Additive Magnesium Alloy Manufacturing

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ABSTRACT: Magnesium alloys are a promising new class of degradable biomaterials with a comparable stiffness to bone, reducing the adverse effects of stress shielding. The use of biologically degradable magnesium implants removes the need for a second repair or replacement operation. There is a increasing interest in capitalizing on the specific design capabilities of additive manufacturing to advance the medicine boundaries. Due to the high chemical reactivity which poses a risk of combustion, magnesium alloys are difficult to print 3D though. Alloying will slow down an order of magnitude or more, which may not yet be enough for many applications. In addition , the low vaporization temperature of magnesium and traditional biocompatible alloying elements further increases the difficulty of printing fully dense structures that meet the requirements of strength and corrosion. The purpose of this study is to survey current techniques for the construction of 3D printing magnesium and provide guidance on best additive practices for these alloys.

KEYWORDS: Alloy Manufacturing Additive manufacturing, Magnesium, Implants, Biomaterials.

INTRODUCTION

Magnesium-based implants:

Magnesium (Mg) alloys have emerged as a promising bio-material degradable to use in orthopaedics, cardiology, respiratory and urology. Mg's primary benefit is that problems in the long term can be reduced or eliminated as the system totally degrades away. Another primary advantage in orthopaedics is that Mg has a more comparable bone modulus that minimizes the harmful effects of shielding stress [1]. Three companies have proven clinical success to date and regulatory approval obtained in Europe and South Korea. Syntellix received CE marking in 2013 for a Magnezix compression fracture screw that sold more than 50,000 units.

In 2015, U&i Corporation obtained regulatory approval from the South Korean Ministry of Food and Drug Health for orthopedic bone screws made of a Resomet alloy called bioresorbable MgCa. U&I manufactures screws, K-wires, suture anchors and pins with a Mg – Ca alloy that will degrade completely depending on the application in 6–18 months. Biotronik was awarded CE marking for Magmaris in cardiovascular health in June 2016 and is the first scientifically validated bioresorbable magnesium scaffold [2]. While success for smaller-scale implants such as screws and pins has been demonstrated, current manufacturing technology can not provide bioresorbable constructs for more load-bearing applications that match strength and corrosion requirements (Figure 1).

Competing technologies that slow the rate of corrosion of biomaterials based on Mg are coatings, alloys, and surface treatments (Fig. 2). Coatings run the risk of scratching and cracking unevenly. They can last from just a few weeks to a few months. This may not be enough for such implants to safely pass the necessary threshold required by restoring structural integrity of the bone (Fig. 3). If the coating is dissolved, uncontrolled alloy corrosion results in excessive build-up of hydrogen gas in the body, and implant strength loss [3]. Alloying can slow down a magnitude or greater order of degradation, which may still not be enough for many applications. Most notably, the introduction of rare earth metals shows the most potential for strength improvement, but biocompatibility remains uncertain [4].

Figure 1. Schematic Representation of (a) Normal Degradation of a Plate/Screw Construct in One Year and (b) Premature Catastrophic Failure Due To Stress Shielding and Stress-Corrosion Cracking.

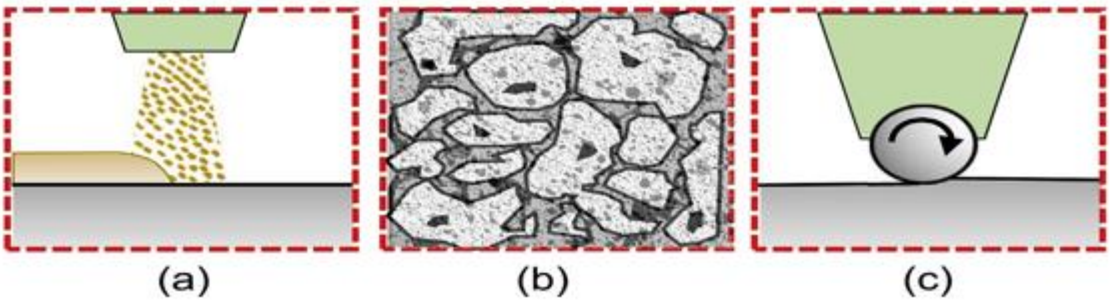

Figure 2. Technologies to Slow Mg Corrosion: (a) Coatings, (b) Alloying, And (c) Surface Treatments.

