¹ sodium hydroxide and 10 g.L⁻¹ sodium silicate in double distilled water. The PEO treatment was performed at a current density of 15 mA·cm⁻², to a final voltage of 420V. The coating process was continued at 420V until the current drifted down close to zero, evidenced by the reduction in sparks. The temperature of the electrolyte was maintained in the range 15°C-25°C and the electrolyte was stirred using a magnetic stirrer.

Electrochemical measurements were made in an ACM Gill AC potentiostat/galvanostat FRA, using a three electrode cell. The corrosion potential of the specimens was measured for a period of 1800 s before performing the electrochemical tests. Electrochemical impedance measurements were performed with an applied amplitude of 10 mV in the frequency range 0.1 Hz to 30000 Hz at the corrosion potential. Potentiodynamic polarisation studies were carried out at a sweep rate of 0.5 mV·s⁻¹. The uncoated specimens were prepared by polishing up to 2500 grit emery for the electrochemical studies, while the PEO coated specimens were used in the as-coated condition. Experiments were made in duplicate for ascertaining the reproducibility, and all the experiments were performed at ambient temperature (21 ± 2°C), in as-prepared, non-deaerated ASTM D1384 solution containing 148 mg Na₂SO₄, 165 mg NaCl and 138 mg NaHCO₃ in one liter of double distilled water.

The tensile specimens for the slow strain rate tensile (SSRT) tests were of cylindrical configuration, with a 5 mm gauge diameter and 10 mm gauge length. The overall length of the specimen was 100 mm. SSRT tests were performed in ASTM D1384 test solution by following the ISO standard 7359—Part 7 [13]. In SSRT tests in air the specimen elongation was measured using a clip-on gauge in addition to the employment of two linear variable displacement transducers (LVDT) attached to the specimen grips.

The optical micrograph of the AM50 alloy in [Figure 1](#) reveals the coarse grained structure of this material, characteristic of gravity cast condition. The near-uniform

distribution of $Mg_{17}Al_{12}$ precipitates in the matrix is also evident in this micrograph. During the PEO process, the sparking and the first discharge were noticed at a voltage level of 240 V in this electrolyte. The sparking was uniform and distributed all across the surface of the specimens treated, and the intensity of sparks was observed to increase with increasing voltage. The maximum voltage for the PEO coating was fixed as 420 V, based on prior optimization experiments to achieve a coating thickness of around 10 μm -15 μm . Further, this voltage level was preferred for treating large sized specimens with the problems of excessive heating of the electrolyte and the consequent burning of specimens. Thickness measurements made using an eddy current probe showed an average thickness of around 12 μm , which was corroborated by the microscopic examination. The cross section of a PEO coated specimen is shown in **Figure 2(a)** and a near-uniform thickness across the section of the specimen can be noticed. The morphology of the PEO coated surface presented in **Figure 2(b)** reveals the presence of fine pores in the oxide structure formed on the surface.

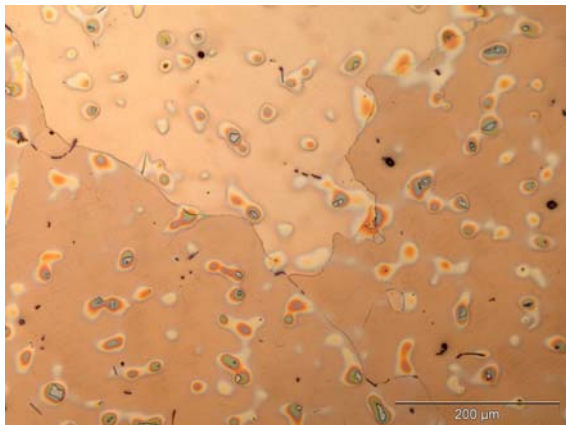
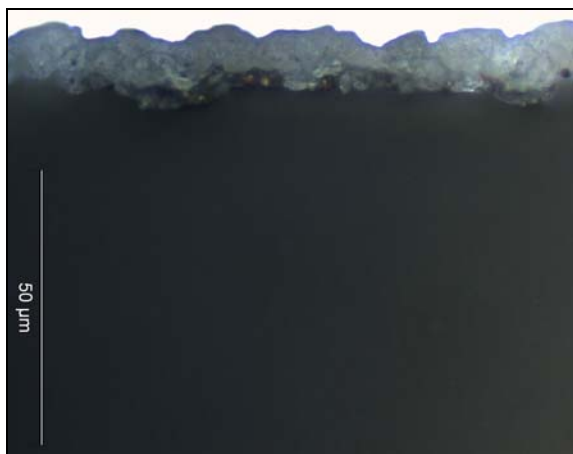
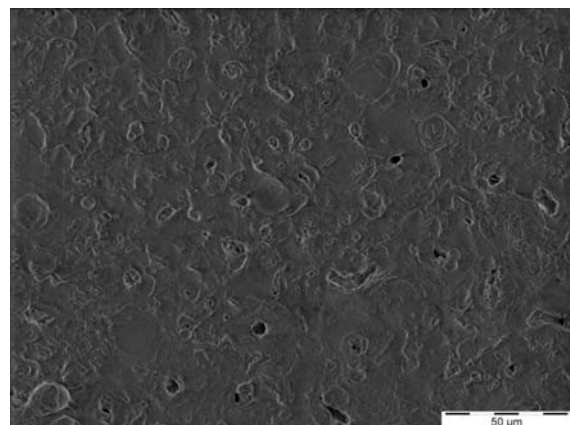


