PROCESSING AND CHARACTERIZATION OF BALL MILLED MAGNESIUM FOR BIOMEDICAL IMPLANT

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UNDER THE SUPERVISION OF

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CERTIFICATE

This is to certify that the thesis entitled "**PROCESSING AND CHARACTERIZATION OF BALL MILLED MAGNESIUM FOR BIOMEDICAL IMPLANT"** submitted by Prasanna Chandra Jha (109BT0624) in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Biotechnology and Medical Engineering at National Institute of Technology, Rourkela is an original work carried out by him under my supervision and guidance.

The matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree.

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Abbreviations

1. Mg	-	Magnesium
2. HA	-	hydroxyapatite
3. AR	-	As received magnesium
4. BM	-	Ball milled magnesium
5. h	-	Hour
6. ml	-	milliliter
7. g	-	gram
8. XRD	-	X-ray diffraction
9. SEM	-	Scanning electron microscopy
10. AMS	-	Absorbable metallic stents
11. SBF	-	simulated body fluid
12. mm	-	millimeter
13.rpm	-	rotation per minute
14. ML	-	mass loss
15. wt	-	Weight
16. FWHM	-	full width at half maximum

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Abstract

Damage and disease in the bone tissue arises the need for developing biomedical implants. Magnesium and its alloys have been intensively studied as biodegradable implant materials, where their mechanical properties make them a potential candidate for orthopaedic applications. As a biocompatible and biodegradable metal, it has several gains over the metallic implants presently in use, including eliminating the effects of stress shielding, improving biocompatibility concerns in vivo and eliminating the requirement of a second surgery.

In this present research work magnesium powder of two different particle size as received (AR) and ball milled (BM) were prepared using powder metallurgy technique. The AR and BM powders were compacted, sintered and characterized using x-ray powder diffraction (XRD) and scanning electron microscopy technique (SEM). The density measurement of AR and BM samples were measured using Archimedes' principle. Bioactivity and degradation studies were evaluated by immersing the samples in simulated body fluid (SBF) for up to 3 weeks. The degradation studies were assessed by determining the weight loss method. The bioactivity was assessed observing the apatite formation when immersed in SBF using SEM and XRD. From this study it was observed that the corrosion resistance of pure magnesium increases with decrease in particle size (i.e. BM samples showed better corrosion resistance).

Keywords: Magnesium, ball milling, sintering, bioactivity, simulated body fluid (SBF)

Chapter 1

Introduction

1. Introduction

Annually several million people suffer bone fractures caused by accidents or diseases. Many of those fractures are too complex for an external medical treatment but have to be surgically fixated by internal bone implants. Traditional methods of osteosynthesis or osteotomy use permanent metal implants e.g. bone screws and bone plates made of steel or titanium alloys, but permanent metal implants have to be excised. Especially young patients in growth require the implant removal. Usually, metal implants should be removed latest one or two years after the first surgery. Biodegradable implants, which dissolve in the human organism, therefore represent an appropriate solution.

Clinical circumstances often require the application of implants that serve temporarily rather than for a permanent purpose (Table 1.1). In these circumstances degradable biomaterials are of interest because the implants fabricated from these materials do not need to be surgically removed. The surgical removal of an implant with a temporary purpose is undesirable, as the process creates another wound with the possibility of surgical complication and infection. Additionally, the use of degradable implants can sometimes sidestep problems related to the long-term safety of permanent implants, such as long-term immune rejection, chronic inflammation at the implant–tissue interface, and failure of the implant. However, degradable implants are not without their own safety concerns, such as the toxicity of their degradation products, and the degradation-related, early failure of the implant.

Therefore, designing a degradable implant requires careful testing for potential toxicity of its degradation products and careful consideration of the implant's mechanical integrity during the required service life of the implant. To facilitate a better understanding of the complex decisions that have to be made during the design of a degradable implant, this work covers the basics of the process of degradation and/or erosion, the most prominent types of metallic biomaterials available today and considerations specific for the design and use of degradable medical biomaterials.

Table 1.1: Medical application of degradable biomaterials

Applications	Comments
Sutures	The earliest successful application of degradable biomaterial in human body.
Orthopedic fixation devices	Requires material of exceptionally strength and stiffness
Temporary vascular grafts and stents made of degradable material	Only investigational devices are presently available.

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1.1 Metallic Biomaterials

1.1.1 Stainless steel: The metallic biomaterial most commonly used for orthopedic applications earlier was the austenitic stainless steel. Its utilization is particularly justified by the combination of properties such as good acceptance by the body; low cost; good machinability; good formability; high strength, especially when cold worked and reasonable corrosion resistance. However, some aspects such as low strength in the annealed condition and susceptibility to localized corrosion often limits the wider use of this type of material in orthopedic applications, mainly when the implanted device must remain in the human body for a relatively long time (more than 12 months). The combination of such aspects favors the failure of orthopedic implants by a synergy called as corrosion–fatigue [1]. Ni and Cr are main components of stainless steel. These implants are reported to release these elements due to corrosion in the body. Ni and Cr released from prosthetic implants have been reported to be toxic. Skin related diseases such as dermatitis due to Ni toxicity have also been reported [2]. In addition, 316L SS possess much higher modulus than bone, leading to insufficient stress transfer to bone leading to bone resorption and loosening of implant after some years of implantation.

The high cycle fatigue failure of hip implants is also reported as the implants are subjected to cycles of loading and unloading over many years [2].

