

## Chapter 2

# Synthesis of Magnesium-Based Biomaterials

**Abstract** Owing to the advantages of magnesium as a biomaterial, study on synthesis of magnesium materials is of prime importance. This chapter introduces potential synthesis techniques for synthesizing both impermeable and porous magnesium-based biomaterials. Primary processing of magnesium-based materials (alloys and composites) can be classified into liquid-state and solid-state processes. The advantages and disadvantages of synthesis techniques are presented and discussed. Even though there are many synthesizing methodologies for magnesium-based alloys and composites, very few were adopted for synthesizing biomaterials, especially porous magnesium materials. Recent technology advancements enable the researchers and engineers to synthesize homogeneous magnesium alloys and composites utilizing high-purity raw materials and continuously strive to achieve repeatability of material properties at all times.

**Keywords** Synthesis • Biomaterials • Impermeable • Porous • Magnesium • Alloys • Composites

## 2.1 Synthesis of Impermeable Magnesium Materials

### 2.1.1 Liquid-State Processing

There are five liquid-state processing techniques for Mg-based materials and they are as follows:

- (a) Conventional casting,
- (b) Liquid infiltration,
- (c) In situ processes,
- (d) Spray deposition, and
- (e) Disintegrated melt deposition technique.

Magnesium materials can be processed by addition of alloying elements/reinforcements into the liquid metal matrix. Advantages of liquid-state processing are as follows:

- (a) Near-net-shape forming capability,
- (b) Faster rate of processing, and
- (c) Relatively low melting temperatures associated with melting most light metals like Mg- and Al-based materials.

### 2.1.1.1 Conventional Casting

Casting is a conventional technique used for synthesizing both magnesium alloys and magnesium metal matrix composites (MMC). Conventional casting technique can be classified into the following:

- (a) Sand casting,
- (b) Die casting,
- (c) Squeeze casting,
- (d) Semisolid metal (SSM) casting, and
- (e) Stir casting.

The advantages, disadvantages, and applications of different casting techniques are discussed in Table 2.1.

Stir casting is the most commonly used technique for synthesis of impermeable Mg materials targeting biomedical applications. Previously, Wan et al. [1] synthesized Mg (0.6, 1.2, 1.6, and 2) wt% Ca alloy for biomedical applications by using stir casting method. High-purity magnesium ingot was melted within a steel crucible at 680 °C under an argon gas (Ar) atmosphere. Calcium particulates were added at higher temperatures, and the liquid metal was held and stirred for some time before casting into the metallic mold. The synthesized Mg–Ca alloys were then solutionized at 550 °C for 8 h followed by aging at 150 °C for 7 h using a resistance furnace with Ar atmosphere. Formation of Mg<sub>2</sub>Ca was found to reduce the compressive, bending, and corrosion properties of pure magnesium. The mechanical properties of the synthesized Mg–Ca alloys are shown in Table 3.6. Mg 0.6 wt% Ca was reported to be a potential material for biomedical applications based on its mechanical and corrosion properties possessing similar elastic modulus as that of cortical bone.

### 2.1.1.2 Liquid Infiltration

This method is primarily used to synthesize MMC. Reinforcing phase is made in the form of a porous object with a mold, and the molten metal matrix is allowed to pour through the interstices to fill the pores and form a composite. Based on the force requirements for infiltration, this technique can be classified into two types:

- (a) Pressureless infiltration (zero force required), and
- (b) Pressure-assisted infiltration (external force required).

**Table 2.1** Conventional casting techniques, their advantages, applications, and disadvantages

Casting technique	Processing description and process control	Advantages	Disadvantages	Applications
Sand casting	Parts are produced by pouring molten metal into a sand mold cavity	Most commonly used casting method	Possibility of metal–mold reactions	To fabricate metallic parts
	Metal–mold reactions can be minimized by controlling moisture content of sand and use of suitable volatile inhibitors. The amount of inhibitors to be added depends mainly on density difference between the raw materials, and temperature of liquid molten metal [50]			
Die casting or high-pressure die casting (HPDC)	Molten metal is forced through a narrow gate at a faster rate and fills the mold cavity. A high pressure of 40–1,000 MPa is applied to force the molten metal into the mold	Faster cooling rate and application of high pressure enables possibilities of fine-grained microstructure with minimal solidification shrinkage	High initial cost, possibilities of hot tearing of as-cast products during solidification, and presence of high porosity [51, 52]	Widely used to produce thin-walled and intricate-shaped metallic parts. Predominantly used to synthesize Mg alloys and seldom for Mg composites. Majority of Mg alloys are synthesized using high-pressure die casting
Squeeze casting	In <i>direct squeeze casting</i> (similar to forging process), the molten metal is poured into a female die (bottom) and male die (top) is lowered down till it closes the female die. Temperature of the fiber and melt, high pressure, and spacing between the fibers are essential process control parameters to obtain high-quality as-cast materials with minimal solidification shrinkage and porosity	Can produce low-porosity Mg materials		Widely used to fabricate metal matrix composites
	In <i>Indirect squeeze casting</i> (similar to die casting process), molten metal is poured into a sleeve in the casting equipment and the melt is injected into the die and then solidified under pressure. Molten metal injection speed has to be carefully selected to achieve less porosity		Low material yield	Widely used to fabricate metal matrix composites

