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Investigating the Degradation Behavior of Grain Refined WE43 Magnesium Alloy Produced by Friction Stir Processing for Medical Implant Applications

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Abstract

Developing Magnesium (Mg) based degradable implants for orthopedic applications is an attractive research area for the past two decades in the biomedical engineering. Mg is well accepted by human system and does not cause any health abnormalities during its degradation in the physiological environment. However, in order to improve its life span by controlling the aggressive degradation, novel Mg alloys are developed and subjected to different treatments to enhance their performance to tailor as promising candidates for implant manufacturing. In this context, recently, a special attention is paid towards using rare earth containing Mg alloys due to their excellent mechanical and corrosion resistance properties. Hence, in the present work, WE43 Mg alloy has been selected and the microstructual modification was carried out by friction stir processing. The role of grain refinement on the degradation behavior of FSPed WE43 Mg alloy was assessed by immersing the samples in simulated body fluids. From the microstructural studies, grain size reduction from 46 ± 4.2 µm to 16.1 ± 5.4 µm was achieved after FSP. The larger intermetallic particles were also observed as dissolved into the solid solution grains and fewer intermetallic particles were remained in the stir zone of FSPed alloy. After immersion studies, the surface of the samples was deposited with mineral phases and were analyzed by X-ray diffraction analysis and scanning electron microscope and found that the grain refinement achieved by FSP has a significant effect on increasing the mineral depositions which helps to control the degradation rate of the samples.

Keywords: *Biomineralization, Degradable Implants, Friction Stir Processing, Grain Refinement, WE43*

1.0 Introduction

Biomaterials are substances consisting of natural or synthetic materials, engineered in a way that they interact with the biological system by replacing the organs or by providing appropriate support to improve the function of the organs. Biomaterials are playing a significant role in enhancing the quality of human life by addressing several challenges in the health care sector, and thus attracting a great deal of attention in materials engineering. Biomaterials are used in numerous applications in different parts of a human body including neural prosthetics, pacemakers and artificial valves for the heart, cardiac stimulators used in the cardiovascular system[1-3], urinary tract reconstruction, bone replacements for wrist, shoulder, knee, ankle, hip, dental and spine etc. Among these biomedical applications, orthopaedic implants have their own prominence due to the increased need of medical remedies to address bone degenerative diseases like arthritis, osteoporosis, trauma and musculoskeletal disorders[4-6].

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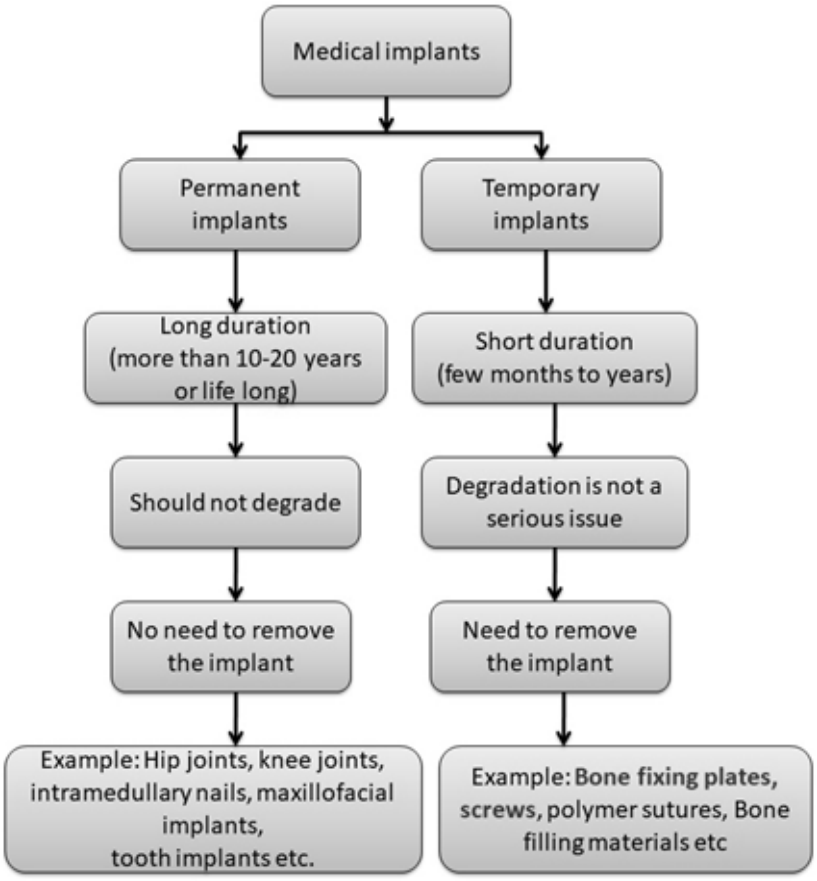

Figure 1. Classification of implants based on the need of function in the human body.