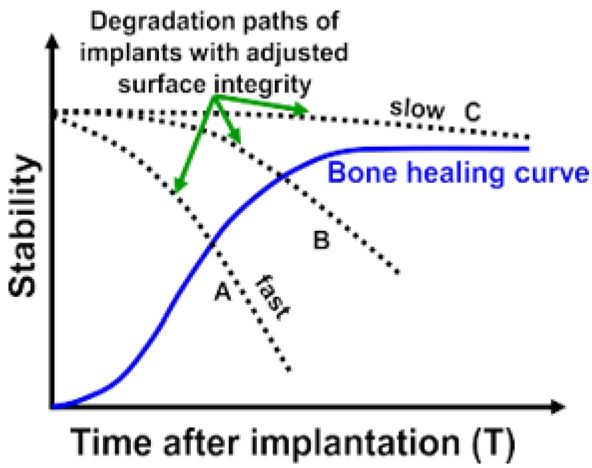

Fig. 3. Schematic Diagram Showing the Intersection Point between Failures of Medical Implant Relative to Bone Recovery.

The alloying elements introduce a new risk of toxicity. Controlled use of such elements as calcium, zinc, and manganese has been shown to be non-toxic to the human body [5][6]. Alloyed implants were functional in the body for 6–8 weeks before material degradation caused a loss of strength The hydrogen gas released during magnesium degradation in small quantities was considered harmless and could be removed using subcutaneous needles. These alloying elements affect size and distribution at the microstructural level. The composition of a grain at the middle is different from that at the boundary of the grain. The internal energy at the grain boundary is higher and thus, at these locations, corrosion occurs first. Another limitation of alloying is that it is usually given regulatory approval for a fixed composition and thus a fixed corrosion rate [7]. Any change in the composition of alloys for a different patient population or application would require additional regulator.

An alternative approach is surface treatment to reduce the corrosion rate. Compared with the other methods, surface treatments provide specific benefits. Laser peening, for example, is a mechanical mechanism in which the pressure waves generated by expanding plasma trigger deep residual compressive stress (CRS) and hardening up to 6 mm below the surface, which in effect improves fatigue strength and corrosion resistance [8]. Moreover, the modification of peening process parameters allows degradation to be adapted to the needs of patients without worries about biocompatibility from changing composition or adding a coating. Preliminary data indicated that mechanical surface treatments de-crease the corrosion rate of Mg. The problem is that structural integrity is prematurely lost if the conventional layer handled with the surface degrades [9].

Need for additive manufacturing of magnesium:

Mg alloys additive manufacturing (AM) is of growing interest in the community because it allows unattainable design capabilities with traditional manufacturing and its potential for biodegradable implant development. Additive magnesium processing has been demonstrated using fusion powder bed, AM wire arc, paste extrusion deposition, AM friction swirl, and jetting technologies. These processes possess different process mechanics and raw material forms. Each process yields AM components with varying structural properties. Through this way, AM can be used for manufacturing components to create extremely complex geometries that are either difficult or impossible to produce using traditional machining processes [10]. AM allows for individualized implants that fit more closely with anatomical geometries. As multiple steps of conventional machining can be eliminated and batch processing becomes feasible, AM also reduces the production time and cost for implants.

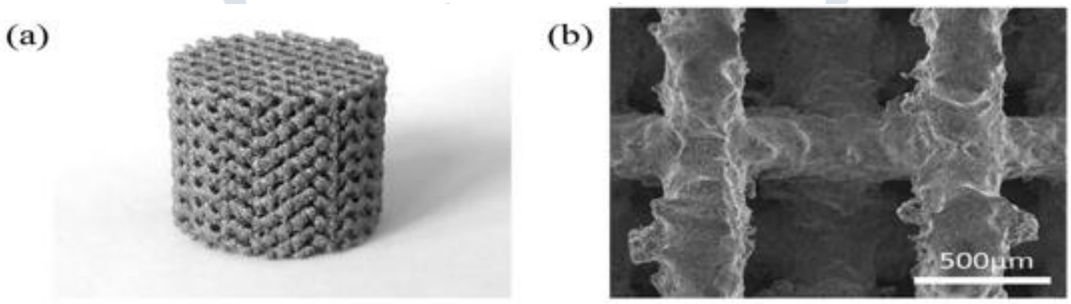

Figure 4. (a) As-Printed WE43 Scaffold and (b) Surface Morphology of As-Polished Strut.