1.1.2 Cobalt chromium alloys: Co–Cr based alloys are the most commonly used representative of Co alloys for biomedical applications. The presence of Cr imparts the corrosion resistance and the addition of small amounts of other elements such as iron, molybdenum or tungsten can give very good high temperature properties and abrasion resistance. The various types of Co – Cr alloys used for implant applications include Co–Cr–Mo, Co–Cr–Mo, Co–Cr–W–Ni and Co–Ni–Cr–Mo–Ti. Clinical applications of such alloys include its use in dentistry and maxillofacial surgery. However high cost, low formability and poor machinability are some of the limitation prevents the use of these metallic materials for orthopedic applications. Also like stainless steel, Co and Cr are toxic and causes skin disease. Co has also been reported to be carcinogenic [2].

1.1.3 Titanium (Ti) and its alloys: Ti and its alloys possess low modulus varying from 110 to 55 GPa [2]. Commercially pure Ti and Ti–6Al–4V are most commonly used titanium materials for implant applications. High corrosion resistance and excellent biocompatibility increases its suitability for biomedical industry. The mechanical strength of the Ti and its alloys is very close to that of 316 L SS, and its density is 55% less than steel. The applications cover joint replacement parts for hip, dental implants, knee, elbow, spine, shoulder etc. Although titanium and its alloys mainly Ti6Al4V have excellent corrosion resistance and biocompatibility, long term use leads to release of Al and V ions. Both vanadium and aluminum ions released from the Ti6Al4V alloy are found to cause long term health problems, like Alzheimer disease etc. [2]. Toxicity of vanadium has also been reported, both in the elemental state and oxides V_2O_5, which are present at the surface. Bio inertness of Ti also restricts its use in biomedical implants [2]. Beside Cp-Ti and Ti6Al4V, β-titanium alloys such as Ti-Ta alloys; Ti-Mo alloys; Ti-Nb and Ti-Ni shape memory alloys are very much attracted as bio implants [1, 9]. These alloys exhibit high corrosion resistance and biocompatibility. Ti-Ta alloys have much lower modulus and a good combination of high strength and low modulus. They have the great potential to become new candidates for biomedical applications.

Adding Zr to the Ti alloy lowers the Young's modulus and other mechanical properties suitable for biomedical applications [2].

1.1.4 Magnesium and its alloys: As an important essential trace element, magnesium participates in almost all the human metabolism, ranking just after calcium, sodium and potassium. Its density (1.74g/cm^3) is close to that of natural bone (1.75g/cm^3) [10].

Meanwhile, its high specific strength (pure Mg, 133 GPa/ ($g \cdot cm^3$)) and specific stiffness, can meet the strength performance requirements of biological implant materials. As a biodegradable implant material, magnesium provides both biocompatibility and sufficient mechanical properties. Mg alloys are very attractive due to their good biocompatibility and especially their degradability. Researchers found that magnesium alloys offer great potential as absorbable implant materials such as cardiovascular tube stent and bone fixation materials for instance as bone screws or plates. Within a certain time span after surgery, they degrade and are completely suitable to medical functions [2-3, 7-8].

However, several problems need to be settled for the application of Mg to the biomedical field, such as poor corrosion resistance in chloride containing solutions and pitting especially in body fluid condition.

1.2 Objective

The objective is to access corrosion behavior of unmilled and ball milled magnesium samples. It is expected that the corrosion resistance of ball milled sample in physiological medium will be better than that of unmilled sample. Corrosion behavior will be estimated by mass loss method. And the results will be correlated with characterization techniques i.e. SEM and XRD.

Chapter 2

Literature review

2. Literature review

2.1. Magnesium

Magnesium is a grayish-white, legitimately tough metal. Magnesium is the eighth most abundant element in the earth's crust even though not found in its elemental form [11]. It is a Group 2 element (Group IIA in older labeling schemes) called alkaline earth metals. Magnesium metal is pyrolitic burns with a very bright light [11].

Magnesium is an important element for plant and animal life. Chlorophylls are porphyrins based upon magnesium. The daily requirement of magnesium for adult human being is about 0.3 g per day [11].

In 1618 a farmer at Epsom in England attempted to feed water to his cows water from a well. They refused to drink because of the water's bitter taste. However the farmer noticed that the water seemed to heal scratches and rashes. The fame of Epsom salts spread. Eventually they were recognized to be magnesium sulphate, $MgSO_4$. Black recognized magnesium as an element in 1755 [11]. It was isolated by Davy in 1808 that electrolyzed a mixture of magnesia (magnesium oxide, MgO) and mercuric oxide (HgO) [11].

Magnesium alloys, as a new kind of biodegradable materials, have attracted great attention recently. The key advantages of magnesium alloys as temporary biomaterials are their good mechanical properties and biocompatibility:

(i) The fracture toughness of magnesium is greater than ceramic biomaterials, while the elastic modulus (41–45 GPa) is close to that of the bone that avoids the stress shielding effect [10].

(ii) Magnesium is essential to human metabolism and is the fourth most abundant cation in the human body, with estimated 25 g magnesium stored in human body and approximately half of the total content stored in bone tissue. Magnesium is a cofactor for many enzymes and stabilized the structures of DNA and RNA [10].

(iii) Magnesium has standard electrode potential of – 2.37 V, and bare magnesium metal exhibits even poorer corrosion resistance in Cl^- containing physiologic environment.

Therefore, magnesium alloys could be developed as a new biodegradable metal, taking advantage of their fast corrosion rate in the physiologic environment [10].

Magnesium and its alloys have been intensively studied as biodegradable graft materials, where their mechanical properties make them smart candidates for orthopaedic applications. As a biocompatible and degradable metal, it has several gains over the permanent metallic materials currently in use, including eliminating the effects of stress shielding, enlightening biocompatibility concerns in vivo and improving degradation properties, removing the requirement of a subsequent surgery for implant removal.