In current orthopaedic implants can be classified as permanent implants and temporary implants based on their life span. A few applications demand the support of the implant for longer periods of for the entire life span such as knee implants, hip implants, dental implants, intramedullary nails and maxillofacial implants which are called as permanent implants. Permanent implants must possess higher compatibility, appropriate mechanical properties and higher corrosion resistance and non degradability[7,8]. On the other hand, a few implants are required to function until the host organ is recovered to its full functioning. Materials used to manufacture temporary implants should have biocompatibility, biodegradability and appropriate mechanical properties until the local host is sufficiently regenerated to its full functioning[9,10]. Figure 1 shows the classification of the implants based on their life span. Table 1 presents the applications of different implants usually found in the biomedical engineering[11].

It is inevitable to use metals and alloys such as steels, titanium alloys and Co alloys for permanent implant applications. In case of temporary implant applications; due to the lack of degradable metals in the commercial applications, permanent implants are used as fixtures and then removed after the diseased or fractured organ or tissue is completely recovered. Additionally, due to the larger difference in the mechanical properties of the local tissue and the implant material, stress shielding phenomenon is another challenge needed to pay attention in developing metallic implants[12,13]. Here comes the necessity of developing novel metallic implants which exhibit safe degradation in the physiological environment.

Among the available materials to manufacture temporary implants, Magnesium (Mg) alloys have the potential as suitable candidates to develop degradable implants. Furthermore, due to the similar mechanical properties to that of natural bone, Mg reduces the stress

shielding effect to a greater extent when used as an implant material. However, controlling the rapid degradation of Mg alloys in biological environment is a limitation which is the interest of several research groups across the globe for the past two decades[14]. Microstrcutural modification through mechanical processing techniques such as Severe Plastic Deformation (SPD) or thermo mechanical treatments is one of the promising strategies to improve the bulk properties and to tailor the degradation of the Mg based implants[15,16]. Friction Stir Processing (FSP) is one of such techniques, in which the substrate is stirred plastically to achieve grain refinement within the solid state[17,18,29]. Pure Mg, and AZ31, AZ61, AZ91, AZ80, ZE41, ZK60, AM60, Mg-RE (Y, Gd, Nd, Zr) Mg alloys were subjected to FSP and improved bulk properties were reported in the literature[14,19,20].

Rare Earths (RE) containing Mg alloys are the new class of alloys which exhibit better mechanical and corrosion properties specifically which are having yitrium and neodenium[21-23]. Addition of Zirconium (Zr) helps to refine the microstructure in Mg. Presence of intermetallics such as $Mg_{41}Nd_5$ and $Mg_{24}Y_5$ due to the addition of Nd and Y in Mg significantly influences the mechanical, corrosion and tribological properties of Mg-RE alloys. The quantity, size and distribution of these intermetallics can be altered by heat treatment or mechanical processing that involves recrystallization. As observed form the earlier reports; the fraction and the distribution of the intermetallics in Mg alloys can be significantly altered by adopting FSP[24,25]. Hence, in the present work, WE43 Mg alloy has been selected and processed by FSP to achieve grain refinement with an objective to investigate the role of modified microstrucutre on the biomineralization of WE43 Mg alloy targeted for degradable implant applications.

2.0 Materials and Methods

WE43 Mg alloy sheets (Exclusive Magnesium, India) of size 100 × 100 × 6 mm^3 with the chemical composition of 3.5% Y, 2.5% Nd, 0.5% Zr and remaining being Mg with negligible impurities were used as the base alloy. Friction stir processing was done on the sheets by using an FSP tool having 20 mm shoulder diameter and a tapered threaded pin with 6 mm to 3 mm radius for a length of 5 mm and the process parameters were obtained from the literature to carry out the procedure with a feed rate of 50 mm/minute and a tool rotational speed of 900 rpm. Figure 2 shows the typical photograph of the process and the surface of the FSPed sample. Specimens were cut across the stir zone of FSPed sample and also from the base alloy for microstructural studies. After systematic metallographic polishing followed by chemical etching of the samples, microstrucutres were recorded by optical microscope (Leica, Germany). The base alloy and FSPed alloy were subjected to X-Ray Diffraction (XRD, Bruker, USA) analysis by using CuKα radiation from 20 to 80 ° range with a scanning rate of 0.1°/s.