The ability to produce complex internal and external geometries using AM enables geometric features to be developed that support cell growth, proliferation, and bone regeneration. WE43 scaffolds, a magnesium alloy with yttrium and rare earth metals, printed with pores as small as 600µm, showed in vitro toxicity of less than 25 percent and maintained structural rigidity for four weeks (Fig. 4 and Fig. 5). In addition, porous depositions can be attained using AM, which can act as favourable tissue adhesion sites that speed up the healing process. Porosity can be adjusted across a 3D construct by manipulating parameters of the print process, which will have a direct effect on corrosion rates and cell behaviour.

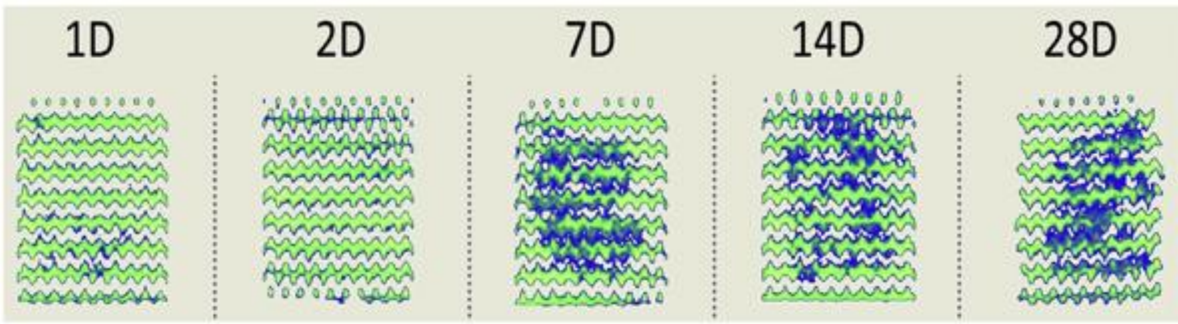

Figure 5. CT-Scans Revealing Evolution of Corrosion Products in A 3D Printed WE43 Scaffold Over 28 Days

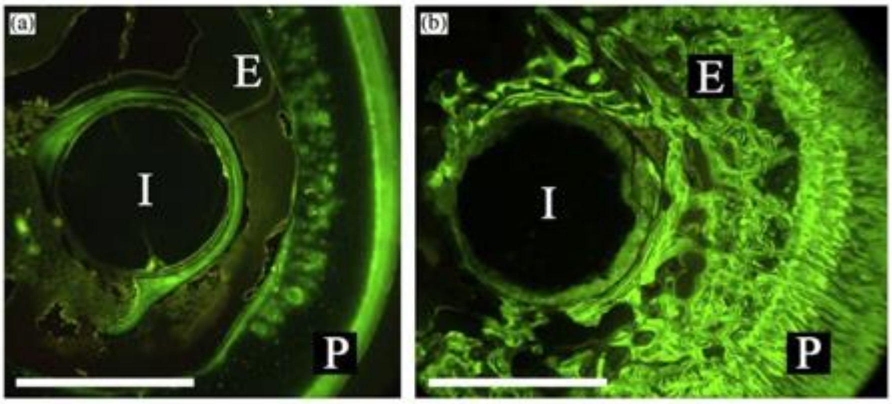

Figure 6. Fluoroscopic Images Of Cross-Sections Of A (a) Degradable Polymer And (b) And A Magnesium Rod With In Vivo Staining Of Newly Formed Bone.