Many artificial bone tissues of ceramics and metals are being developed. A biodegradable orthopedic implant should have an excellent biocompatibility and bioactivity. Beside these, the degradation rates of the implant material must match the rate of bone healing. Also they should possess mechanical properties similar to that of the damaged or diseased bone. High corrosion and wear resistance also plays an important role [12].

2.2 Ball milling

The process of ball milling or mechanical alloying (MA) starts with mixing of the powders in the right proportion and charging the powder combination into the vial along with the grinding medium (generally steel balls). This combination is then milled for the desired span of time until a steady state is reached when the composition of every powder particle is the same as the proportion of the elements in the starting powder mix. The milled powder is then consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties. Thus the important components of the MA process are the raw materials, the mill, and the process variables [13].

Some of the important parameters that have an effect on the final constitution of the powder are:

- type of mill
- milling container
- milling speed
- milling time
- type, size, and size distribution of the grinding medium

- ball-to-powder weight ratio
- extent of filling the vial
- milling atmosphere
- process control agent
- Temperature of milling

All these process variables are not fully independent. For example, the optimum milling time be influenced by on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio, etc.

Marie-Helene et. al, 2004, varied the particle size of pure magnesium by high energy by varying the milling time and reported that various particle size of pure magnesium were obtained. Also it was reported that the corrosion improvement was attributed to the increase through the milling process of the density of surface defects and grain boundaries susceptible to increase the number of nucleation sites for Mg hydroxylation in aqueous media, leading to the rapid formation of a dense and protective Mg(OH)2 layer [14].

M. Zidoune et. al, 2004, reduced the particle size of pure magnesium by ball milling and did the comparative study on the corrosion behavior of unmilled and milled magnesium and it was reported that ball milling can be used as a simple and low cost technique in the preparation of materials (magnesium) with improved corrosion resistance [15].

2.3 Compaction

Powder compaction, also known as powder pressing, is the process of compacting metal powder in a die by the application of high pressure. Typically the tools are held in the vertical orientation with the punch tool forming the bottom of the cavity. The powder is then compacted into a shape and then ejected from the die cavity [13].

A controlled amount of powder is fed into a precision die and is compacted. Dimensions and density are closely controlled in this process. The compacted component is said to be in the "green" state. The density of the compacted powder is directly proportional to the amount of pressure applied.

2.4 Sintering

Sintering is a method used to create objects from powders. It is based on atomic diffusion. Diffusion occurs in any material above absolute zero, but it occurs much faster at higher temperatures. In most sintering processes, the powdered material is held in a mold and then heated to a temperature below the melting point [16]. The atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece. Because the sintering temperature does not have to reach the melting point of the material, sintering is often chosen as the shaping process for materials with extremely high melting points. After pressing, the "green compacts" are sintered by passing them through a furnace in which both temperature and atmosphere are strictly controlled. The part is heated to just below the melting point of the principal material so that the particles are fused, or sintered, together into a solid mass.

Yamaguchi et. al, 1997, studied the compaction and sintering characteristics of composite metal powders and reported that the hardness of the sintered part increases remarkably, which is approximately 15 to 20 times [17].

2.5 Simulated body fluid (SBF)

There are many chemicals present around the inserted orthopedic implant in body, in the form of various body fluids. This is due to diverse composition of body fluid. The composition of the environment changes depending on the location of the implant. The factors found in the body fluid effects the corrosion of the magnesium implant are pH, certain proteins, ion concentrations and water. New implants may be tested in simulated body fluid (SBF) to determine the rate of corrosion. A simulated body fluid (SBF) is a solution with an ion concentration close to that of human blood plasma, kept under mild conditions of pH and identical physiological temperature. A material able to have apatite formed on its surface in SBF, is considered to bond to living bone through this apatite layer. This relationship holds as long as the material does not contain a component that induces toxic or antibody reactions [18].

There are a few materials that directly bond to living bone without the formation of detectable apatite on their surfaces. Despite this limitation, examination of apatite formation on the surface

of a material in SBF is useful for predicting the in vivo bone bioactivity of the material, not only qualitatively but also quantitatively [18]. This method can be used for screening bone bioactive materials before animal testing.

Kokubo et. al, 2006, reported that apatite formation on a material in SBF is useful for predicting the in vivo bone bioactivity of a material, and the number of animals used in and the duration of animal experiments can be reduced remarkably by using this method, which can assist in the efficient development of new types of bioactive materials. [18].

Guang.Ling et. al, 2006, studied the corrosion behavior of pure magnesium in SBF and reported that after some proper measures are taken to retard corrosion reaction, Mg can be successfully employed as a degradable and absorbable implant material [19].

2.6 Mass loss as a measure of biodegradation

Mass loss (ML) experiments typically require only a sample, degradation medium and an accurate microbalance. The sample is placed in the degradation medium for a period of time, after which the specimen is removed and the resultant change in mass is measured. Prior to measuring the final mass, a cleaning solution such as dilute chromic acid is used to remove degradation products from the surface (via dissolution of any Mg-hydroxide ($Mg(OH)_2$) surface product).

N.T. Kirkland et al, 2012, reported that results obtained from ML tests are typically accurate. ML experiments conceal how much degradation has occurred, they do not divulge the mechanisms involved in the degradation process. Although it may be observed that one alloy corrodes faster than another, ML does not provide the information required to determine why this happens [12].

2.7 Magnesium as degradable orthopedic implant material.

Magnesium as a degradable implant material provides both biocompatibility and sufficient mechanical properties. Studies have shown that magnesium, which is an essential element of the human organism, is suitable as a degradable biomaterial for use in medical implants. Due to mechanical properties comparable the bone, magnesium implants show biomechanical properties

comparable to conventional steel implants in standardized biomechanical tests. Also an influence of surface properties on the degradation behavior is already known. Interdisciplinary research between medical and engineering sciences focuses on the development of degradable magnesium implants for osteosynthesis.