In vitro degradation studies were carried out by immersing the samples in a Simulated Body Fluid (SBF) solution. Specimens of size 10 x 10 mm^2 were cut from the base alloy and FSPed alloy sheets for the immersion studies. Lab grade chemicals as listed in Table 1 are added in one liter of deionized water and a pH of 7.4 was

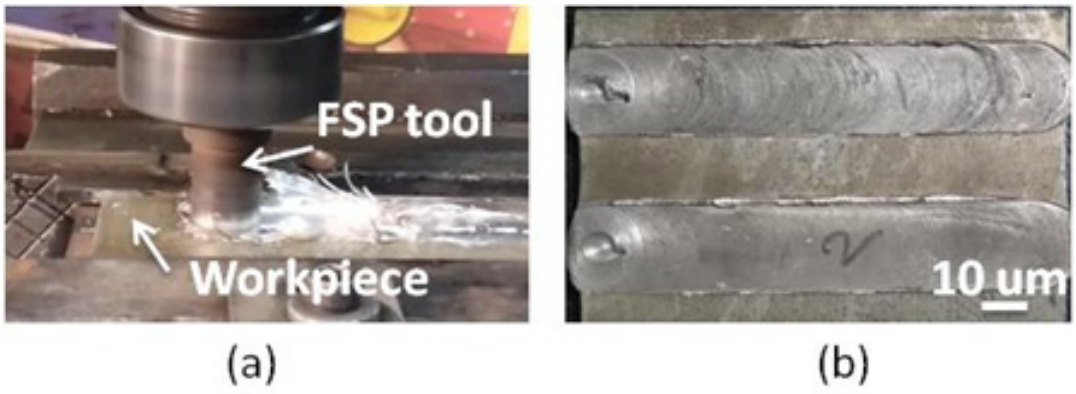

Figure 2. Photograph showing FSP of WE43 Mg alloy.

Table 1. Sequence of adding the chemicals and their amounts to prepare 1 liter of SBF solution as per Kokubo protocol[26].

Order	Reagent	Amount
1	NaCl	8.035g
2	$NaHCO_3$	0.355g
3	KCl	0.225g
4	$K_2HPO_4.3H_2O$	0.231g
5	$MgCl_2.6H_2O$	0.311g
6	1.0 M-HCl	39ml
7	$CaCl_2$	0.292g
8	Na_2SO_4	0.072g
9	Tris - $(HOCH_2)_3CNH_2$	6.118g
10	1.0M-HCl	0-5 ml

maintained. The protocol to prepare SBF was adopted from *et al*[26]. The base and FSP samples were immersed in 50 ml of SBF and the containers were placed in a constant temperature water bath maintained at 37°C. The weights before the immersion and after immersion were noted. The surface morphologies of the immersed samples were observed by Scanning Electron Microscope (SEM, TESCON, Czech Republic).

3.0 Results and Discussions

The microstructures of base alloy (WE43) and processed alloy (FSP WE43) are presented in Figure 3. It is clearly noticed that FSP led to develop fine grains in the alloy. Form a starting size of 46 ± 4.2 µm in the base alloy, FSP resulted in grain refinement up to 16.1 ± 5.4 µm as measured from the microstructures. Additionally, presence of several intermetallics was also observed in the base alloy as indicated with the white arrows in the base alloy (Figure 3(a)). These intermetallics ($Mg_{24}Y_5$, $Mg_{41}Nd_5$) are usually developed when Y and Nd elements are added to Mg and appear at the grain boundaries as indicated with arrows in Figure 3(a). In addition to grain refinement, the size of the intermetallics was appeared as decreased due to the dynamic recrystallization. This kind of behavior was also observed with other Mg alloys such as AZ91 and ZE41 Mg alloys after FSP[24,27]. This finding also suggests the development of the supersaturated gains in the FSP WE43 sample. Several twins were also observed in the FSP We43 sample in the newly developed grains. Twin boundaries also behave like grain boundaries and hence, the effect of grain size