The current biodegradable implants based on polymers lack the necessary strength to be used as orthopaedic implants with load bearing [11][12]. The identical rigidity between human bone and magnesium prevents tension shielding and allows a perfect candidate for such implants for bearing loads. In addition, a comparison of magnesium alloys with polylactide polymer, which is an existing biodegradable polymer used for non-load - bearing implants, showed a higher generation of bone cells in magnesium implants (Fig . 6).

Challenges with additive manufacturing of magnesium:

AM of reactive materials, especially magnesium, has been of interest to the research community in recent years, and technology is being developed to minimize the difficulties associated with 3D printing. Because of their highly reactive nature, magnesium is a difficult metal to 3D print. Magnesium oxidizes in its pure form uncontrollably, and must be handled in a way that avoids oxygen exposure. Raw AM materials are available in forms of powder, liquid resin, or wire. During this condition, the metal's surface energy rises and poses a greater risk of reacting with atmospheric oxygen to allow for combustion. Such risks have led to insufficient research into magnesium production processes that could be used as a possible biodegradable alloy. Specialized equipment that can print magnesium in an inert atmosphere is required, while also ensuring safe material handling methods.

Powder bed fusion of magnesium alloys:

Powder bed fusion (PBF) is an AM procedure used to selectively fuse regions of a powder bed using thermal energy. The powder bed contains, as feedstock, metal, polymer, or ceramic powder. An energy source selectively scans and melts the top layer of the powder bed into the powder bed. The powder bed then decreases, and a fresh powder layer is applied over the melted layer (Fig. 7).

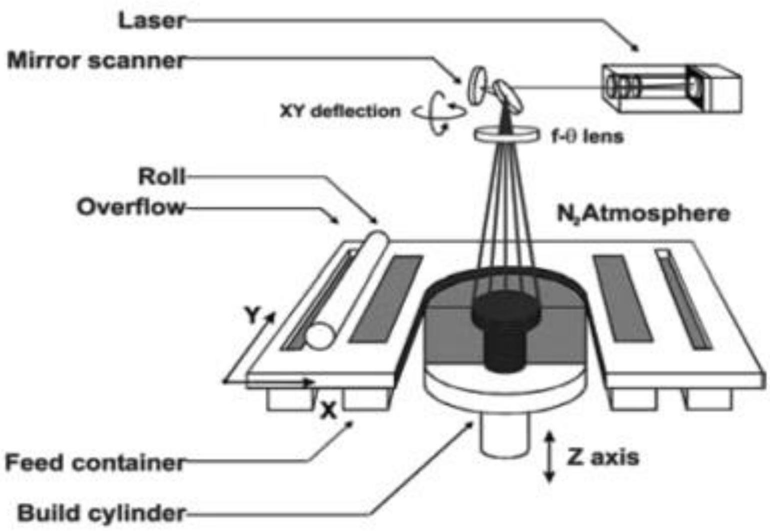

Figure 7. Schematic Diagram of A PBF System.

The cycle continues until all of the structure is created by piling melted powder layers. The powder used in PBF varies from 20µm to 150µm but it usually tends to be at the bottom end of this range. PBF has a broad range of parameters which can cause variations in the chemical composition, mechanical properties and geometry of the components produced. It'll be boring to account for all of the parameters. Therefore, important parameters such as laser strength, scanning speed, and layer need to be defined and centred heavy duty. One way was printed on a PBF device to assess the relevant parameters in AZ31, consisting of aluminium, zinc, and manganese. The parameters affecting AZ31's PBF have been analysed using DOE, and high laser power has been seen dramatically reducing porosity. It also shows that a reduction in the speed of laser scanning at constant laser powder has produced porous parts. Therefore laser power and scanning speed during Mg PBF must be carefully considered. The parameters which affect Mg's PBF are outlined below.

ZK60 is a zinc- and zirconium-rich magnesium alloy. Magnesium and zinc elements within the powder underwent strong vaporization when ZK60 powder was subjected to very high energy density of 1250 J/mm3. Once the laser intensity decreased to 250 J / mm3 the melting pool increased and the vapour pressure decreased. As a result, incomplete powder particle fusion leads to 82.25 per cent weak relative density (Fig. 8). At an energy density of 416.67 J / mm3, a maximum relative density of 94.05 percent was achieved.

