Materials Science Forum *Online: 2012-01-24*
ISSN: 1662-9752, Vol. 710, pp 264-269
doi:10.4028/www.scientific.net/MSF.710.264

Bioactive grain refined magnesium by friction stir processing

B. Ratna Sunil [a], T. S. Sampath Kumar [b] and Uday Chakkingal [c]

Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras,

Chennai 600036, India.

[a] bratnasunil@gmail.com, [b] tssk@iitm.ac.in, [c] udaychak@iitm.ac.in

Keywords: friction stir processing, pure magnesium, grain refinement, bioactivity

Abstract. Magnesium and its alloys are promising candidates for temporary implant applications due to their combination of mechanical properties, biocompatibility and biodegradation. But higher degradation rate restricts their wider applications. Recently friction stir processing (FSP) has emerged as a promising tool to attain near surface fine grain structure in materials. In the present work commercial purity magnesium was processed by FSP to obtain fine grain structure and the effect of the grain refinement on the bioactivity was investigated. The microstructural observations were carried out at different locations of the processed regions, from an original grain size of 1500μm, grain refinement was achieved to a level of 6.2μm at the nugget zone. Microhardness was measured across the processed regions and improvement was observed at the nugget zone. Contact angle measurements were carried out to estimate the wettability of the material and the measurements indicate increased wettability due to the increased surface energy induced by grain refinement. For studying the bioactivity, the FSPed samples were immersed in simulated body fluids (SBF 5X) for different intervals of time. The phases formed on the samples were investigated by X-ray diffraction (XRD) method, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The phases on the samples after 72hr of immersion were confirmed as magnesium hydroxide, hydroxyapatite and magnesium phosphate by XRD. Controlled degradation due to formation of these phases was observed. FSPed samples have more deposition of Ca/P than non FSP samples which implies better control over the degradation. Hence grain refinement by FSP can be a simple technique to control the degradation of magnesium for temporary implant applications.

Introduction

Magnesium, being a promising biodegradable metal has attracted considerable attention in the past decade for temporary hard tissue applications. The elastic modulus, compressive yield strength and density of magnesium are nearer to natural bone compared to other metallic biomaterials. However the higher rate of degradation is one of its main limitations for wide applications. As controlled degradable magnesium by biocorrosion seems to be a realistic alternative to permanent implants, research efforts have been focused to overcome the issues associated with rapid degradation in biological environment. Witte *et al* [1] have reported the degradation behavior of magnesium and its alloys in simulated body fluids (SBF). Pure magnesium heterogeneously corrodes in SBF. The corrosion rate decreases with increase in immersion time of samples. Since the biological environment has a complex ionic concentration, studying the degradation behavior is immensely important especially in the early hours of immersion. Need for developing tailored surfaces is growing in the biomaterials field as the implant surface plays a crucial role in biological interactions. Ability to form hydroxyapatite (HA), a calcium phosphate mineral phase similar to inorganic part of human bone on an implant material, called bioactivity, can be enhanced by grain refinement [2]. Friction stir processing (FSP), a new solid-state processing technique was developed as a generic tool for microstructural modification based on the basic principles of friction stir welding (FSW) [3]. There have been few reports on FSP of magnesium alloys for biomedical applications. Studies concerning microstructure evolution of pure magnesium by FSP and bioactivity are lacking. In the present work pure magnesium was processed by FSP and the impact of the induced grain refinement on the surface hardness, wettability and bioactivity was investigated.

Materials and methods

Samples of size 100 X 100 X 5 mm were cut from commercially available pure magnesium billet and were annealed at 340°C for 1h. Fig.1 shows schematic representation of the FSP process. The FSP tool was made of H-13 tool steel and has a tapered pin at the working end with a cylindrical shoulder. Annealed samples were processed with a single pass at different combinations of rotational (800–1200 rpm) and translational (6 – 60 mm/min) speeds to obtain optimized processing parameters. A rotational speed of 1200 rpm, load of 5000N and translational speed of 12 mm/min were selected for this study.