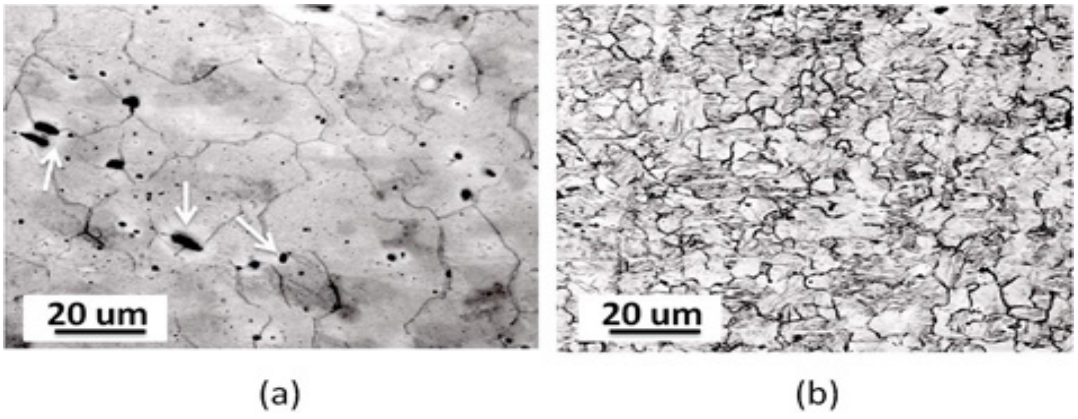

Figure 3. Microstructure of the samples. **(a)** WE43 and **(b)** FSP WE43.

Table 2. Weights of the samples measured before and after immersion studies

Samples	Immersion time (days)	Weight before immersion (g)	Weight after immersion (g)	Change in weight (%)
WE43	1	0.557	0.574	3.5
	3	0.559	0.62	12
	7	0.555	0.610	9.9
FSP WE43	1	0.28	0.296	5.71
	3	0.296	0.372	24
	7	0.293	0.337	15

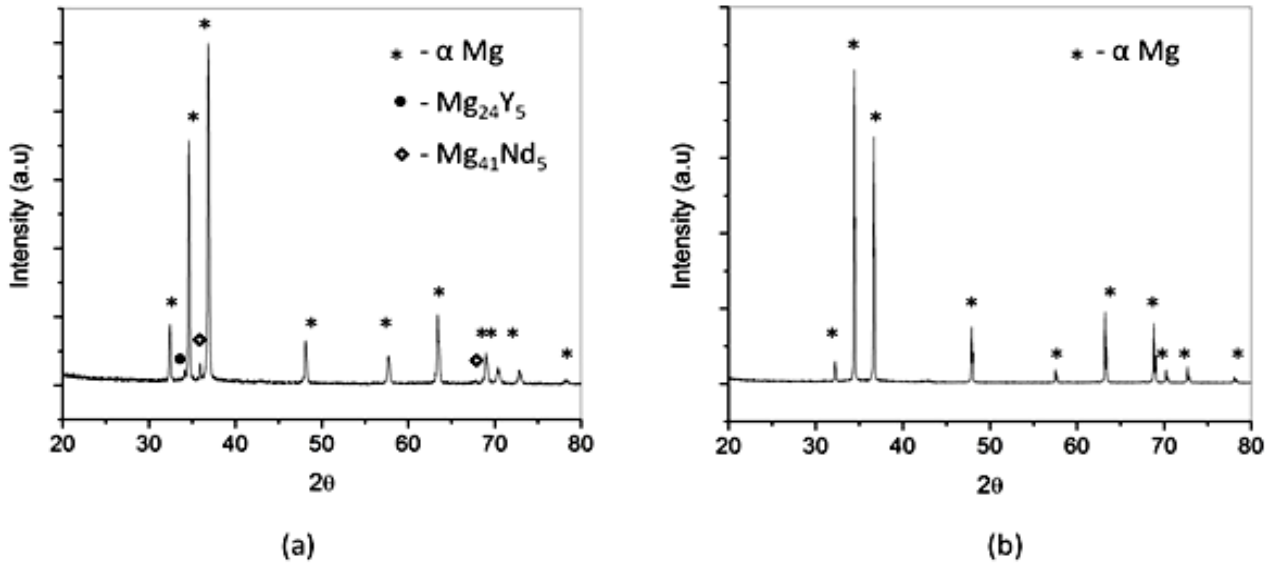

Figure 4. XRD analysis of the samples. **(a)** WE43 and **(b)** FSP WE43.

reduction is increased with the presence of twins in the microstrucutre.