Figure 1 Optical micrograph of the AM50 alloy



(a) Cross section



(b) Surface morphology

Figure 2 Optical (a) and scanning electron (b) micrographs of a PEO coated AM50 alloy

The electrochemical impedance and polarisation behaviour of the untreated and PEO coated specimens are presented in **Figures 3(a) and (b)**, respectively. The corrosion resistance of the untreated AM50 alloy was observed to be around 4900 ohm.cm^2 . On the other hand, the PEO coated specimen registered a resistance value of $6.3 \times 10^5 \text{ ohm.cm}^2$, showing nearly a two orders of magnitude enhancement in corrosion resistance. The corrosion potential of the PEO coated specimen based on 30 minutes rest potential measurements, and also obtained from the E_{corr} value, seems to be nobler than that of the untreated counterpart. The corrosion current density values were $1.2 \times 10^{-2} \text{ mA.cm}^{-2}$ and $4.3 \times 10^{-5} \text{ mA.cm}^{-2}$ for the untreated and PEO coated specimens, respectively. The above observations, with respect to the corrosion behaviour, were in agreement with some of the documented literature [11, 14-15].

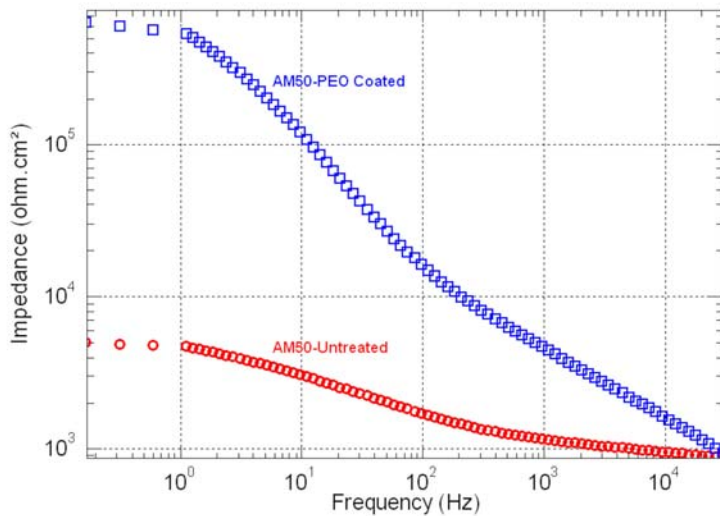


Figure 3(a) Electrochemical impedance behaviour (Bode plot) of untreated and PEO coated AM50 alloy