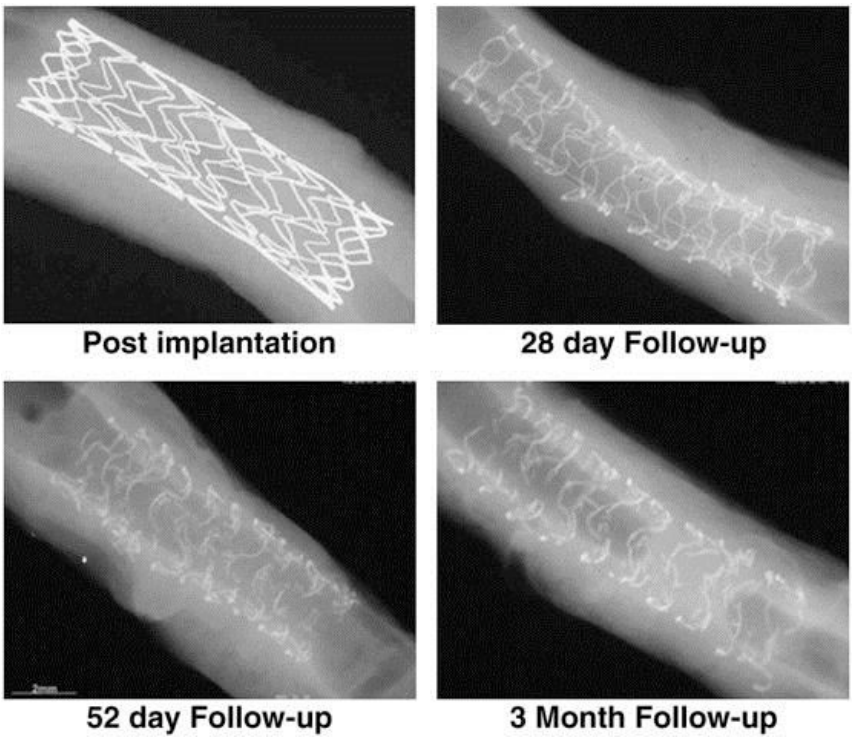


Fig. 2.1 Radiological pictures of biodegradable magnesium implant [20]

M.P. Staiger et al, 2006, reported that magnesium is an osteoconductive metal and can be used as bone substituent if the corrosion process in physiological medium can be controlled [21].

Erbel R et. al, 2007, reported that the AMS stent was evaluated in a multicenter and nonrandomized study of 63 patients at nine clinical sites with a single de novo native coronary lesion. The results showed that 71 stents, 10–15 mm in length, 3.0–3.5 mm in diameter, and about 3mg in weight, could achieve an immediate angiographic result similar to the result of other metal stents and can safely degraded after 4 months [20].

The removal of those implants after convalescence of the fractured bone is no longer necessary, resulting in a considerable benefit for patients and the public health care system.

Chapter 3

Materials and Methods

3. Materials and methods

Pure Magnesium powder was obtained from Himedia. As received powder was processed and coded as shown in Table 2

Table 3.1: Sample code

S.no	Sample code	Description
1.	AR	As received Magnesium powder (mesh size 300)
2.	BM	Ball milled Magnesium compacted (8 h)

3.1 Sample preparation

The as received Magnesium powder (mesh size 300) was ball milled in a planetary ball mill machine (Fritsch Planetary Ball Mill – Puluerisette 5) for 8 h.

Fig. 3.1 Ball milling machine

Ethanol was used as wetting media. Ball milling was done using stainless steel vial and stainless steel balls and the ball to powder mass ratio 20:1 was maintained. The ball milling was done at 150 rpm and milling was done in a cycle of 15 min and was put on rest for next 15 min. This cycle was continued till 8 h of effective milling time.

The milled powders were compacted in uniaxial single action (SOILLAB, Delhi) hydraulic compaction machine, using a 15 mm diameter die and using 10 ton load.

Fig. 3.2 Punch press (15 tons capacity)

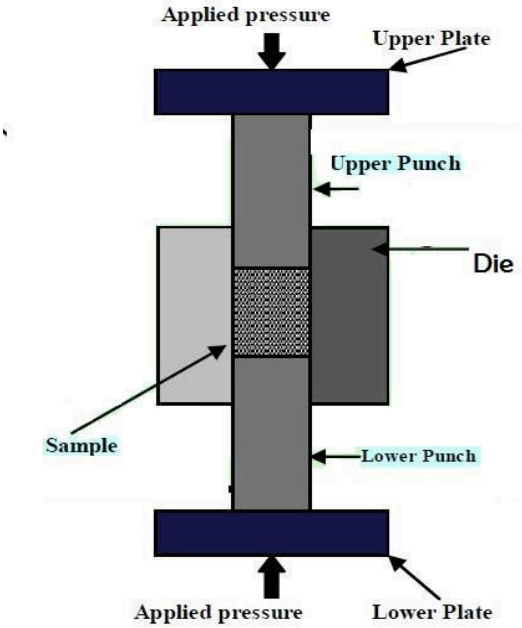


Fig. 3.3 punch press mechanism

Zinc stearate was used as lubricant. The green compact was then sintered in muffle furnace (SEMAG Industries).

3.2 Sample characterization

The as milled and sintered samples were characterized using scanning electron microscope (SEM), (JEOL JSM – 6480LV) and XRD (PANalytical - Xpert 3040Y00) for morphology and phase contamination. The scanning range for XRD was between 20^{o} -80^{o} with a step size of 3°/min.