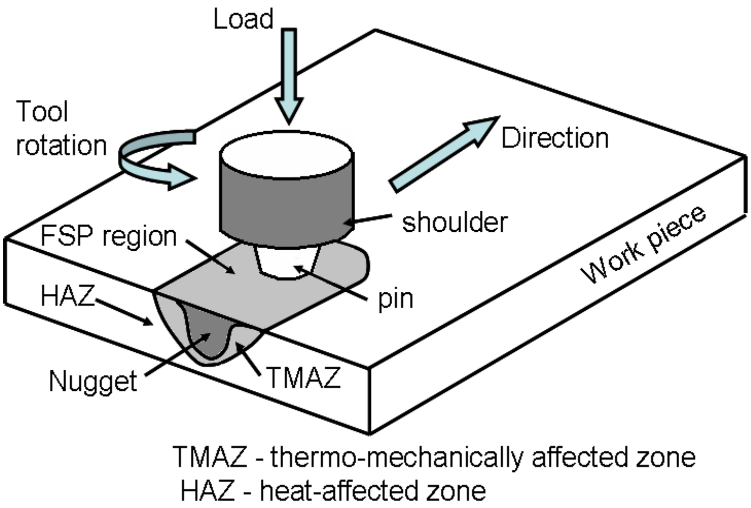

Fig. 1 Schematic representation of friction stir processing

The samples were mechanically polished and etched for microstructural observations. Vickers microhardness was measured with 100 g load applied for 10 s. Contact angle measurements were carried out using distilled water as the contacting solvent. From the FSP samples, specimens of size 10 X 10 X 5 mm were cut from the nugget zone (where dynamic recrystallization takes place due to intense plastic deformation with in the stir zone results fine grain evolution) and named as friction stir processed (FSP). Bioactivity studies were carried out in SBF 5X. The SBF solution has ionic concentration similar to those of human extracellular fluid and SBF 5X has a concentration of ions five times of that of the SBF [4]. Both the as-annealed (AS) and FSP samples were immersed into SBF 5X at a constant temperature of 37°C. The samples were removed from the SBF, rinsed with de-ionized water and further characterized by X-ray diffraction (XRD) method, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis.

Results and discussion

Fig.2 shows the microstructures at different regions of the FSPed samples. Initial average grain size was measured as 1500 µm and grain refinement was achieved in nugget zone up to 6.2 µm. Twin bands, which are common in deformation of hcp metals like magnesium, appeared in heat affected zone (HAZ). Microstructural evolution from coarse grains to fine grains can be observed at the interface region of thermo - mechanically affected zone (TMAZ) and nugget zone (Fig 2(f)). Micro hardness measurements across the processed region on the surface (Fig. 3) shows increased hardness at nugget zone and gradual decrease towards HAZ and unprocessed region. Both the unprocessed and nugget regions were found to be hydrophilic. Average contact angles of water droplet were measured as 76° and 63° for unprocessed and FSPed regions respectively (Fig. 4).