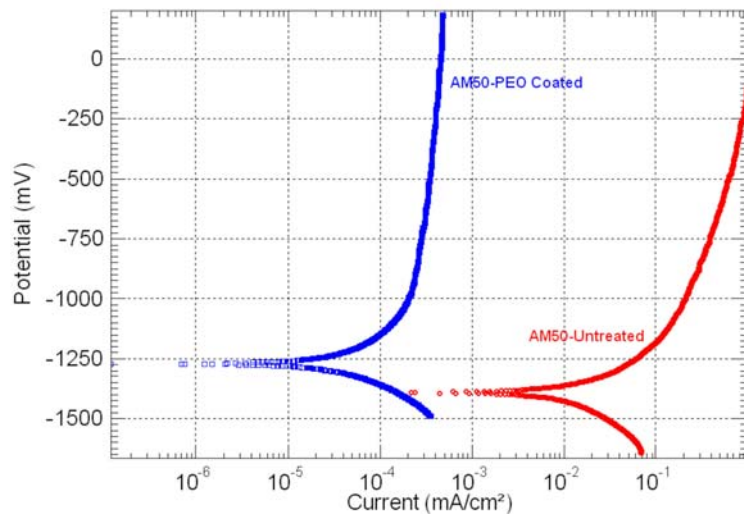
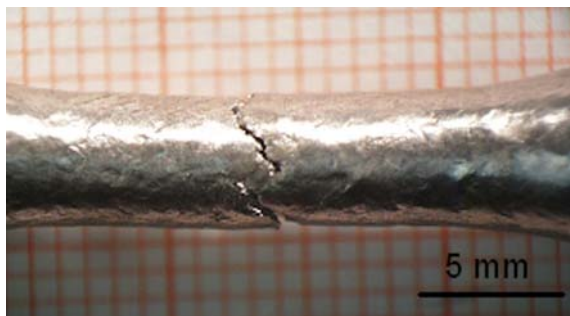
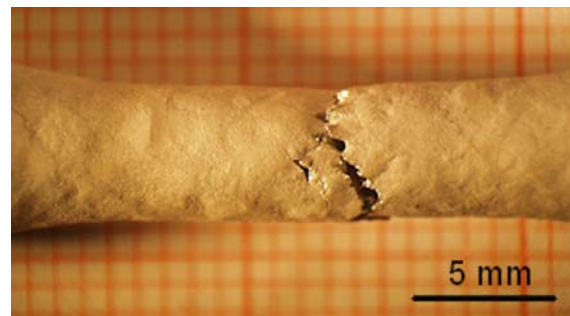


Figure 3(b) Potentiodynamic polarization behaviour of untreated and PEO coated AM50 alloy

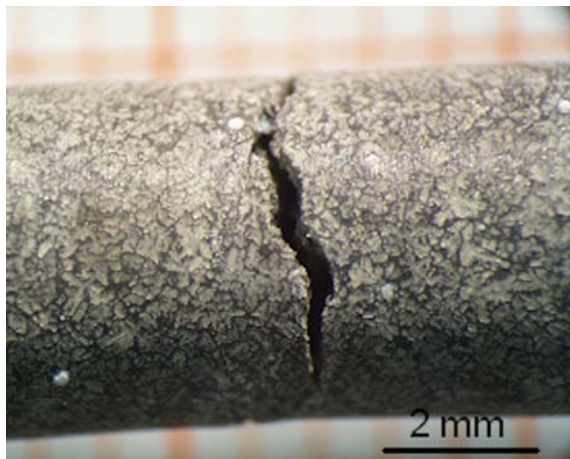
The ultimate strength and the elongation values of the untreated specimen were 200 MPa and 24%, respectively and that of the PEO coated specimen were 185 MPa and 23%, respectively. The optical macrographs of the untreated and coated specimens subjected to tensile tests in air, shown in **Figures 4 (a) and (b)**, suggest that the tensile deformation behaviour in both these specimens could have been similar. However, there was a marginal difference in the elongation values between these specimens, which could be attributed to the presence of this brittle ceramic coating of the PEO specimen. On the other hand, the reason for the marginal lowering of the tensile strength in the PEO specimen is not known. In a work on nitrocarburising, the development of hard nitride/carbonitride layer was reported to lower the ultimate tensile strength of austenitic stainless steel [16]. Correlating the cited literature, it is postulated that there could have been differences in the work hardening behaviour during the tensile tests, in the presence of the PEO coating. The higher magnification scanning electron micrograph (**Figures 4 (c) and (d)**) did reveal the presence of cracks in the PEO coating and also the damaged regions exposing the substrate. This suggests that the deformation characteristics were distinctly different for these two cases and this requires further attention for a better understanding.