3.3 Density measurement

Compacted and sintered samples were immersed in a measuring cylinder containing distilled water. The corresponding change in the volume of the water was measured. The densities of the

samples were calculated using Archimedes' principle. According to the Archimedes principle, the increase in volume of water corresponded to the volume of the immersed sample. The density of the samples was calculated from the fundamental formula, density = mass/volume.

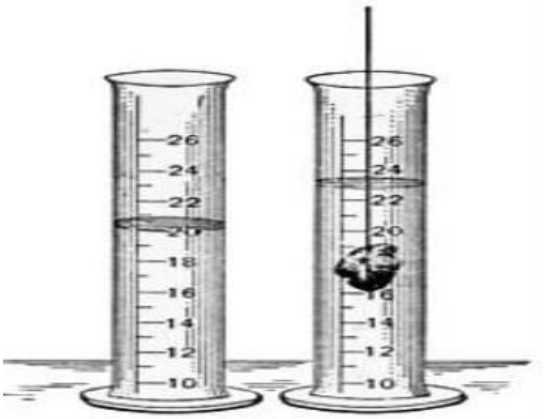


Fig. 3.4 Density measurement by Archimedes principle

3.4 In-vitro bioactivity study in SBF and weight loss measurement (biodegradation)

Compacted and sintered (as received powder and ball milled) cleaned in distilled water and then acetone for 15 min and dried. The samples were soaked in freshly prepared SBF for 3 weeks. The SBF is a solution with ion concentration close to that of human blood plasma and is kept under mild conditions of pH and identical physiological temperature.

The following electrochemical half-reactions occur during the corrosion process:

Anodic reaction:

$Mg \rightarrow Mg^{2+} + 2e$

Cathodic reaction:

$2H_2O + 2e \rightarrow 2OH^- + H_2$

Product formation:

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$

General reaction:

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

Corrosion mechanisms in the body

Table 2 shows the amount of reagents required to prepare 1 liter of SBF [14].

Table 3.2: Reagents for the preparation of one liter SBF

S.No	Reagents	Amount
1	NaCl	8.035g
2	$NaHCO_3$	0.355g
3	KCl	0.225g
4	$K2HPO_4.3H_2O$	0.231g
5	$MgCl_2.6H_2O$	0.311g
6	1.0M HCl	39-44 ml
7	$CaCl_2$	0.292g
8	Na_2SO_4	0.292g
9	Tris	6.118g

SBF was prepared by following Kokubo's protocol [14]. The pH of the finally prepared sample was adjusted to 7.40 by adding 1.0 M HCl. SBF was stored in clean plastic container in refrigerator at 4^oC. Each sample was kept in 50 ml plastic falcon tube. The falcon tube was then kept in a constant temperature water bath at 37^oC. SBF volume is calculated by

$$v = \frac{Sa}{10} \ldots\ldots\ldots\ldots [14]$$

v= volume of SBF

Sa= surface area of sample in mm^2

For porous materials, the volume of SBF should be greater than the calculated V_s. Since magnesium is porous so we took $V_s = S_a/10 + 5$ ml.

After each week the samples were taken out, washed with distilled water, dried and characterized using SEM and XRD for apatite morphology.

For degradation studies, the sample is placed in the SBF for a period of 3 weeks. Every day the mass loss was measured by removing the sample from the corrosion medium, dried and weighed the resultant change in mass is measured.

Chapter 4

Results and discussion

4. Results and discussion

4.1 Density measurement

The densities of the samples after compaction and sintering were calculated by Archimedes' principle. Table 4.1 shows the results of the density measurement by Archimedes' principle as well as by theoretical density calculation. The results showed that the density increased after ball milling and sintering.

Table 4.1: Density measurement by Archimedes principle

Sample code	Density by Archimedes Principle (g/cc)	Theoretical Density (g/cc)
AR	1.52	1.65
BM	1.43	1.62

The density of ball milled magnesium decreased with ball milling, indicating increase in porosity in the structure.

4.2 Powder morphology

Physical observations of the Mg powders indicate that milling affects the morphology .The milled powders consist of irregular particles. The large particles are due to the well-known cold welding of the particles occurring concomitantly to the repeated fracturing of the powder during milling. Fig 4.1 show the image of the Mg pellets obtained after cold compaction at 10 tons cm^{-2} of the unmilled Mg and milled Mg powders.

Fig. 4.1 compacted pellets

4.3 Powder structure

Fig. 4.3 shows the X-ray diffraction patterns of as received Mg powder and 8 h ball milled Mg powder. It shows the phase composition of unmilled and ball milled samples. The position of the diffraction peaks remains constant indicating that the lattice parameters are unchanged by the ball milling, i.e. solid solution resulting from possible contamination with milling tools does not occur. On the other hand, extra peaks attributed to an MgO phase are noticeable. The peak width of ball milled sample increased indicating refinement of crystal size. This decrease in the intensity of ball milled Mg peaks shows a refinement of crystal size. Table 4.2 shows that size of unmilled powder is 300 mesh sizeafter8 h of ball milling, the crystallite size of the BM powder was found to be 76 nm. Slight shift in the peaks were observed which was due to strain imposed on the powder due to ball milling and from XRD analysis and from table we can see that strain percentage of ball milled sample is 0.264. The strain induced in powders due to crystal imperfection and distortion was calculated using the formula:

$$\varepsilon = \frac{\beta hkl}{4\ tan\theta}$$

Where ε is strain and βhkl is FWHM at 2θ angle. And the average crystalline size was calculated using Debye-Scherrer's formula:

$$D = \frac{K\lambda}{\beta hkl Cos\theta}$$

Where D= crystalline size, K= shape factor (0.9), and λ= wavelength of x-ray. The source of oxygen during milling can be residual/leaking air present in the container and more largely, oxides present at the surface of the milling tools.