(continued)

Table 2.1 (continued)

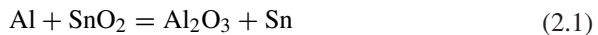
Casting technique	Processing description and process control	Advantages	Disadvantages	Applications
SSM casting	<i>Thixomolding</i> is similar to plastic injection molding. The raw material in the form of chips is heated below the liquidus temperature under Ar gas atmosphere. Heating takes place within a screw which can rotate and thereby forms slurry. The slurry is then injected at higher speeds into the die	Higher-dimensional precision products and complex net-shaped products can be produced	High initial cost when compared to die casting	Developed for Mg alloys
	<i>Rheocasting</i> uses raw material in the form of molten alloy. It involves formation of slurry (in the form of semisolid state) followed by high-pressure die casting (HPDC). For fabrication of metal matrix composites, the reinforcements are added within the semisolid temperature and the slurry is stirred followed by HPDC	Low possibilities of shrinkage pipe and crack formation. Slurry with non-dendritic microstructure with excellent rheological properties can be obtained which enables to cast complex shapes		Used to fabricate both Mg alloys and composites
Stir casting	The raw materials are melted within a graphite crucible in the presence of inert gas (Ar) atmosphere using a resistance heating furnace. After reaching adequate temperature, the molten metal is then stirred and allowed to downpour into the mold	High material yield and comparably low initial cost	Possibilities of agglomeration of reinforcements, sedimentation of reinforcements at the bottom of the as-cast, and high interfacial reactions	Used to fabricate Mg alloys and composites
	Critical decisions on stirring speed and time have to be established based on the difference in the densities between the metal matrix and reinforcing phases			

Pressureless infiltration is also called as spontaneous infiltration technique. It does not require any external force to infiltrate the molten metal into the pores of the preform. Due to the absence of pressure, there are possibilities of high porosity in the materials synthesized using this technique. Composites synthesized using pressure-assisted infiltration are usually denser. Either an inert gas or a mechanical device is utilized as a pressurizing medium. Major advantage of this process is the possibility of synthesizing near-dense materials with unappreciable porosity levels. Some of the major drawbacks of this process are possibilities for reinforcement particulates to break during infiltration and formation of heterogeneous microstructures.

Previously, Gu et al. [2] synthesized Mg 1 wt% Ca–HAp/TCP composite by using pressure-assisted liquid metal infiltration technique. Molten Mg 1 wt% Ca alloy was infiltrated into a porous scaffold using vacuum suction casting machine prepumped to 0.02–0.03 MPa. The porous HAp/TCP ceramic was preheated at 150 °C and positioned in a vacuum suction casting machine. Initially, Mg–Ca alloy was melted in an inert atmosphere at 700–720 °C and vacuum drives the molten alloy to infiltrate into the porous ceramic. The molten metal was held in the pores for 2 min to allow complete solidification. The synthesized composites were then characterized for mechanical and corrosion properties. Uniaxial compression test, electrochemical measurements, immersion test at 37 °C (within Hanks balanced solution for 20 days), and cytotoxicity of the synthesized composites were investigated and compared to that of Mg 1 wt% Ca alloy. The composite exhibited inferior compression properties (decreased by 50 %), but the corrosion resistance of the composite was found to surpass that of Mg 1 wt% Ca alloy by 68 %. Mg 1 wt% Ca alloy was found to dissolve gradually leaving behind the ceramic scaffold which has lower degradation rate.

### 2.1.1.3 In Situ Process

It is a process for synthesizing composite materials where the reinforcements are formed in the matrix by controlled metallurgical reactions [3]. For synthesizing MMC, ceramic particulates are formed by reaction between the metal matrix and a master alloy to obtain a composite of desired reinforcement volume fraction. Reinforcement is one of the final reaction products, and it is uniformly distributed throughout the metal matrix [3]. Alumina ( $\text{Al}_2\text{O}_3$ ) as reinforcement particulates is generated by the reaction shown in the following Eq. 2.1:



Reaction temperature between the metal matrix and the master alloy can be used to tailor the desired reinforcement particulate size. The major advantage of in situ reaction is the elimination of problems typically associated with wetting of the particulate, so a relatively clean and strong interface is typically formed. The number of composite systems where reaction processing is beneficial, however, is limited.