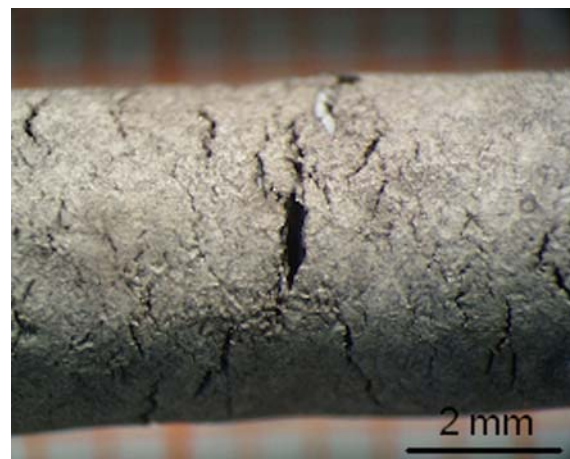
(a) Untreated



(b) PEO coated



(c) Untreated



(d) PEO coated

Figure 4 Optical macrographs and scanning electron micrographs showing the surface appearance of the SSRT tested AM50 alloy in air

The stress vs. strain plots of the untreated and PEO coated specimens in air at a strain rate of $1E-6$, and that of the same in ASTM D1384 test solution at a strain rate of $1E-7$ are presented in **Figure 5**. As it was difficult to use a clip gauge in tests involving solutions, the displacement measurements were made only with LVDTs, and for uniformity and comparison purposes, the strain values measured with LVDTs are presented in this figure for all the conditions.

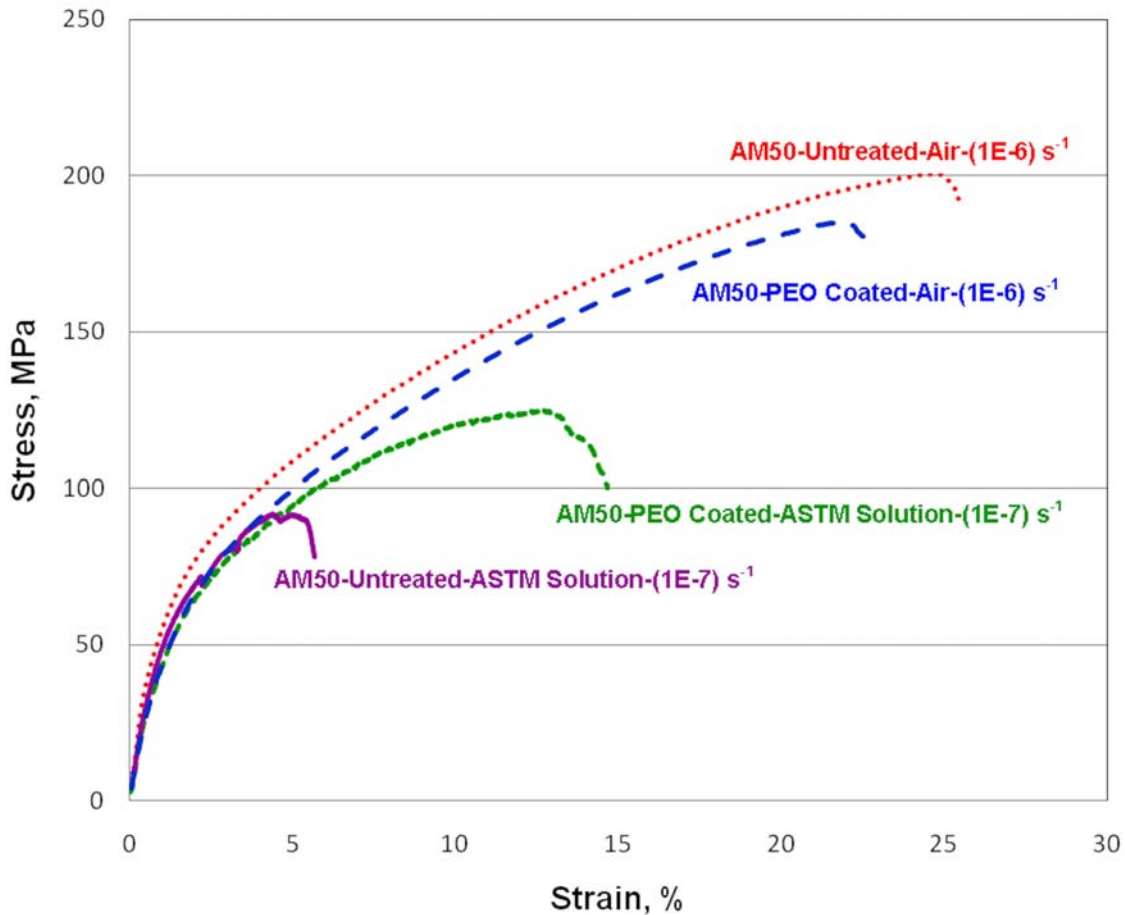
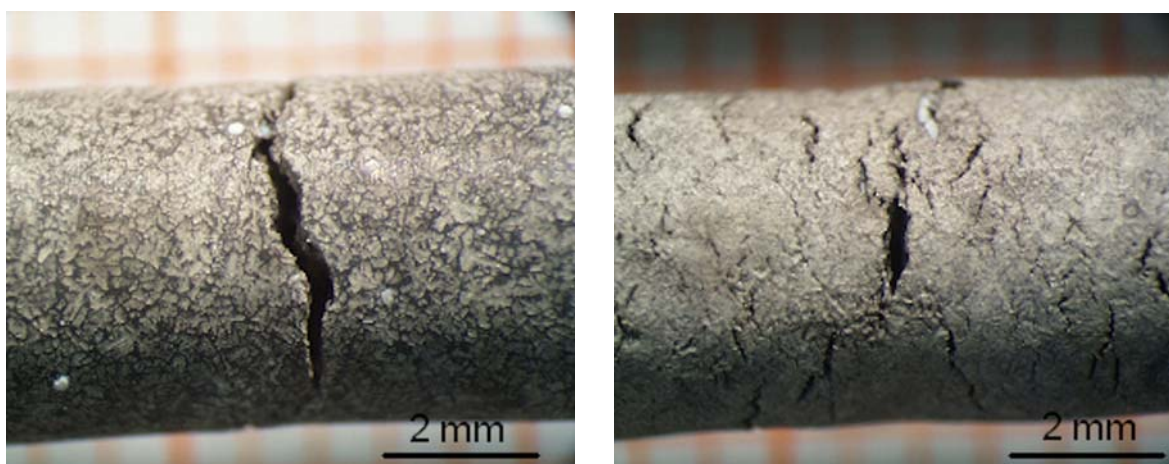


