A study on the effect of plasma electrolytic oxidation on the stress corrosion cracking behaviour of a wrought AZ61 magnesium alloy and its friction stir weldment

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ABSTRACT

Friction stir weldments of a wrought AZ61 magnesium alloy produced in a robotic friction stir welder under optimised welding conditions were characterised for microstructure, mechanical properties, corrosion and stress corrosion cracking (SCC) behaviour. The effect of surface modification in the form of a plasma electrolytic oxidation (PEO) coating on the corrosion behaviour of the weldment was assessed. The weldment exhibited a joint efficiency of 94%, nevertheless, the weld nugget region was found to have a higher susceptibility to SCC than its parent material counterpart. Even though the PEO coating had provided a good resistance to general and pitting corrosion, it could not completely prevent SCC of this weldment in ASTM D1384 solution.

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1. Introduction

Magnesium alloys are an attraction for the automobile industry, on account of their light weight, castability, workability and mechanical properties [1]. Welding of magnesium alloys to achieve acceptable quality joints is a difficult task. Fusion welding of magnesium viz., gas tungsten arc welding, plasma arc welding is, however, a difficult task since these processes generally result in joints with lower strength levels in comparison to the base material due to high levels of porosity entrapment in the resultant welds [2–4]. This has prompted the use of low heat input, high energy density laser beam and electron beam processes for welding of magnesium alloys [5,6]. Friction stir welding (FSW) patented by TWI in 1991 [7], has successfully been employed for the joining of light alloys, especially for aluminium but also for magnesium, in recent times. Microstructural evolution and the resultant mechanical properties of friction stir weldments of many magnesium alloys have been well documented [8–10]. Despite having favourable properties and positive outcomes in the processing, magnesium alloys still suffer from their inherent poor corrosion resistance and for many applications surface treatments are necessary for meeting the demands. A number of surface modification technologies are contemplated for this purpose [11], and in recent times the anodic treatments, especially the plasma electrolytic oxidation has gained in popularity [12]. There are a few investigations on the corrosion and stress corrosion cracking (SCC) behaviour of magnesium alloy weldments [13–15]. Even though one of the recent publications of the authors addressed the SCC behaviour of surface modified cast magnesium alloy [16], there is no published information on the effect of surface modification
on the SCC behaviour of magnesium alloy weldments. Hence, in this work an attempt has been made to understand the effects of plasma electrolytic oxidation (PEO) treatment on the SCC behaviour of a wrought AZ61 magnesium alloy friction stir weldment.

2. Experimental

A wrought AZ61 magnesium alloy sheet of 2.5 mm thickness with a nominal composition of 6%Al, 1%Zn, 0.2%Mn, balance Mg (by weight), supplied by M/s Salzgitter AG, Germany was employed in this investigation. Butt joints were produced by friction stir welding technique, utilising a Neos Tricept TR805 robotic FSW machine. The welding parameters included the tool rotational speed of 475 rpm, weld travel speed of 75 mm min⁻¹ and axial or forging load of 6.5 kN. Metallographic specimens were prepared by polishing successively with 220, 320, 400, 800, 1200 and 2500 grit emery sheets followed by polishing in 1 µm diamond paste. Finally, the specimens were polished in colloidal silica emulsion and etched in a solution comprising 3.5 g picric acid, 6.5 ml acetic acid, 20 ml water and 100 ml ethanol. Macro and micro examinations were performed in a Leitz light optical microscope. Microhardness measurements were made under a load of 5 N, as hardness survey across the weldment, at the mid section thickness and the tests were performed in duplicate.

The PEO treatment was carried out using a simple DC power supply source with a capacity of 600 V and 4 A in an electrolyte consisting of 10 g l⁻¹ potassium 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 420 V. The coating process was continued at 420 V until the current decreased to zero due to increasing layer thickness, evidenced by a reduction in spark density. The total duration of the PEO treatment was approximately 10 min.