Previously, Lei et al. [4] synthesized Mg 20 wt% ZnO MMC by using ball milling and hot press sintering. Under an Ar atmosphere, pure Mg (100  $\mu\text{m}$ ) and 20 wt% ZnO (36 nm) were ball milled and hot pressed from room temperature to 550  $^{\circ}\text{C}$  at the rate of 10  $^{\circ}\text{C}$  per min under 30 MPa for 4 h in a graphite crucible to form a disk of 30 mm diameter and 65 mm thickness, respectively. When ball-milled powders of Mg and ZnO are subjected to sintering at 550  $^{\circ}\text{C}$ , two possible reactions were highlighted [4] leading to the formation of MgO(s) reinforcement and Mg–Zn(l) intermetallic, where “s” and “l” represent solid and liquid states, respectively. Uniform distribution of MgO and Mg–Zn intermetallic was observed along with significant grain refinement of pure magnesium with improvements in its mechanical properties and corrosion resistance. The synthesized Mg–MMC was highlighted as a potential fully degradable biomaterial.

#### 2.1.1.4 Spray Forming

In *spray forming* or *spray deposition*, the metal or alloy is melted and the liquid stream is atomized using an inert gas. The atomized droplets are then directed or spray deposited onto a substrate to build up bulk metallic materials [3]. In spray forming, the metal is usually melted in an induction furnace and the reinforcing particulates may be introduced into the molten metallic spray. The major disadvantages of magnesium materials synthesized by spray forming technique are the following:

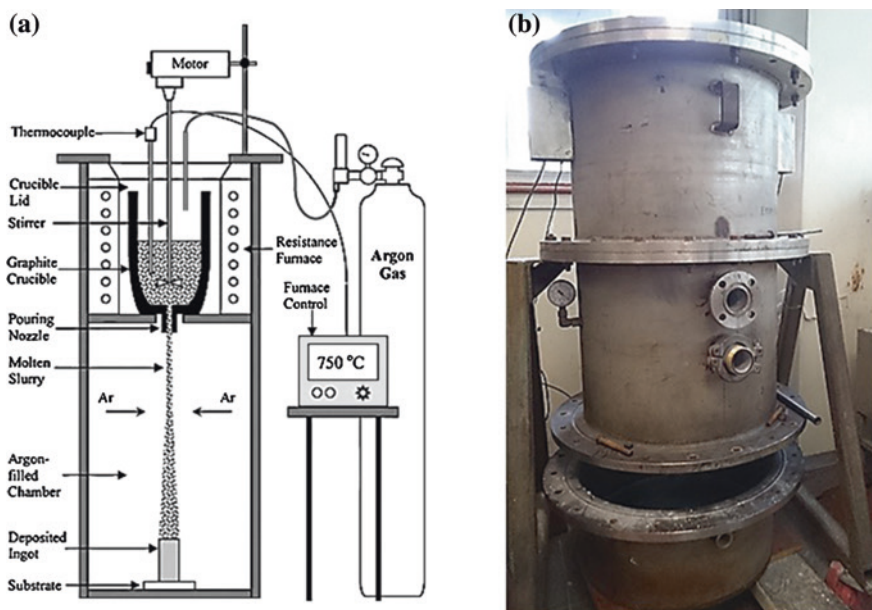
- (a) Non-uniform distribution of reinforcement particulates and
- (b) Possibilities of high porosity may be due to very high cooling rate employed in the process.

The distribution of reinforcement particulates in the liquid droplet depends on the size of the reinforcement and the process sequence at which the reinforcements are injected into the metal matrix. When the particulates are injected into the liquid metal matrix immediately after atomization, the particulates are able to penetrate themselves into the liquid droplet, and a relatively homogenous distribution of particulates in the matrix is obtained following deposition. Injection of the particulates later in the process, i.e., when the matrix droplet is in semisolid state, incorporation of the particulates into the matrix is restricted, causing the particulates to reside on the surface of the matrix droplet. Even though there are a number of studies on magnesium materials synthesized by spray forming technique [5–8], to the best of the author’s knowledge, this technique was not utilized to synthesize magnesium materials targeting biomedical applications.

#### 2.1.1.5 Disintegrated Melt Deposition Technique

Disintegrated melt deposition (DMD) technique was developed in early 1990s [9]. A representative schematic diagram of DMD technique and a photograph of its

actual setup developed at National University of Singapore are shown in Fig. 2.1a, b, respectively. DMD is a unique technique which brings together the cost-effectiveness associated with conventional casting process and the scientific innovativeness and technological potential associated with spray forming process. However, unlike spray forming, DMD technique uses higher superheat temperatures and lower impinging gas jet velocity. Within a graphite crucible, the magnesium materials along with alloying elements or reinforcements are superheated to 750 °C under an Ar gas atmosphere using a resistance heating furnace. For achieving homogeneous Mg material, the superheated slurry is stirred at 465 rpm for 5–10 min using a twin blade with a pitch of 45°. ZIRTEX 25 (86 %  $\text{ZrO}_2$ , 8.8 %  $\text{Y}_2\text{O}_3$ , 3.6 %  $\text{SiO}_2$ , 1.2 %  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ , and 0.3 % trace inorganic) coating is applied on the stirrer to avoid iron contamination of the molten metal. After stirring, the molten metal is then allowed to downpour into the mold, under the influence of gravity, through a 10-mm hole in the crucible. Before entering the mold, the molten metal is disintegrated by two jets of Ar gas oriented normal to the melt stream. The flow rate of Ar is maintained at 25 L/min, and an ingot of 40 mm diameter is normally obtained. The 40-mm ingots obtained were then machined to a diameter of 36 mm. The literature search reveals that DMD is a suitable processing method for synthesizing new magnesium materials including alloys [10, 11], bulk metallic glass [12], and composites with reinforcements of micron, submicron, and nanolength scales [13–20]. Recently, the authors synthesized and studied the effects of  $\text{TiO}_2$  nanoparticulates