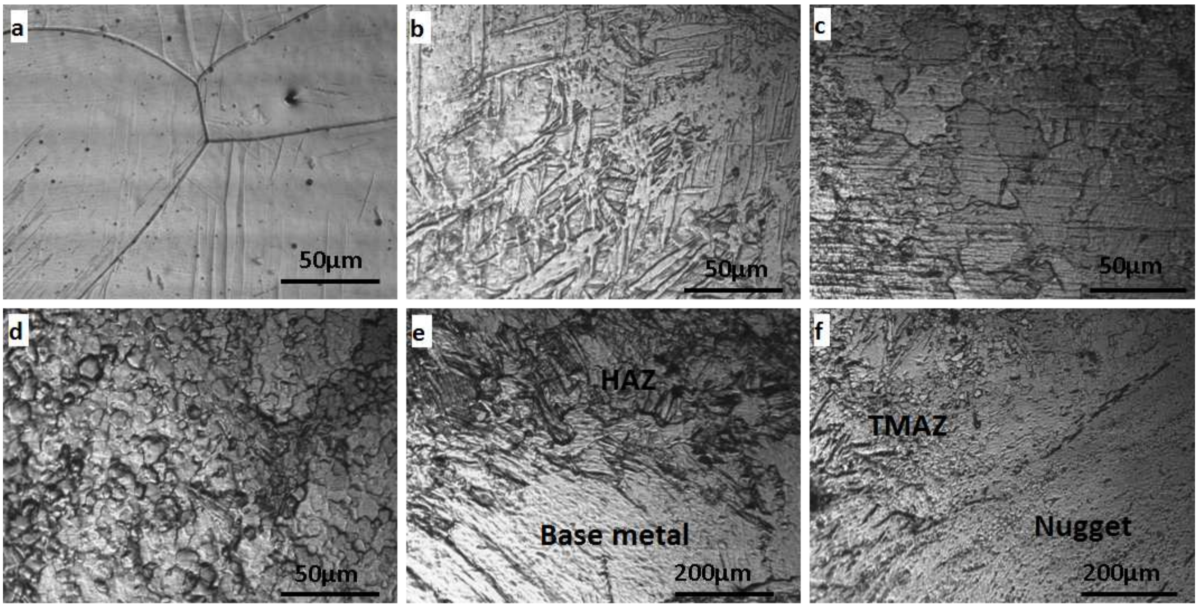

Fig. 2 Optical micrographs of FSPed magnesium (a) unprocessed zone, (b) heat affected zone (HAZ), (c) thermo-mechanically affected zone (TMAZ), (d) nugget zone, (e) base metal-HAZ interface, (f) TMAZ- nugget interface.

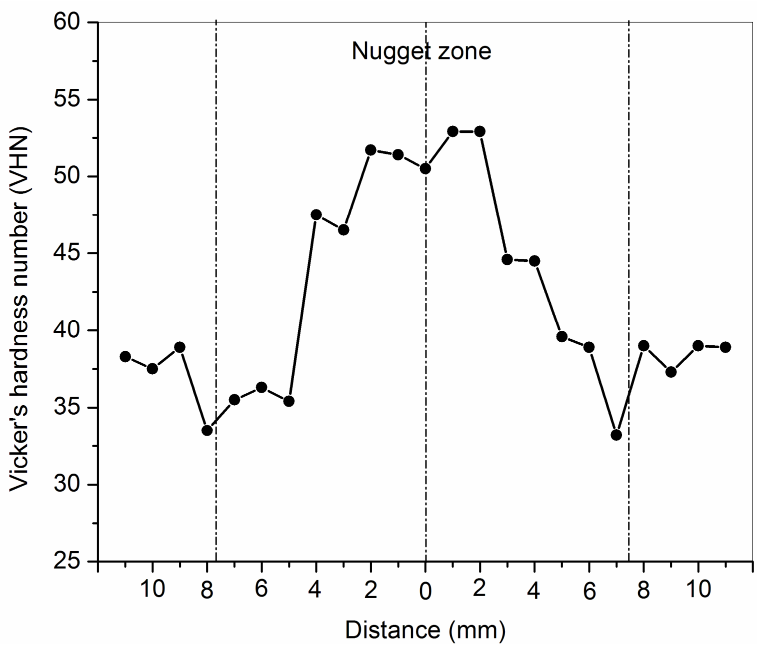

Fig. 3 Vickers micro hardness across the processed region

A hydrophilic surface is favorable for the adsorption of specific proteins, cell-attachment and proliferation kinetics which can subsequently lead to the formation of a strong bonding between the implant and tissue. The surface of the magnesium before FSP can be considered as a hydrophilic surface (θ <90°). The droplet contact angles resulting from FSP fall into the lower value than that prior to FSP. The reduction of droplet contact angle indicates improved wettability due to grain refinement in the FSP sample. The surface energies have been calculated from the contact angle measurements and the FSP sample has been found to have higher surface energy (33 mJ/m^2) than the annealed sample (17 mJ/m^2). Fig 5 shows SEM images of the samples immersed in SBF 5X for different intervals of time. Network-like cracks and pits of magnesium hydroxide were formed as a result of corrosion during the process of degradation after 24h of immersion for both the samples. This is similar to that reported earlier by Witte *et al* [1]. Plenty of precipitates white in color were observed on both the samples. These precipitates were found to be increased as immersion time increases to 48h. After 72h of immersion, a thick layer of white precipitates was observed on both the samples. However, it was observed that with increasing of immersion time to 72h, formation of these white phases was found to be more and more on FSP sample than annealed sample.