Table 4.2: Crystallites size and strain (estimated from a Scherer refinement analysis of the X-ray patterns)

Parameter	AR	BM
Crystallite size	300 mesh size	76 nm
% strain	0.0	0.264

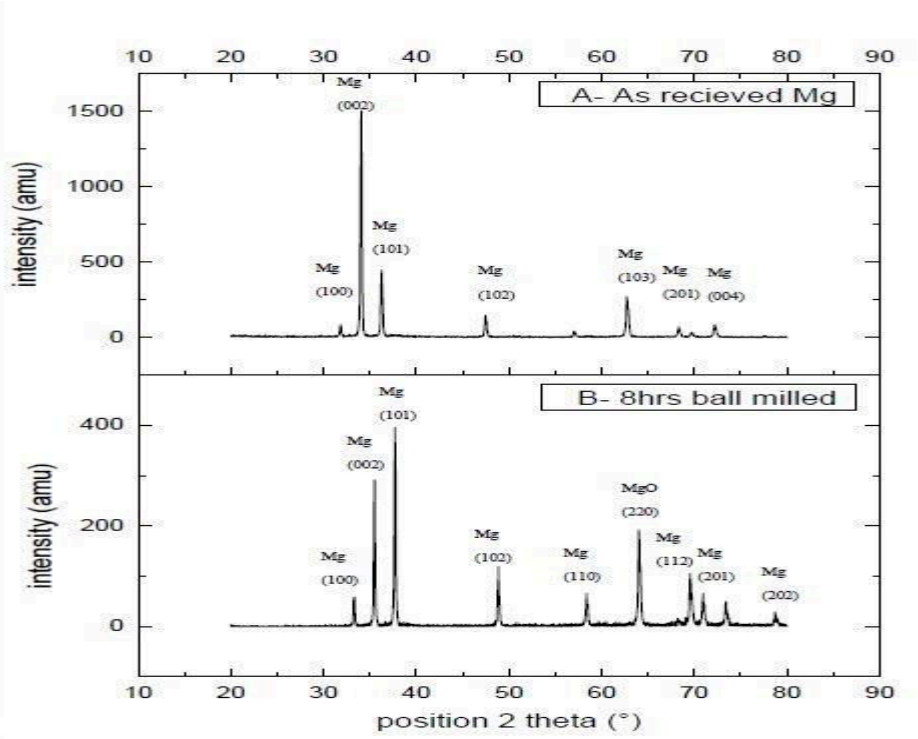


Fig. 4.2 X-ray diffraction patterns of as received Mg powder and 8 h ball milled Mg powder.

A Scherer's refinement analysis of the X-ray patterns was performed to determine the crystallite sizes and the internal strain and the results are presented in Table 4.2. The crystallite size is reduced to 76 nm after 8 h of milling. The decrease of the crystallite size is accompanied by the increase of the internal strain associated to the presence of lattice distortion at the grain boundaries and the accentuation of the dislocation density with prolonged milling.

4.4 Mass loss as a measurement of corrosion

Immersion tests were carried out for three weeks, SBF as corrosion medium. The corrosion rate is given by Eq. (1) [17]:

$$C.R = \frac{(kXw)}{(SXTXD)} \qquad (1)$$

Where the coefficient K = 8.76 X10^4 g cm^{-3}, W is the weight loss (g), S is the sample area exposed to solution (mm^2), T is the exposure time (day) and D is the density of the material (g cm^{-3}), C.R is corrosion rate. Here surface area of A= 495.55 mm^2, surface area of B = 423.9 mm^2 density of A= 1.65 g cm^{-3}, density of B = 1.56 g cm^{-3}

Table 4.3: corrosion measurement

Day (Time)	Mass of A (in g)	Mass of B (in g)	C.R for A (g mm^{-2} d)	C.R for B (g mm^{-2} d)
1	1.026	0.502	0	0
2	1.040	0.510	1.5	1.06
3	1.104	0.520	4.18	1.19
4	1.121	0.527	3.39	1.1

5	1.149	0.533	3.3	1.02
6	1.156	0.536	2.7	0.9
7	1.159	0.541	2.37	0.86
8	1.101	0.528	1.15	0.49
9	1.103	0.536	1.03	0.56
10	1.207	0.533	2.15	0.45
11	1.218	0.539	2.05	0.49
12	1.287	0.543	2.54	0.49
13	1.338	0.544	2.78	0.46
14	1.335	0.547	2.54	0.46
15	1.203	0.522	1.35	0.19
16	1.278	0.534	1.8	0.28
17	1.287	0.541	1.74	0.32
18	1.312	0.543	1.8	0.32
19	1.323	0.542	1.76	0.29
20	1.334	0.544	1.73	0.29
21	1.348	0.547	1.72	0.30