**Fig. 2.1** **a** Schematic diagram of DMD and **b** photograph of actual DMD setup developed at National University of Singapore

on mechanical response of pure Mg targeting biocompatible applications [20]. The room temperature tensile properties of the nanocomposites revealed >2 vol% TiO<sub>2</sub> is required for strength improvement of pure Mg.

### **2.1.2 Solid-State Processing**

When the syntheses of materials are done at a temperature below the solidus temperature of the metal matrix phase, the syntheses are termed as solid-state syntheses. The advantages of solid-state processing are as follows:

- (a) Metastable phase formation is possible in the microstructure, and
- (b) Materials with superior strength levels can be obtained.

#### **2.1.2.1 Powder Metallurgy Technique**

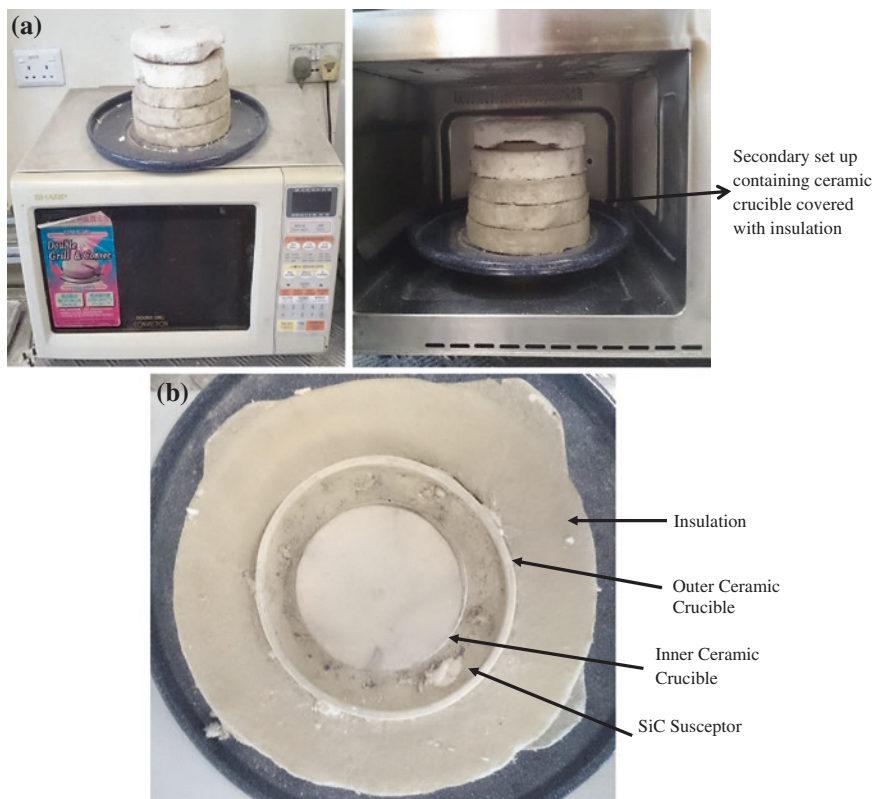
The most common solid-state processing technique for synthesizing magnesium-based materials is powder metallurgy (PM) technique. Raw material (metal or ceramic) in the form of powders is formed into specific shape and subsequently sintered at a temperature just below the melting temperature of the primary constituent (magnesium) of the powder mixture. PM technique has the capability of forming near-net-shaped products. Initial stage of this PM technique is blending where the powders (raw material) are mixed homogeneously. The blending conditions mostly depend on the density difference between the constituents of the powder mixture. After blending, cold press or hot press or hot isostatic press is employed to produce a “green compact,” which is about 80 % dense and then followed by sintering.

Sintering should be effective enough to improve the bonding between the powders and thereby to minimize porosity. It can be done by using a traditional resistance heating furnace [21, 22] where the direction of heating is from outside to inside of the powder compact resulting in poor microstructural characteristics of the core of the material [23]. Microwave can also be utilized to sinter the green compact where both electric and magnetic field act together to sinter the compact. When compared to the conventional sintering, heating in microwave sintering is able to achieve comparably higher densities [24]. Desirable properties of materials can be achieved through microwave sintering due to the following [24]:

- (a) Shorter sintering time and
- (b) Lower sintering temperatures.