XRD analysis before and after FSP suggest the development of texture (Figure 4). After FSP, the intensities of peaks corresponding to intermetallics ($Mg_{24}Y_5$, $Mg_{41}Nd_5$) were identified as decreased. This can be attributed to the heat generated during FSP which increased the solubility limit of the alloying elements and dynamic recrystallization which led to the evolution of new grains with the more solubility of alloying elements. Hence, the resulted grains are believed to be super saturated due to the dissolution on more amount of alloying elements. Furthermore, a significant change in the intensities of the peaks after FSP also suggests the development of texture during the material flow in the stir zone.

The weight measurements of the samples before and after immersion in SBF are presented in Table 2. The immersion of the samples was done for three different intervals of times including 1 day, 3 days and 1 week. From the weights before immersion and the weights after the immersion, the % of change in the weight of the sample was calculated and presented in Table 2. It was observed that the weight gain has been increased with the immersion time for both the samples. Compared with the base alloy, FSP WE43 sample has higher weight gain at all the immersion times. Figure 5 presents the typical surface morphologies of the samples observed by SEM after 24 h

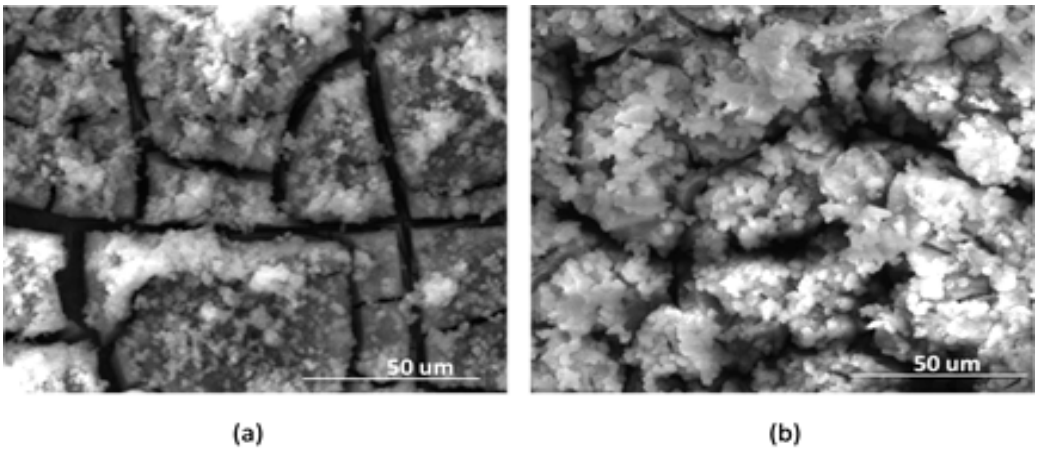

Figure 5. Surface morphologies of the immersed samples after 24 h of immersion. **(a)** WE43 and **(b)** FSP WE43.