Electrochemical characterization of the parent material and the weld nugget was carried out using a Gill AC potentiostat/galvanostat FRA system with a three electrode cell set up. The free corrosion potential measurements were made for 30 min prior to the electrochemical tests on specimens which were ground to a final finish of 2500 grit emery. Potentiodynamic polarisation studies were performed in non-deaerated ASTM D1384 solution containing 148 mg Na₂SO₄, 165 mg NaCl and 138 mg NaHCO₃ in 1 l of double distilled water with a sweep rate of 0.5 mV s⁻¹ starting at −200 mV relative to the free corrosion potential.

Slow strain rate tensile (SSRT) tests in ASTM D1384 solutions were conducted with flat tensile specimens of 2.5 mm thickness. The gauge section of the parent specimens was 6 mm×10 mm, whilst in friction stir weldment specimen it was 6 mm×22 mm in order to accommodate the nugget, thermo-mechanically affected zone and the parent regions in the gauge section. SSRT tests were performed in ASTM D1384 test solution at a nominal strain rate of 10⁻⁶ s⁻¹ by following the ISO standard 7359—Part 7 [17]. As for the SSRT tests in corrosive test environment it was too difficult to use a clip-on gauge for the measurement of elongation, hence, for all the SSRT tests (both in air and in solution), the specimen elongation was measured by employing two linear variable displacement transducers attached to the specimen grips. It is pointed out here that the elongation values measured in these tests do not represent the precise strain levels of the
specimens, and hence are referred to as “apparent strain” in the discussions. The fracture surface analysis was done in a Cambridge Stereoscan 200 scanning electron microscope.

3. Results and Discussion

3.1. Microstructure and Mechanical Properties

A 3D-optical micrograph of the extruded AZ61 magnesium alloy presented in Fig. 1 reveals the considerably uniform equiaxed re-crystallized grains in the center of the plate (2.5 mm thickness sheet) with more grain deformation close to the surface. The optical macrograph of the friction stir weldment shown in Fig. 2 reveals the profile of the weld nugget. The microstructures of the parent alloy and the weld nugget depicted in Fig. 3(a) and (b) reveal clearly the differences in the grain sizes in these two regions. The average grain size of the parent alloy was found to be around 40 µm and that of the weld nugget was only in the range of 5–15 µm. It is well known that finer grain sizes evolve in the nugget region of friction stir weldments owing to the severe plastic deformation and dynamic recrystallisation due to the heat generated during welding [18,19]. However, there are contradictory reports concerning grain refinement in the stir weld nuggets in magnesium alloys. Afrin et al., for example, reported the development of much larger grain sizes in the weld nugget region compared to its parent metal counterpart in 5 mm thickness AZ31B friction stir weldments [20]. Fig. 3(a) reveals the Al₆Mn₅ particles dispersed over the α-phase, and also the existence of highly fragmented β-phase (Mg₁₇Al₁₂) is visible in the parent alloy. According to the Mg-Al phase diagram, the β phase starts to dissolve in the matrix when the temperature of processing exceeds 370 °C [21]. Peak temperatures in the range of 350 °C to 380 °C, as measured by k-type thermocouples embedded in the backing bar directly below the weld nugget; indicate the dissolution of β phase which was possible in the nugget region of the joint. However, the micrograph of this region shows some secondary phases, which appear to be fragmented β phase particles. Hence, from this evidence it is not clear whether the temperature and its duration were sufficiently high enough to facilitate the complete dissolution of the β phase in the weld nugget region.

Fig. 4 – Micro hardness profile across the AZ61 friction stir weldment.

Fig. 5 – Stress vs. apparent strain plots of the AZ61 parent alloy and friction stir weldment specimens SSRT tested in air at a nominal strain rate of $10^{-6}$ s⁻¹.
Nevertheless, the observation of the evolution of finer grain sizes in the weld nugget in the current investigation is in line with the literature documented by Feng et al. [22] and Xunhong et al. [10].

Micro hardness measurements performed at the mid-thickness section of the weldment at a load of 5 N presented in Fig. 4 show marginally higher hardness levels in the weld nugget region; however, the hardness of the entire weldment was in the range of 66±3 HV0.5. Other researchers reported similar marginal increase in hardness values in friction stir weldments as an influence of the FSW process [23,24]. However, considering the differences in the values, it is appropriate to state for the current study that the welding conditions had no significant influence on the hardness.