Unlike in traditional heating, the direction of heating in microwave is from inside to outside of the powder compact which results in poor microstructural characteristics of the surface [23]. A recent work on microwave sintering with two-directional heating employing microwaves together with microwave-coupled external heating source is shown in Fig. 2.2a, b. It is utilized for rapid sintering which effectively mitigates the drawbacks of the former sintering processes

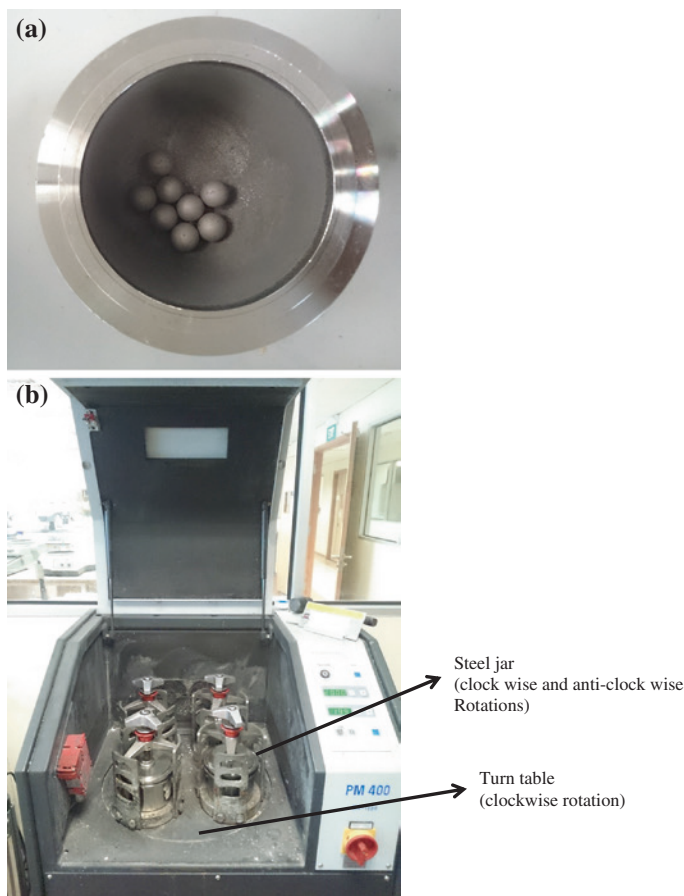




**Fig. 2.2** **a** Photograph of hybrid microwave experimental setup and **b** photograph showing the top view of the setup

such as microstructural non-uniformity and the presence of poor microstructural characteristics of the core as well as surface of the material [23]. A layer of silicon carbide (SiC) is placed between the inner and outer crucibles (as shown in Fig. 2.2b). The SiC layer absorbs microwave energy readily and thereby is heated up quickly. The green compact placed within the inner crucible is heated up by both the microwaves and SiC susceptor. To the best of the authors' knowledge, magnesium materials targeting biomedical applications have not been synthesized using PM-assisted microwave sintering process with two-directional heating.

Mechanical alloying or high-energy milling method involves repeated cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Figure 2.3 shows a typical planetary ball mill. The required amounts of powder (raw material) are placed within the steel jar (as shown in Fig. 2.3a). As per the output powder size requirements, the powder charge ratio, that is, ball to powder ratio is carefully selected. The required amounts of steel balls are then put along with the powder and mechanically milled by using the planetary ball milling machine (as shown in Fig. 2.3b). Planetary ball milling machine consists of a turn table and usually four jar



**Fig. 2.3** **a** Accessories for mechanical milling namely steel jar and steel balls and **b** planetary ball milling machine

mountings (as shown in the Fig. 2.3b). The turn table rotates clockwise, whereas the jar mountings can rotate in both the directions. The rotation of the jars changes as per the user inputs. The rotations of turn table and steel jars are about their respective axis and in opposing directions which creates centrifugal forces within the steel jars and effectively pushes the steel balls to mill the powders. Chemical compositions that are difficult or impossible to obtain by traditional casting methods such as nanostructured and amorphous powders can be synthesized using this methodology. Mechanical alloying can be of three different forms and they are as follows [3]:

- (a) Milling of metallic and ceramic powder to reduce the powder size,
- (b) In situ synthesis of nanocomposites by reducing oxide from a powder with a metal powder, and
- (c) In situ formation of secondary particles by direct milling of elemental powders.

### 2.1.3 Additive Manufacturing

Additive manufacturing is used to create metal and polymer parts layer by layer. It is also called as rapid manufacturing or rapid prototyping or solid-free form fabrication which enables fabrication of highly complex physical objects assisted by computer-aided design (CAD) systems. The model generated using CAD software is sliced into many layers with every layer defined by a layer thickness, and the object is built in a layer-by-layer fashion [25]. Selective laser melting (SLM) is an additive manufacturing process which uses energy from laser beam to selectively melt powders. Bottom-to-top approach is usually utilized such that once a layer of available powder is sintered, a new layer of powder is deposited and is subsequently sintered. No support structures are utilized to build parts. Components utilizing polymers, ceramic powders, and metallic powders can be synthesized by using SLM method. The microstructure and mechanical properties of SLM-sintered parts largely depend on the laser power and laser scan speed utilized during synthesis [26].