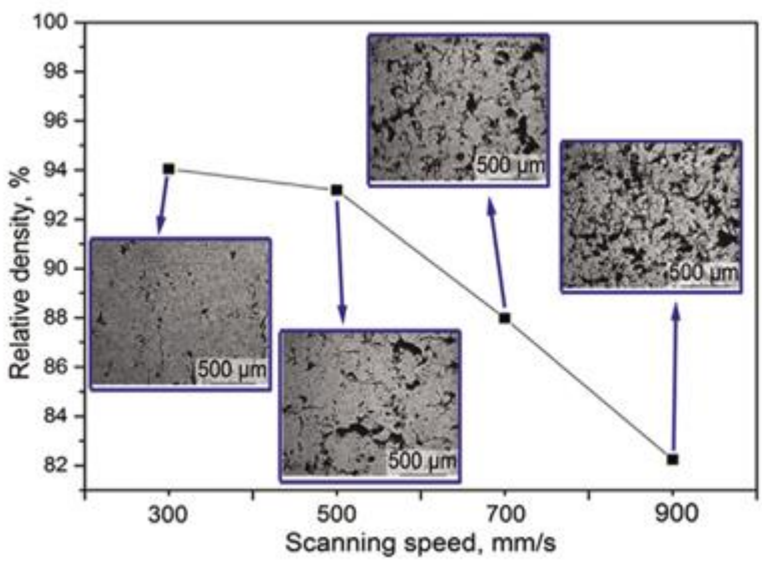

Figure 8. Influence of Laser Scanning Speed on Relative Density of ZK60.

Laser power and scanning speed:

Lasers are the energy source of magnesium alloys most commonly studied for PBF. Lasers allow a high concentration of heat to be concentrated for a limited period of time to melt the powder over small regions of the powder surface. This short-term heat flux allows the molten powder to rapidly heat and quench, resulting in a rapid solidification. The effect of this rapid solidification is grain refinement, which helps the material to withstand greater loads.

When magnesium alloy powder undergoes high temperatures, some elements in the powder are subjected to vaporisation. Powder vaporization during deposition of material leads to a localized build-up of vapour pressure at the melting pool. The pressure causes the molten material to spatter outward in the melt tank, which results in a low-density structure being formed. This also contributes to variations in chemical composition as opposed to the original material. Good alloying element solubility during AM is critical to reduce the formation of galvanic cells in impressed components that would interfere with corrosion behaviour.

Laser strength and speed of scanning greatly influence the melting stream, vaporization and the subsequent deposition in PBF. While the effects of varying laser power and scanning speeds cause individual changes in deposition quality, individual explanations of their effects are difficult to explain. They play a significant role together in deciding the laser's energy density transferred to the magnesium powder. PBF is the experiment architecture (DOE)[40]. DOE is a statistical method that helps to reduce the cost and time required to find the significant Most of the magnesium printing literature pertains to alloys; however, pure magnesium powder with spherical particles of a mean size of 24 μm used at a relatively low energy density of 155.56 J/mm3 yielded 97.5 percent dense deposits. The material's relative density and mechanical resistance decreased as the energy level increased or decreased.

CONCLUSION

This dissertation summarizes the magnesium-printing techniques used in additive manufacturing. Magnesium reactivity makes it difficult to print biodegradable implants because of the high surface energy of the powder and high alloy electronegativity which drives the rapid rate of corrosion within the human body. Nevertheless, several approaches in AM are gradually overcoming those challenges. The attempts to print Mg using PBF, WAAM, paste extrusion deposition, FSAM, and jetting technologies have been identified with a focus on their parameters for the process. Due to the relatively small heat flux and complex internal and external geometries enabled by this technology, Powder bed fusion is the most widely researched method for printing magnesium alloys. Parts with a density of 96.13 percent have been achieved, depending on the type of magnesium alloy used. A critical challenge in magnesium AM remains the development of nearly completely dense structures above 99 percent. Despite the relatively high porosity levels, the manufactured components have limited the ability to maintain stiffness in vitro for up to four weeks.

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