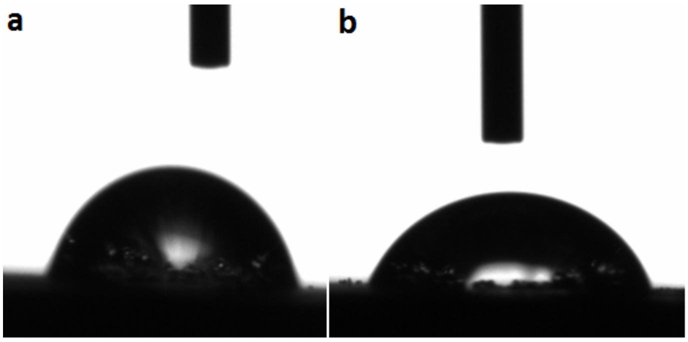

Fig. 4 Photograph of water droplet on (a) as annealed and (b) FSPed magnesium

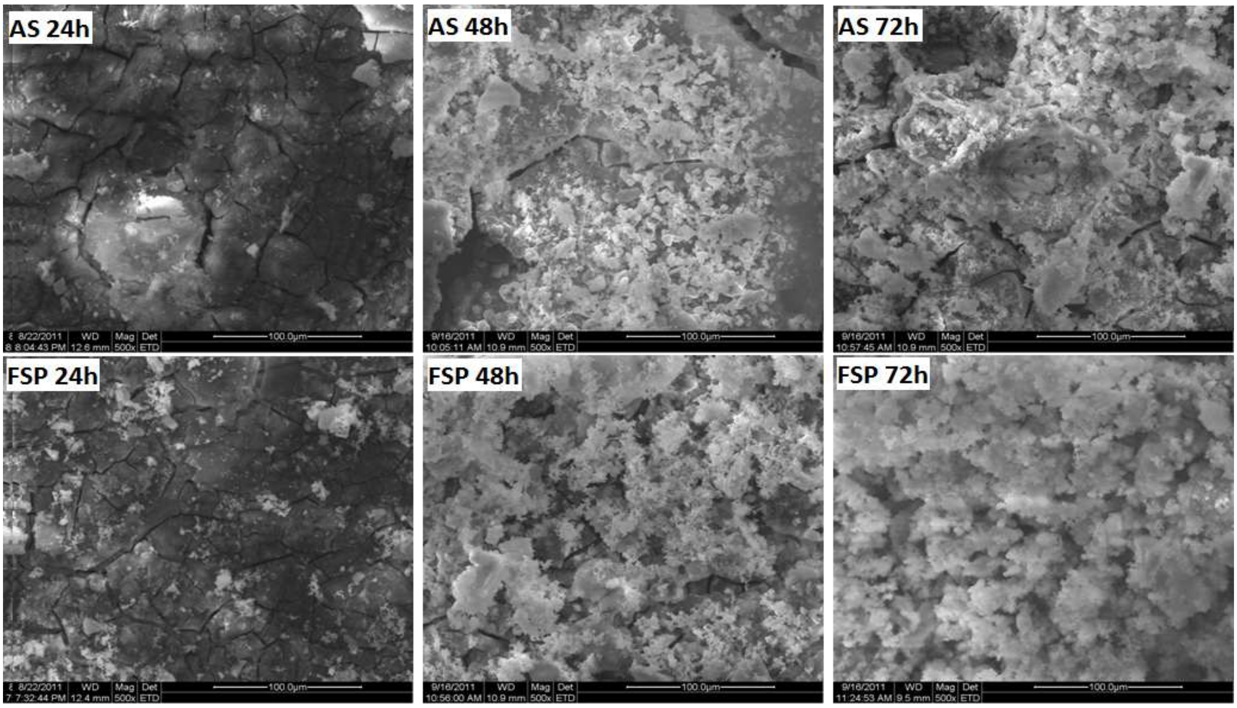

Fig. 5 SEM images of FSPed samples immersed in SBF 5X

These white precipitates were confirmed with XRD (Fig. 8) as hydroxyapatite and magnesium phosphate. These phosphorous containing compounds, together with magnesium hydroxide, promote protection against the aggressive action of chloride (Cl^-) ions [5]. Fig. 6 shows low magnification morphologies of the samples after 48h of immersion. Many round corrosion pits were observed on annealed sample compared to the FSP sample and EDX analysis around the pits showed presence of less Ca/P and more Cl on annealed sample. In the case of FSP