Previously, Ng et al. [25] utilized two grades of magnesium powders of sizes 75–150 and 5–45  $\mu\text{m}$  with irregular and spherical shape, respectively. The SLM setup was powered with Nd:YAG laser with a scanning speed of 0.2–300 mm/s and laser current operated between 0 and 35 A. The entire setup was operated within a shield cover circulated with Ar gas which is provided to mitigate surface oxidation problems. Energy density is given by the ratio of laser power to the product of laser scan speed and laser scan spacing. Low energy density which may be due to low laser power or very high laser scan speed and laser scan spacing leads to poor fusion of powders and thereby leads to poor mechanical properties. For optimal process control of SLM, the authors varied the laser scanning speed (10–300 mm/s) and laser current 0–35 A. It was observed that coarse Mg powders (75–150  $\mu\text{m}$ ) did not melt at various combinations of laser scan speed and laser current. With finer Mg powders, sintering was observed with increase in energy density ( $\sim 0.66 \text{ J/mm}^2$ ). Further increase in energy density ( $\sim 0.99 \text{ J/mm}^2$ ) leads to agglomeration of Mg powders and formation of disrupted surface with increase in surface oxidation by  $\sim 5\%$ . Further, the authors synthesized single tracks of 20-mm-long Mg and investigated the laser process parameters on the microstructure and mechanical properties [27]. Microstructural characterization, hardness, and modulus measured through nanoindentation technique were studied for different SLM process parameters. When compared to as-cast Mg (7  $\mu\text{m}$ ), the grain size of laser-melted magnesium was found to be less (2–5  $\mu\text{m}$ ) with very fine and equiaxed grains. A maximum hardness and modulus values of  $\sim 0.95$  and  $\sim 38.18 \text{ GPa}$ , respectively, were observed for SLM-sintered Mg utilizing energy density of  $1.13 \times 10^{12} \text{ J/m}^2$  with a finer grain size of  $\sim 2.33 \mu\text{m}$ . Further increase in energy densities was found to increase grain size and thereby decrease both hardness and modulus values. A minimum hardness and modulus values of  $\sim 0.67$  and  $\sim 27.41 \text{ GPa}$  were observed for Mg synthesized using SLM with energy density of  $9.80 \times 10^{12} \text{ J/m}^2$ . The authors concluded that the hardness and modulus values of

SLM-synthesized magnesium closely match with that of human bone when compared to other conventional biomaterials.

Other synthesis techniques seldom utilized for fabrication of Mg-based materials are as follows:

- (a) Zone solidification technique [28] and
- (b) Conventional PM followed by spark plasma sintering technique [29].

### ***2.1.4 Secondary Processing of Impermeable Mg Materials***

Through extensive literature survey, it was observed that hot extrusion and hot rolling are the two most commonly used secondary processing techniques for synthesizing impermeable Mg materials.

#### **2.1.4.1 Hot Extrusion**

Extrusion is a forming process where a block of metal is forced through an orifice of a die under high pressure. During extrusion, high compressive forces act on the extrusion billet (raw material) which mitigates the cracking of primary processed materials. Based on the direction of extrusion process, it is classified into two types and they are as follows:

- (a) Direct or forward extrusion and
- (b) Indirect or back extrusion.

In direct extrusion, billet is between the die and the ram and the extrusion rod is obtained in the same direction at which the pressure is applied, whereas in indirect extrusion, the die is between the billet and the ram and the extruded rod is obtained opposite to the applied pressure direction. The following are the process control parameters of hot extrusion process:

- (a) Extrusion ratio,
- (b) Working temperature, and
- (c) Deformation speed.

The extrusion ratio is defined as the ratio between the initial cross-sectional area of the billet to the final cross-sectional area of the extrusion rod. Most of the metals are hot extruded as the deformation resistance of metals decreases with an increase in temperature. Extrusion working temperature should be well below the melting point of metals. Lower working temperature is advisable to mitigate problems such as oxidation of materials and softening of working tools at higher temperatures [30]. Usually, the experiments are standardized with best process control parameters through many trials. During standardization, different combinations of experiment parameters are usually employed on many materials for achieving the best desirable properties.

### 2.1.4.2 Hot Rolling

Rolling is a forming process where the metal is plastically deformed by passing it through the rolls. By this process, the metal is subjected to high compressive stresses due to squeezing action of the rolls and surface shear stresses due to friction between the rolls [30]. The main objective of this process is to reduce the thickness of metal. Through this process, thin plates are produced directly from ingots.