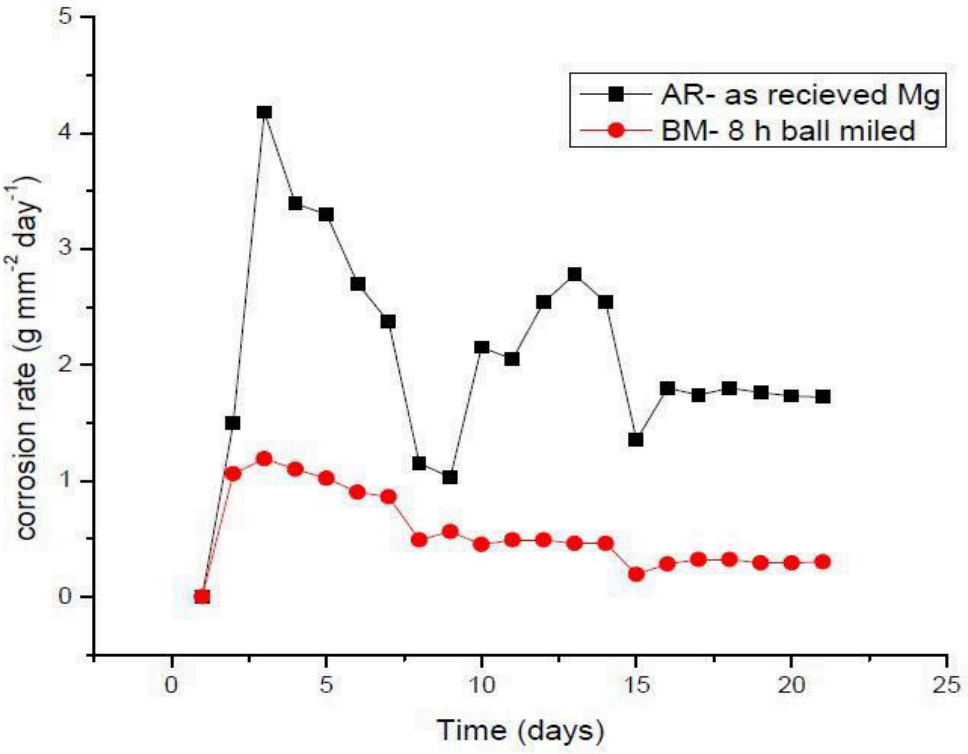


Fig. 4.3 Graph of degradation behavior of as received Mg powder (AR) and 8 h

Ball milled Mg (BM) in SBF

Immediately upon immersion, some small bubbles began to appear on the surface of the samples in SBF solution. Samples were covered with white degradation products and detached degradation products were present on the bottom of the tube. To the naked eyes, the entire samples were covered with white precipitates and the shape of sample was severely destroyed. The unmilled sample after 3 weeks became puffed and bulky whereas ball milled sample remained compacted. The mass loss was taken continuously for 3 weeks and the result is shown in table 4.3 and corresponding graph fig. 4.3 is presented. As the immersion time increased, the amount of degradation products on the samples increased. In case of ball milled sample, there were no detached corrosion products throughout the immersion test, while in case of unmilled sample lot deposition was observed at the bottom of the falcon tube, indicating the degradation of ball milled sample was much milder than that of unmilled one. The surface of the ball milled sample was relatively flat and compact as compared to unmilled sample, suggesting that ball milled sample was more corrosion resistant than the unmilled one. At the initial time of

immersion, the unmilled samples suffered from a high degradation rate and the surface was rapidly covered with apatite nucleation, which slowed down further corrosion attack.

From the results of the immersion test, it might be stated that the protectiveness of the ball milled sample was almost the same for the whole degradation time. Such a protection behavior (apatite formation) of ball milled sample over time is just desirable for degradable implants because a low initial corrosion rate allows the implant to maintain mechanical integrity in the bone-healing phase. After this period, the implant is expected to degrade with the freshly formed bone. It is considered that the high Cl^- concentration in SBF causes Mg to corrode fast. The mass loss was not as fast as before. The possible reason is that the Ca–P–Mg deposition on Mg would inhibit further corrosion

4.5 In-vitro bioactivity study in SBF

Fig.4.4 shows the XRD pattern of the unmilled and ball milled sample soaked in SBF for 3 weeks. XRD plot of the sample soaked in SBF shows the formation of apatite after immersing in SBF.

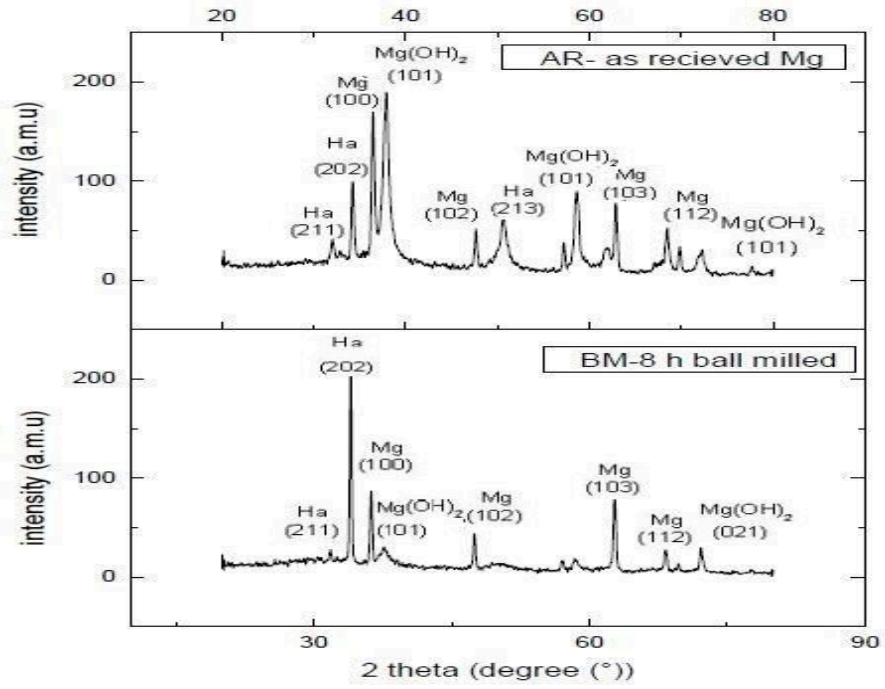
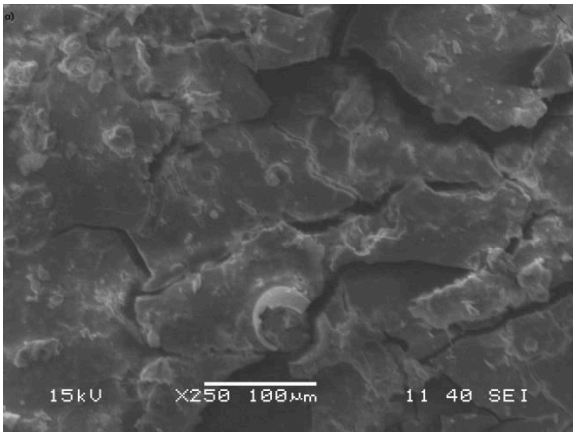
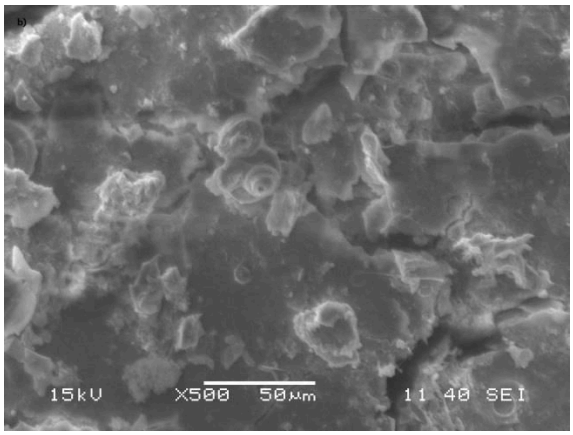