Figure 5 Stress vs. strain plots of the untreated and PEO coated AM50 alloy specimens in air and ASTM solution

The untreated AM50 specimen exhibited its susceptibility to stress corrosion cracking in the SSRT tests performed at $1E-7$ s⁻¹. The specimen failed at a stress level of around 90 MPa, with an elongation of only around 5%. Kannan et al., [17] have reported the SCC susceptibility of AZ31 wrought alloys in ASTM solutions in a recent work and Song et al., [18] have documented the SCC behaviour of the same class of alloy even in double distilled water. Hence, it is not surprising that this cast alloy exhibited SCC in this electrolyte. The PEO coated specimen, despite showing an excellent corrosion resistance in the short term electrochemical tests, has also failed at a much lower stress level than its counterpart in air. The ultimate tensile stress value of 125 MPa is only marginally higher than that of the untreated specimen. However, the elongation was much higher, registering around 13%. The experiments were stopped as the load

started to drop 20 MPa below the maximum stress values, for the assessment of the surface of the specimens. The optical macrographs of the specimens presented in **Figures 6(a) and (b)**, give an account of the type and extent of damage on these two specimens. The untreated specimen has apparently had a large crack, causing the damage, while the PEO coated specimen had been observed to have developed multiple cracks. The size of the cracks that were observed in this specimen were quite large compared to those observed in the PEO coated specimen tested in air. It is quite evident that the PEO coating, despite being thin, was cracking under conditions of constant/continuous straining, thus developing numerous microcracks. Thus, on account the synergistic dissolution and straining at these defect sites, the cracks have opened up wider and longer, leading to SCC. The formation of numerous cracks and their widening is plausibly the reason for the higher elongation values registered for the coated sample.



(a) Untreated

(b) PEO coated

Figure 6 Optical macrographs showing the surface appearance of the SSRT tested (ASTM D1384 solution) AM50 alloy

In summary, the PEO coated specimen despite showing a very good resistance to corrosion in the electrochemical tests and also enduring the environment for a relatively longer test duration (in SSRT tests), it could not obviate the SCC process. It remains to be seen whether the other types of PEO coatings and/or thicker coatings from this same type of PEO solution would help palliating further the SCC problems of susceptible magnesium alloys.

Acknowledgement

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