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Full Length Article

Influence of bimodal grain size distribution on the corrosion behavior of friction stir processed biodegradable AZ31 magnesium alloy

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Abstract

In the present study, AZ31 magnesium alloy sheets were processed by friction stir processing (FSP) to investigate the effect of the grain refinement and grain size distribution on the corrosion behavior. Grain refinement from a starting size of 16.4 ± 6.8 μm to 3.2 ± 1.2 μm was attained after FSP. Remarkably, bimodal grain size distribution was observed in the nugget zone with a combination of coarse (11.62 ± 8.4 μm) and fine grains (3.2 ± 1.2 μm). Due to the grain refinement, a slight improvement in the hardness was found in the nugget zone of FSPed AZ31. The bimodal grain size distribution in the stir zone showed pronounced influence on the corrosion rate of FSPed AZ31 as observed from the immersion and electrochemical tests. From the X-ray diffraction analysis, more amount of $Mg(OH)_2$ was observed on FSPed AZ31 compared with the unprocessed AZ31. Polarization measurements demonstrated the higher corrosion current density for FSPed AZ31 (8.92×10^{-5}A/cm^2) compared with the unprocessed condition (2.90×10^{-5}A/cm^2) that can be attributed to the texture effect and large variations in the grain size which led to non-uniform galvanic intensities

Keywords: AZ31 Mg alloy; Biodegradable implants; Grain size distribution; Corrosion; Friction stir processing, texture

1. Introduction

Magnesium (Mg) and its alloys are now gaining immense importance as promising candidates for load bearing temporary implant applications in biomedical engineering. Biocompatibility, biodegradability and mechanical properties close to that of natural human bone are the advantages with the magnesium [1]. Avoiding the necessity of second surgical procedure to remove the implant after the tissue is healed and reducing the other complications such as restenosis, thrombosis, permanent physical irritation, and inability to adapt to growth and changes in human body are the major benefits with the magnesium based temporary implants [1,2]. However, the high corrosion rate of magnesium in the biological environment is the major concern in developing magnesium based implants which also influences the healing rate [3,4]. Therefore, different strategies such as developing new alloys, composites and coatings have been widely adopted to address the uncontrolled degradation issue of magnesium [4–13]. Microstructural modification is another interesting route recently gaining wide popularity to alter the corrosion rate of magnesium [14–22].

AZ series (Aluminum and zinc) is the well-known Mg alloy system commonly used in the structural applications [23]. Mg alloy with 3% Al and 1% Zn (AZ31) is one of the most widely investigated compositions among the other AZ series Mg alloys for biomedical applications because of less aluminum content. If aluminum content is increased more than 3%, the presence of more $Mg_{17}Al_{12}$ phase at the grain boundaries significantly influences the mechanical and corrosion properties of Mg alloys [24]. Additionally, good fatigue and corrosion resistance also made AZ31 Mg alloy as first choice for medical implant applications [20].

It is an interesting observation in the literature that the grain refinement has increased the corrosion resistance [14–22] and also as reported in some studies, decreased the corrosion resistance [20–22,25] of Mg alloys. Usually the grain boundaries are

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the high energy sites so that the corrosion is initiated preferentially from the grain boundaries. Fine grain structure increases the fraction of grain boundary and hence reduces the corrosion resistance of the material in the aggressive medium. However, ability to quickly form a protective passive layer helps to reduce the corrosion rate of fine grained metals in the neutral electrolyte and such behavior can be found in metals like Mg alloys. Therefore, microstructural modification can be adopted as a promising method in corrosion management of reactive metals like Mg alloys. In addition to this, the level of secondary (β) phase distribution in the alloy or some dissolved elements in the alpha phase (solid solution) also improve the corrosion resistance.