Fig. 4.4 XRD pattern of 3 weeks ball milled and unmilled samples soaked in SBF.

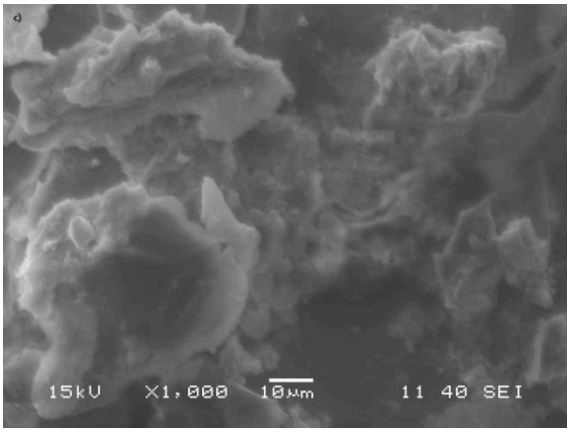
XRD pattern of the ball milled 3 weeks soaked sample showed higher number of HA peaks as compared to unmilled sample indicating more apatite has formed on milled sample's surface. The intensity of the Mg peaks of ball milled is lower than that of unmilled sample after 3 weeks indicating that uniform layer of Ha has formed all over sample. XRD patterns of both the samples soaked in SBF for 3 week shows the presence of Ha, $Ca_3(PO_4)_2$ and CaO phases. $Mg(OH)_2$ phase is more significant in unmilled sample indicating more degradation has occurred.



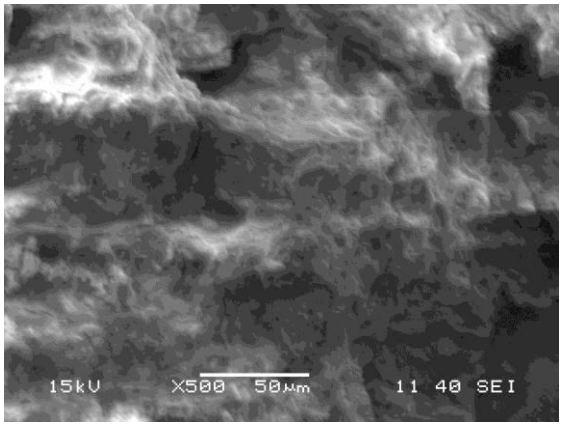
(a)



(b)



(c)



(d)

Fig. 4.5 SEM micrographs of a) 8 h ball milled Mg sample soaked in SBF for 1 week, b) 8 h ball milled Mg sample soaked in SBF for 3 weeks, c) unmilled Mg sample soaked in SBF for 1 week and d) unmilled Mg sample soaked in SBF for 3 weeks.

With increasing time the apatite layer grew thicker as shown in SEM micrographs, indicating better bioactivity of samples. Fig. 4.5 shows that globular apatite particles have been deposited on the sample and more globular apatite was deposited after 3 weeks of immersion. Hydroxyapatite is formed only if the material is bioactive when immersed in SBF. Since more apatite is formed on unmilled sample, so it can be more bioactive but a uniform apatite is observed in case of ball milled sample.

In fig 4.5 we can see that thick globular apatite is formed on the surface of unmilled sample whereas in case of uniform apatite layer which acts as protection layer over its surface thus increases the corrosion resistance in physiological medium.

Chapter 5

Conclusion

5. Conclusion

Porous magnesium sample was successfully prepared by powder metallurgical route using a high energy ball milling with subsequent compaction and sintering. Density, degradation and bioactivity of the sintered samples were assessed in simulated body fluid. From the study the following conclusions were drawn.

1. The crystallite size of Mg decreases with ball milling.
2. Density of ball milled sample decreased indicating that the sample is more porous.
3. The degradation studies clearly indicate that with decrease in crystallite size the corrosion resistance of magnesium is improved when immersed in SBF.
4. It was also observed that the bioactivity of the ball milled magnesium enhanced when compared to unmilled specimen. (i.e. specimen with coarser particle size)

Future scope: the degradation behavior of pure magnesium can be controlled if the particle size of magnesium is reduced. Hence magnesium can be used as a biodegradable implant material.

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