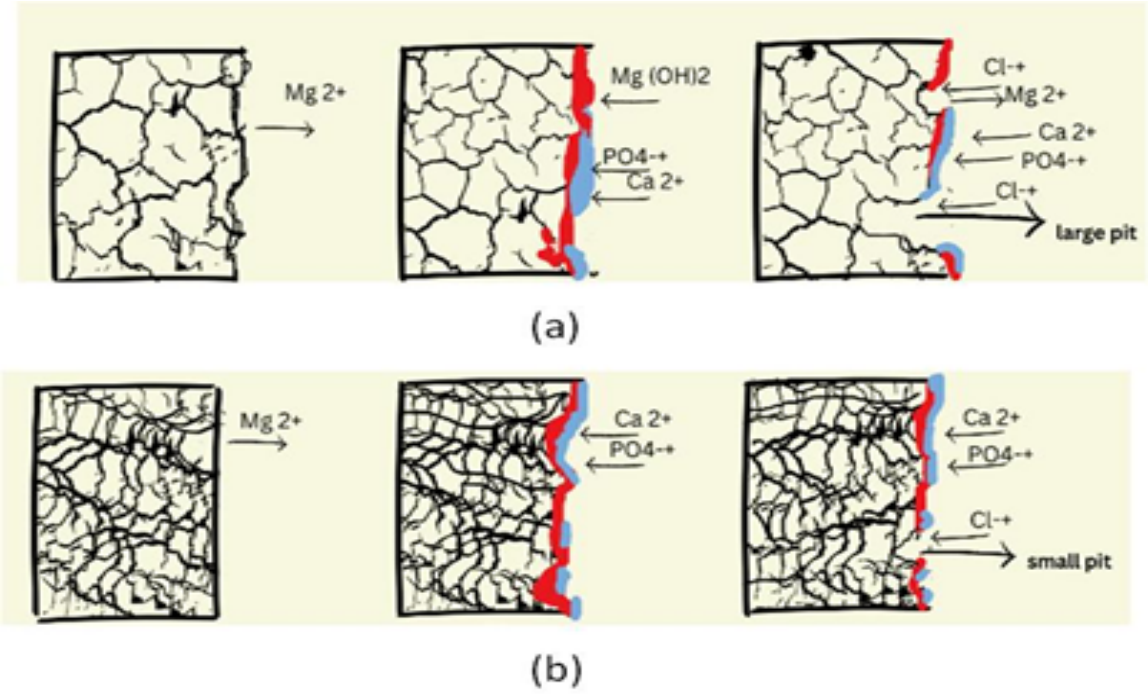

Figure 6. Schematic representation of the degradation of WE43 with two different grain sizes. **(a)** Coarse grains and **(b)** Fine grains.

of immersion. More surface cracks were appeared on the base alloy compared with FSP WE43. On the other hand, more mineral phases were deposited on the FSP WE43 alloy which suggests the increased biomineralization.

In the biomineralization and degradation perspective, Mg forms magnesium hydroxide layer on the surface for protection against the corrosion. Since, the biological solutions contain more concentration of Cl^- ions, magnesium hydroxide is unstable and results magnesium chloride. If the stability of magnesium hydroxide is increased by controlling the formation of magnesium chloride, the degradation of Mg alloys can be reduced[19,28].

Equations (1), (2), (3) and (4) explain the development of magnesium hydroxide when immersed in the aqueous solution.

$$Mg \rightarrow Mg^{2+} + 2e^{-} \quad (1)$$

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \uparrow \quad (2)$$

$$Mg^{2+} + 2OH^{-} = Mg(OH)_2 \uparrow \quad (3)$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow \text{ (Overall reaction)} \quad (4)$$

In addition to stabilizing the magnesium hydroxide corrosion layer, deposition of calcium based or phosphorous based mineral phases on the surface of Mg alloys from the physiological solution helps to improve the degradation resistance of Mg alloys. It was observed from the earlier works that grain refined AZ31 Mg alloy has more amounts of hydroxyapatite and magnesium phosphate mineral depositions on the surface due to the grain refinement which helped to increase the corrosion resistance. As schematically explained in Figure 6, coarse grained WE43 base alloy has larger surface cracks and pits compared with the FSP WE43. The formation of magnesium chloride is delayed due to the deposition of the more mineral phases on FSP WE43 samples as reflected in the increased % of weight of the samples after immersing them in the SBF. With the increased grain boundary in FSP WE43 Mg alloy, higher surface energy is achieved which increases the biomineralizaiton from the SBF. These deposited mineral phases helps to protect the surface of the Mg alloy and prolong the life of the implants. Hence, from the results, it is understood that FSP can be conveniently adopted to produce grain refined WE43 mg alloy. The altered microstructure has a significant effect on increasing the biomineralization which controls the degradation of WE43 Mg alloy for temporary implant applications.

4.0 Conclusions

In the present work, WE 43 Mg alloKokuboy has been processed by friction stir processing to investigate the role of modified microstructure on the degradation behaviour. From the microstructural studies, grain refinement from 46 ± 4.2 µm to 16.1 ± 5.4 µm was achieved after FSP. The intermetallics were observed as decreased as also confirmed from the XRD analysis which suggests the development of supersaturated grains. From the immersion studies carried out in simulated body fluids clearly demonstrate increased weight gain for the FSPed samples at all of the immersion times compared with the base alloy. More number of surface cracks has been observed on the surface the base alloy compared with the FSP WE43 samples. Higher biomineralization was observed on the surface of the FSP WE43 samples which helped to protect the magnesium hydroxide layer and protected the surface. Hence, it is concluded that FSP can be adopted to process WE43 Mg alloy and higher biomineralization can be achieved to tailor the alloy for degradable implant applications.

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