sample a good amount of Ca/P with decreased Cl was observed. Fig. 7 shows the magnified morphology of the white deposits on the samples after 72h of immersion. Prominent amounts of Mg, O and Cl along with Ca and P were observed for annealed sample from the EDX analysis. But the EDX of the FSP samples revealed that the layer is rich in Ca and P with less Mg, O and Cl suggesting that FSP has thick HA formation than annealed sample.

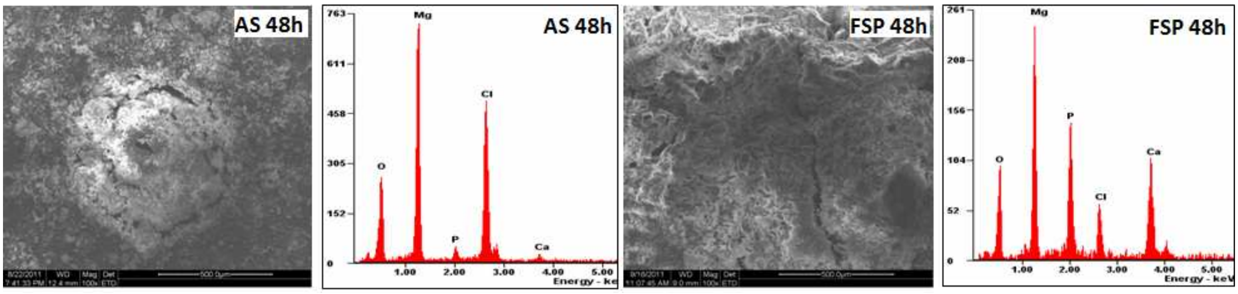

Fig. 6 SEM images and corresponding EDX of the samples immersed in SBF 5X: round corrosion pit formation

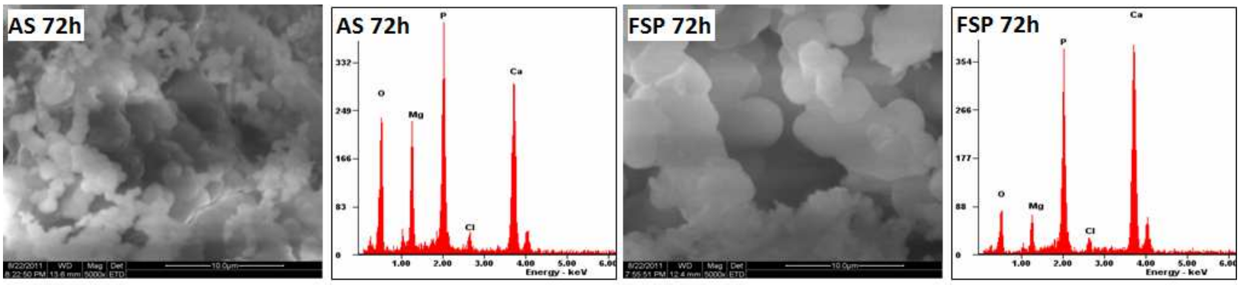

Fig. 7 SEM images and corresponding EDX of the samples immersed in SBF 5X: deposition of a thick white layer on the surfaces