Previously, Li et al. [31] synthesized Mg (1, 2, and 3) wt% Ca alloy by using conventional casting. As-cast Mg 1 wt% Ca alloy was further hot extruded and hot rolled. As-cast Mg 1 wt% Ca alloy ingots were cut into 5-mm-thick plates along the longitudinal direction. The plates were preheated to 400 °C for 1 h and hot rolled to 2-mm-thick sheets. Hot extrusion of Mg 1 wt% Ca was performed at an extrusion temperature of 210 °C and extrusion ratio of 17. The corrosion properties of the as-cast Mg–Ca alloy and secondary processed Mg 1 wt% Ca alloy were studied and compared by using both *hydrogen gas measurement studies* and *polarization studies*. The experimental procedures of *hydrogen gas measurement studies* and *polarization studies* are explained in detail under Sect. 4.1. Immersion test (for 5 h and 250 h) of the synthesized Mg–Ca alloys was performed within SBF medium maintained at a temperature of 37 °C and pH of 7.4. After immersion, surface of the samples was studied by using a scanning electron microscope (SEM). After 5 h of immersion, deep pits were observed on as-cast Mg 3 wt% Ca alloy samples. Within 24 h of immersion, as-cast Mg 3 wt% Ca alloy degraded into fragments. After 250 h of immersion, a corrosion product coating was found on both as-cast Mg (1 and 2) wt% Ca samples. On higher magnifications, micropores on the coating of as-cast Mg 2 wt% Ca was visible. Among the as-cast Mg–Ca alloys, Mg 1 wt% Ca alloy samples exhibited best corrosion properties. Further, X-ray diffraction studies conducted on the immersed samples of as-cast Mg (1 and 2) wt% Ca indicated formation of hydroxyapatite. The pH of corrosion medium increased from 7.4 to 10.5 after 24 h and stabilized at 9.8. When compared to as-cast Mg 1 wt% Ca, the pH of the secondary processed Mg 1 wt% Ca (hot rolled and hot extruded) alloy degraded slowly. Further, the hydrogen evolution in extruded Mg 1 wt% Ca was very less (0.04 ml/cm<sup>2</sup>/h) when compared to as-cast (0.136 ml/cm<sup>2</sup>/h). The electrochemical test utilized three electrodes, platinum, saturated calomel electrode and sample for counter electrode, reference electrode, and working electrode, respectively. The ratio of exposed area of the working electrode to the solution (SBF at 37 °C) was maintained at 0.385 cm<sup>2</sup>. The test was carried out at a scan rate of 1 mV/s. It was observed that the cathodic polarization current of hydrogen evolution reaction on as-cast Mg 3 wt% Ca alloy was much higher than that of as-cast Mg (1 and 2) wt% Ca. Further, from the potential range of current plateau for as-cast Mg (1, 2, and 3) wt% Ca samples, corrosion film formed on Mg 1 wt% Ca was found to be more protective. Higher potentials were observed on the secondary processed Mg 1 wt% Ca which indicate highly protective corrosion surface films when compared to as-cast Mg 1 wt% Ca alloys. Further, when compared to as-cast and as-rolled Mg 1 wt% Ca alloy,

as-extruded Mg 1 wt% Ca alloy exhibited higher tensile properties with a maximum 0.2 % TYS, UTS, and elongation of ~135, ~230 MPa, and ~10.8 %, respectively. Mechanical and corrosion properties of the synthesized Mg–Ca alloys are discussed in Tables 3.6 and 4.1, respectively.

## 2.2 Synthesis of Porous Magnesium Materials

Porous materials are important for biomedical applications as their structure allows adequate spaces for transportation of nutrients and for growth of living tissues [32]. In case of orthopedic applications, by adjusting the porosity, modulus of materials can be greatly controlled which provides an opportunity to design materials with modulus more closer to that of natural bone, thereby mitigating problems related to stress shielding [33]. Recently, many researchers focused on synthesis and characterization of porous Mg materials owing to the advantages of magnesium as a biomaterial (as discussed under Sect. 1.4). The following techniques are utilized to synthesize porous magnesium materials:

- (a) PM using space holder technique [34–36],
- (b) Negative salt pattern molding [37],
- (c) Laser perforation [38],
- (d) Directional solidification metal–gas eutectic method (GASAR process) [39],
- (e) Plaster casting [40], and
- (f) Injection of an inert gas into the melt [41].

To achieve biocompatibility of the resulting material, critical selection of reagents and methods for synthesizing porous magnesium materials is essential. It has been reported that among the reported synthesizing methodologies, plaster casting and PM technique produces viable products [34–36, 40, 41]. By utilizing injection of inert gas and GASAR methodologies, open-cell structures are difficult to be achieved [42]. Production of porous Mg materials utilizing foaming by injection of Ar gas approach has been abandoned as the molten metal produces products with inconsistent morphology [41]. Further, corrosion and contamination of the final product was more prevalent in materials synthesized using plaster casting and negative salt pattern molding [42, 43]. Due to the disadvantages of other synthesizing methodologies, more researchers are focusing on PM method utilizing space holder technique as a potential route for synthesizing porous Mg materials.