The tensile behaviour of the parent alloy and of the friction stir weldment assessed at a nominal strain rate of 10^{-6} s^{-1} at ambient conditions are depicted in Fig. 5. The ultimate tensile strength and apparent strain to failure for the parent alloy were 320 MPa and 37.5%, respectively whereas the friction-stir weldment specimen registered values of 300 MPa and 17%. In terms of reduction in cross sectional area both the specimens have shown values of around 30%. Considering the strength levels, the joint seems to be under matched, showing an efficiency of around 94%, despite the fact that the hardness of the weld nugget was marginally over matched in comparison to the parent material. Macroscopic examination of the fractured specimen revealed that the fracture was in the region away from the nugget, but in the TMAZ/HAZ region (Fig. 6). Fractographs of the tensile tested parent and friction stir weldment specimens (Fig. 7(a) and (b)) reveal the dimpled structure, characteristic of ductile fracture. However, the dimples were finer in the friction stir welded specimen, suggesting that the tensile fracture was at the weld nugget/TMAZ interface, and similar observations have been reported by Arfin et al. [20]. The above observations are in line with some of the recently published literature on structure-property relationships in magnesium alloy friction stir weldments [10,23,25].

3.2. Surface Modification and Electrochemical Characterisation

Fig. 8(a) and (b) show the features of the surfaces of PEO coated AZ61 parent alloy and the weld nugget regions. Even though these two regions had distinctly different microstructures in terms of grain sizes, both these regions had very similar features on the surface in the PEO coated condition. The pore sizes were in the range of 1 µm to 5 µm. The PEO coating thickness was around 12 µm in both specimens and the coating was found to be constituted by MgO and Mg2SiO4.

The potentiodynamic polarisation behaviour of the untreated and PEO coated parent and friction stir weld
nugget regions in ASTM D1384 solution are shown in Fig. 9 and the electrochemical data are presented in Table 1. The corrosion potential and the corrosion current density of the untreated parent specimen were $-1325$ mV vs. Ag/AgCl and $2.5 \times 10^{-3}$ mA cm$^{-2}$, respectively. The specimen had shown a breakdown at a potential of around $-1075$ mV vs. Ag/AgCl. The friction stir weld nugget region in the untreated condition recorded a relatively more noble corrosion potential ($-1293$ mV vs. Ag/AgCl), and a slightly lower corrosion current density level compared to the parent material. The fine grained structure of the nugget region is reported to facilitate formation of a more dense passive film providing a better corrosion resistance [13,26]. However, the breakdown potential of the friction stir weld nugget region was lower than that of the parent alloy, suggesting the higher degree of susceptibility to pitting.

In the PEO coated condition, both the parent alloy and the FSW nugget regions have shown very similar polarisation behaviour, registering a corrosion potential of around $-1250$ mV vs. Ag/AgCl and a corrosion current density of $2 \times 10^{-5}$ mA cm$^{-2}$. The potential was nobler than that of the untreated counterparts and the corrosion current density was by more than two orders of magnitude lower. Further, the PEO coated specimens did not show any sign of breakdown until 0 mV vs. Ag/AgCl in this electrolyte, demonstrating the superior corrosion protection offered by the PEO coating.

### 3.3. Stress Corrosion Cracking

The stress vs. apparent strain plots for the untreated and PEO coated parent alloy specimens obtained from the SSRT tests in air and ASTM D1384 solution at $10^{-6}$ s$^{-1}$ are presented in Fig. 10. In the tests in air, the parent alloy registered an
ultimate tensile strength (UTS) of around 320 MPa in both the untreated and PEO coated conditions. In a recent work, on a cast magnesium alloy with a coarse grain size, a marginal difference in UTS value was observed in the specimens with and without PEO coating, which was attributed to the strain hardening effect [16] and it is probable that in the wrought condition of AZ61 in this work, the effect is not felt. A slightly lower apparent strain value was noticed for the PEO coated specimen compared to the untreated counterpart. Similar observation was made in the earlier work [16,27], and was attributed to the early cracking of coating during deformation. These cracks may continue to grow into the bulk, thus resulting in a marginally lower ductility.