Severe plastic deformation (SPD) techniques are the recently emerged potential top-down methods used to achieve grain refinement in metals [26]. Friction stir processing (FSP) is one of such methods in which the microstructure of metallic sheets or plates can be modified by using a non-consumable rotating tool consisting a shoulder and pin. The mechanism behind grain refinement during FSP has been explained elsewhere [27]. There are a few reports clearly demonstrating the improved corrosion resistance of Mg alloys after FSP [15–18,28]. A few studies have also clearly shown the abnormal change in the electrochemical behavior due to texture [29–32]. However, the information regarding the electrochemical behavior of Mg alloys which exhibit varying levels of grain refinement (bimodal grain size) is lacking. It has been well understood that FSP does not always yield uniform grain refinement which depends on various process parameters [27]. Therefore, in the current study, AZ31 Mg alloy was selected and was processed by FSP to modify the microstructure. Corrosion studies were carried out by the immersion test and electrochemical method with an aim to understand the corrosion behavior of AZ31 Mg alloy with bimodal grain size distribution. The effect of distributed grain size on hardness was also measured and discussed.

2. Materials and methods

2.1. Experimental details

AZ31 Mg alloy rolled sheets (Exclusive Magnesium, Hyderabad) of chemical composition 2.75% Al, 0.91% Zn, 0.001% Fe, 0.01% Mn and remaining being Mg were cut into 100×100×4 mm^3 size and annealed at 340 °C for 1 h. Friction stir processing (FSP) was carried out using an automated universal milling machine (Bharat Fritz Werner Ltd., India). FSP tool made of H13 tool steel was used to process the samples. FSP tool has a shoulder of diameter 20 mm and a tapered pin with root diameter of 3 mm, end diameter of 1 mm and a length of 3 mm. Initially, trial experiments were conducted to optimize the process parameters to get defect free stir zone. Then the FSP was carried out with a tool travel speed of 100 mm/min at a tool rotational speed of 1100 rpm. The penetration depth (3 mm) was given such a way that the tool shoulder touches the work piece surface. The processed AZ31 was coded as FSPed AZ31.

2.2. Material characterization

Specimens of 30 mm length were cut across the FSPed zone and metallographic polishing was done using different graded emery papers. The specimens were then polished using diamond paste of 3 μm size using a disc polishing machine. After each step, the samples were cleaned in distilled water, wiped with cotton and soaked in ethanol to remove any water remaining on their surface. Picric acid reagent comprised of 5 g picric acid, 5 ml acetic acid, 5 ml distilled water and 100 ml ethanol was prepared as etching agent. The polished samples were etched in the solution for 20 seconds and then cleaned in distilled water followed by cleaning in ethanol. The microstructural observations were carried out using an optical microscope (Leica, Germany) at different areas of interest on the surface and cross sections of FSPed regions. Average grain size was measured by linear intercept method.

2.3. Microhardness

Microhardness measurements (Omnitech, India) were carried out on polished specimens by applying 100 g load with 10 sec dwell period. One measurement was obtained for each 1 mm distance. The indents were placed across the FSPed regions at the surface and cross sections. Microhardness was measured over a distance across the stir zone such a way that the base material hardness was also measured up to 5 mm away from the stir zone.

2.4. Corrosion studies

2.4.1. Immersion test

Immersion studies were carried out in 0.9% NaCl solution for 1, 2 and 3 days to assess the corrosion rate of the samples. Lab grade NaCl (Merc, India) was used to prepare 0.9% NaCl solution using de-ionized water and the samples of size $10 \times 10 \times 1.5$ mm^3 were immersed in the solution and the containers were kept at 37 °C in a constant temperature water bath. The ratio of the volume of the solution to the surface area of the specimens was kept more than 1:10. Weights of all these samples before and after immersion were measured. For each group (Unprocessed and FSPed), three samples were considered (n = 3) and immersion studies were carried out. The samples were taken from the solution after each day and gently rinsed in stable de-ionized water and dried. The samples were then immersed in boiling solution of chromic acid (180 g/one liter of de-ionized water) to remove the surface corrosion products. Then the samples were dried in air before measuring the weight loss. Corrosion rate was calculated according to ASTM standard NACE TM0169/ G31 – 12a as given below [33].

$$\text{Corrosion rate}\,(\text{mm/year}) = k \times \Delta W/(A \times T \times D) \quad (1)$$

where $k = 8.76 \times 10^4$, T = time of exposure in hours, A = area of the specimen in cm^2, ΔW = weight loss in g, D = density in g/cm^3.

2.4.2. Electrochemical test

Electrochemical studies were carried out using 0.9% NaCl solution as the electrolyte using Gill AC potentiostat (ACM