Fabrication of Mg materials with interconnected pores is possible by using conventional PM technique (as discussed under Sect. 2.1.2) with green compact of material containing space holder particles. The particles are later leached out by dissolving the material in a suitable solution or evaporated by thermal decomposition during sintering. Selection of such particles is very critical, especially for materials targeting biomedical applications, and they should evaporate or leach out from the material without any contamination [43]. The following are the commonly used space holder particles:



- (a) Sodium chloride [44],
- (b) Ammonium bicarbonate, [45] and
- (c) Carbamide ( $\text{CO}(\text{NH}_2)_2$ ) [46].

Selection of quantity and size of the space holder particles depend on the size and porosity-level requirements of Mg material. When the space holder particles are removed through leaching by dissolving the samples in a medium, there are possibilities for incomplete leaching of the particles as well as corrosion of Mg samples when immersed in the medium. When carbamide particles were leached out from Mg through immersion within 0.001 M NaOH [47], it was highlighted that oxidation of Mg particles is highly possible [48]. Complete thermal decomposition of carbamide requires temperature higher than the melting point of pure magnesium [49], whereas ammonium bicarbonate decomposes at 36–60 °C [34]. At lower temperatures, only partial decomposition of carbamide is possible leading to contamination of the final product [49]. Therefore, ammonium bicarbonate is a more suitable space holder than carbamide for fabricating porous Mg materials using PM technique [43, 45].

Previously, Čapek et al. [45] synthesized porous magnesium materials using ammonium bicarbonate as space holder. Mg (0, 5, 10, 15, 20) vol% ammonium bicarbonate materials were synthesized using pure Mg powder (75–150  $\mu\text{m}$ ) and ammonium bicarbonate powder (250–500  $\mu\text{m}$ ). Initially, the powders were mixed manually for 30 min with 30 vol% liquid hexane to avoid segregation of powders. The powders were then uniaxially cold compacted at a pressure of 265 MPa into cylindrical green compacts. The green compacts were then heat treated at 130 °C for 4 h using a muffle furnace followed by sintering at 550 °C for 6 h using a tubular furnace. Ammonium bicarbonate gets decomposed at 130 °C. After sintering, the measured porosity of initial Mg (0, 5, 10, 15, 20) vol% ammonium bicarbonate was found to be 12, 23, 28, 33, and 38 vol%, respectively. The samples were then characterized for microstructure, flexural strength, and corrosion properties under physiological conditions. Magnesium with least porosity (12 vol%) exhibited the best flexural strength and corrosion properties. Flexural strength of porous Mg (up to 28 vol% porosity) was found to be greater than that of other common implantable porous materials such as hydroxyapatite and composite bioglass. The mechanical properties of the synthesized materials were comparable to that of natural bone. Recently, the authors [43] studied the effects of sintering conditions on microstructural and mechanical properties of Mg with (29–31) vol% porosity following the same experimental procedure discussed initially. The green compacts were sintered for 0, 3, 6, 12, and 24 h using two types of Ar atmospheres at a flow rate of 0.1 l/min: (a) Ar with 99.996 vol% “technical” purity and (b) Ar purified by Mg chips (250–550  $\mu\text{m}$ ) placed around the sintered material which acts as a “getter.” The samples were characterized for flexural strength, compression properties, and Vickers hardness. The authors concluded that for sintering time up to 6 h, the mechanical properties of the synthesized porous Mg was found to increase, but for sintering time greater than 6 h, the purity of Ar atmosphere plays an important role and gettered Ar atmosphere leads to better mechanical properties when compared

to technical Ar for Mg materials. The ultimate flexural strength, compressive yield strength (0.2 % CYS), and ultimate compressive strength (UCS) of the synthesized porous (29–31) vol% Mg material with varying sintering conditions range between 3–5 MPa, 13–53 MPa and 20–70 MPa, respectively, which were found to surpass those of other nonmetallic porous implant materials. The mechanical properties of porous magnesium-targeting biomedical applications are discussed in Table 3.10.

## 2.3 Summary

This chapter illustrates the various synthesizing methodologies available up to date for fabrication of impermeable and porous magnesium materials. It is observed that due to the reactivity of magnesium materials, most of the synthesis techniques use preventive mechanisms such as fluxes and inert gas atmospheric conditions to prevent interactions with oxygen environment. Liquid synthesis through stir casting route and PM using space holder technique are the most commonly used fabrication methodology for synthesizing impermeable and porous Mg materials, respectively. Synthesis and characterization of impermeable and porous magnesium materials using PM (assisted by microwave sintering process with two-directional heating) has not been investigated. It will be interesting to study and investigate the microstructural and biomechanical characterization of Mg materials adopting PM-assisted microwave sintering process with two-directional heating owing to the advantages of the technique, as discussed under Sect. 2.1.2. Further, research on porous Mg materials is at a very early stage. Owing to its importance and applications, synthesis and characterization of new porous Mg-based composites provides an exciting opportunity to the researchers.

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