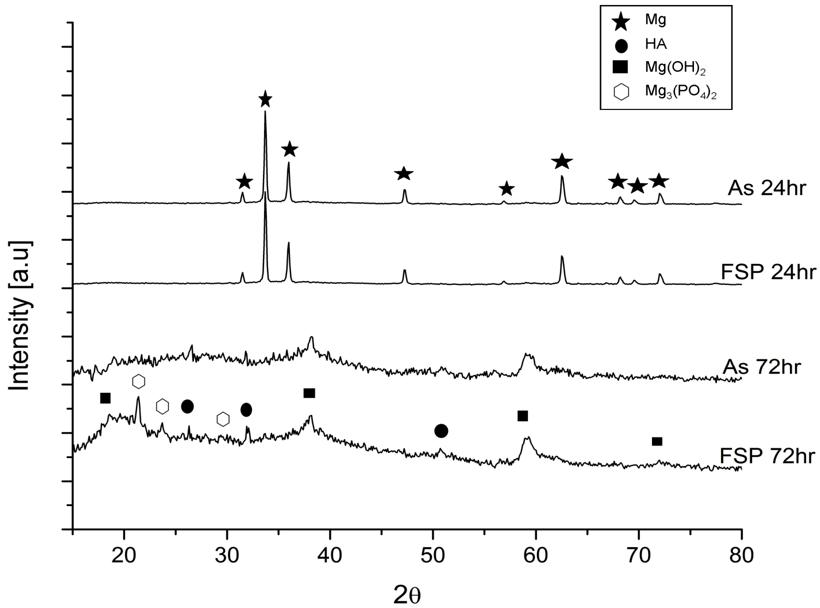

Fig. 8 XRD patterns of the specimens immersed in SBF 5X.

Magnesium undergoes pitting corrosion when exposed to chloride ions. Discrete areas of the samples undergo rapid attack while the vast majority of the surface remains unaffected. Porous Mg $(OH)_2$ formation at the early stage of corrosion process acts as a barrier for further degradation but the presence of Cl^- ions contributes to the breakdown of the $Mg(OH)_2$ by producing $MgCl_2$ and thereby pit formation which increases the degradation rate [6]. As a result the corrosion of magnesium alloys in chloride containing solutions takes the form of pitting. In both the cases complete coverage of surfaces by HA was not observed. However, formation of more amount of HA and with dense surface layers were observed at many locations for the FSP sample compared to annealed sample. EDX analysis shows that the FSP magnesium has deposition of more HA than annealed sample and with increase in Ca/P deposition, presence of Cl^- was found to be reduced. The presence of HA and magnesium phosphate deposition on the surfaces reduces the action of Cl^- and there by increases dissolution time. These results clearly suggests that the aggressive action of Cl^- can be controlled by enhancing the bioactivity of magnesium by FSP.

Summary

Friction stir processing (FSP) of pure magnesium shows fine grain refinement and increased hardness at the nugget zone. Wettability of pure magnesium was also improved after FSP due to the increased surface energy resulting from the fine grain structure. Enhanced bioactivity was observed in FSP sample. A thick layer of hydroxyapatite along with magnesium phosphate was observed on the FSP sample at many locations and this results in reducing the degradation rates. Hence, FSP can be a promising technique to enhance the bioactivity of pure magnesium by inducing grain refinement.

Acknowledgement

The authors would like to thank Prof. K. Prasad Rao, IIT Madras, for providing the FSP facility.

References:

[1] F. Witte, J. Fischer, J. Nellesen, H-A. Crostack, V. Kaese, A. Pisch, Felix Beckmann, Henning Windhagen Biomaterials 27 (2006) 1013–1018.

[2] A. Thirugnanam, T.S. Sampath Kumar, Uday Chakkingal Materials Science and Engineering C 30 (2010) 203–208.

[3] R.S. Mishra, M.W. Mahoney, S.X. McFadden, N.A. Mara, A.K. Mukherjee, Scripta Materialia 42 (2000) 163-168.

[4] T. Kokubo, H. Takadama, Biomaterials 27 (2006) 2907-2915.

[5] M. Alvarez-Lopez, Maria Dolores Pereda, J.A. del Valle, M. Fernandez-Lorenzo, M.C. Garcia-Alonso, O.A. Ruano, M.L. Escudero Acta Biomaterialia 6 (2010) 1763–1771

[6] Yong Wang, Mei Wei, Jiacheng Gao, Jinzhu Hu, Yan Zhang Materials Letters 62 (2008) 2181–2184