In ASTM D1384 solution, the untreated parent alloy showed signs of stress corrosion cracking at a stress level of around 215 MPa with an apparent strain value of 7%. The PEO coated specimen reached a maximum stress of 245 MPa before cracking, registering a 9% apparent strain value, suggesting that PEO coating has some beneficial influence on the SCC behaviour. Macroscopic examination (by optical and scanning electron microscopy) of the failed specimens revealed that the PEO coating cracked during straining in the SSRT tests, thus allowing permeation of the electrolyte towards the substrate through these defective sites.

The fractographs of the SSRT tested PEO coated parent specimen (in air) and of the untreated and PEO coated specimens tested in ASTM solution are presented in Fig. 11(a), (b) and (c), respectively. The fracture surface of the PEO coated specimen tested in air showed dimples characteristic of ductile fracture (Fig. 11(a)), and the features are similar to that observed for the untreated parent alloy (Fig. 7(a)). In the ASTM solution the fracture appearances of the untreated and PEO coated specimens were different from those tested in air. Both the untreated and PEO coated specimens have had features of transgranular and intergranular cracking as is evident in Fig. 11(b) and (c), respectively. Both these specimens have shown a reduction in cross section of less than 5% as against 30% in the tests in air, which further illustrates the SCC susceptibility.

The stress vs. apparent strain plots of the friction stir weldment specimens with and without PEO coating obtained from the SSRT tests are shown in Fig. 12. In air, the untreated friction stir weldment specimen exhibited a strength level of around 300 MPa with an apparent strain level of around 17% compared to a stress of 290 MPa and 12.5% apparent strain in the PEO coated condition. The straining in the different regions of the friction stir weldment is different, and this

![Fig. 12 – Stress vs. apparent strain plots of the friction stir weldment specimen with and without PEO coating.](image)
further causes a difference in straining of the PEO coating resulting in slightly lower stress and apparent strain levels. The fracture location in the case of the PEO coated FSW specimen was in the TMAZ/HAZ region, similar to that observed in the case of its untreated counterpart, and it is no surprise that the fracture surface (Fig. 13(a)) had fine dimples like in the untreated counterpart.

On the other hand, in the tests in ASTM solution the untreated FSW specimen failed at a much lower stress level (around 150 MPa), registering an apparent strain of only around 2%. The PEO coating seems to have provided a marginal increase in resistance to SCC in this case, too, registering a stress level of 190 MPa and an apparent strain of around 3%. Fractographic examination of the specimens tested in solution revealed features of transgranular fracture (Fig. 13(b) and (c)). Macroscopic examination of the SSRT tested untreated FSW specimen showed that the fracture was in the nugget region (Fig. 14) and it appears that the fracture could have originated at the root region of the weld and propagated into the weld nugget. These observations further reaffirm the fact that PEO coating can offer an excellent resistance to general and pitting corrosion, but it does not prevent SCC of this AZ61 magnesium alloy and its friction stir weldment.

4. Conclusions

The following broad conclusions are drawn based on this investigation:

• Friction stir welding of AZ61 alloy can give joints with efficiency levels close to 95% under optimised welding conditions.
• The hardness of the weld nugget does not differ much from the parent region; however, fracture location in the tensile tests suggests that the TMAZ/HAZ region is the weakest zone in the joint.
• PEO coatings obtained from a silicate based electrolyte does not seem to be influenced by the grain size differences in the weldment, and an average layer thickness of 10–12 µm was developed in the weldments.
• The general and pitting corrosion behaviour of the PEO coated parent and FSW nugget regions were nearly the same, even though they were different in the untreated condition and PEO coating improves the corrosion resistance by two orders of magnitude.
• Both the parent alloy and the friction stir weldment specimens exhibited stress corrosion cracking in ASTM D1384 solution. But the friction stir weld nugget has a higher susceptibility to SCC in this weldment.
• Even though the PEO coatings offer an excellent corrosion general/pitting resistance, they do not provide adequate protection to prevent the SCC of this magnesium alloy in ASTM D1384 solution. However, the coating provides a marginal improvement in the SCC resistance.

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