Ref. Ares(2023)5923193 - 31/08/2023

Project Number: [956004]
Project Acronym: [BioTrib]
Project title: [**Advanced Research Training for the Biotribology of Natural and Artificial Joints in the 21st Century**]

Mg-based powder adequate for printing

Deliverable D 3.1

Month Due: PM31

Month Delivered:

Project coordinator name	Prof. Richard M Hall
Project coordinator organisation name	UNIVLEEDS
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Dissemination Level of Report

PU	Public	X
PP	Restricted to other program participants (including the Commission Services)	
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The BioTrib ETN project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 956004.

Version	Date	Comment	Modifications made by
D3.1.1	01-08-23	First Draft circulated to Project Coordinator	
D3.1.2	14-08-23	Review and Amendment	Giulio Cavaliere, Francesco D’Elia, Cecilia Persson
D3.1	**31-08-23**	**Submitted to Commission**	**JS (UNIVLEEDS)**

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Executive Summary

Magnesium (Mg)-based alloys have emerged as promising biomaterials for orthopaedic applications due to their advantageous mechanical properties, biocompatibility, and osteopromotive effects. The low density of Mg, coupled with its similarity to human bone in terms of Young's modulus, reduces stress shielding and promotes bone regeneration. Additionally, Mg-based implants can fully degrade under physiological conditions, eliminating the need for secondary surgeries and enhancing patient comfort. However, the rapid corrosion rate of Mg presents a significant challenge, as it can compromise the mechanical support of the implant during the healing process. Among the Mg-based alloys studied, WE43 has received clinical approval for specific applications; however, the presence of rare earth elements (REEs) in WE43 raises concerns regarding potential cytotoxicity and long-term safety as a biomaterial.

To address these limitations, we aimed to develop a novel REE-free Mg-based powder for biomedical applications adequate for Powder Bed Fusion-Laser Beam (PBF-LB). This technique offers advantages in fabricating Mg alloys, including the ability to produce complex geometries and patient-specific implants with minimal material waste.

The composition of the powder was carefully selected to include only highly biocompatible elements and to target a degradation rate in the range of the recommended limit of 0.5 mm/year. The produced powder was then characterized and compared to a benchmark WE43 Mg-powder. The printability was demonstrated using a PBF-LB system (Aconity MIDI, Aconity 3D GmbH).

Introduction

Mg-based alloys are emerging as promising biomaterials in orthopaedic applications in virtue of their favourable mechanical properties, high biocompatibility and osteopromotive properties. Mg has a significantly lower density (1.74 g/cm³) than other commonly used biomaterials like stainless steel and titanium while still maintaining a high fracture toughness. Moreover, having an elastic modulus closer to human bone, the risk of stress shielding is significantly reduced when compared to alternative metal implants (E in the order of 40 GPa rather than above 120 GPa) [1].

Magnesium is also crucial in human metabolism and naturally present in bone tissue, being the fourth most abundant cation in the human body [2]. Moreover, it has been reported that Mg-based implants stimulate the formation of new bone tissue [3]. Another advantage is that Mg can completely degrade under physiological conditions. This avoids the need for a secondary surgery to remove the implant after complete bone healing, thereby avoiding risks related to infections and decreasing the discomfort to the patient[4].

However, despite the advantage of the ability to corrode in body fluid, the too high corrosion rate attributed to Mg is a main challenge currently limiting the possible applications of this metal. A too rapid degradation can result in an implant not offering mechanical support while the bone tissue is still healing (more than 12 weeks). Also the H_2 generated as a by-product during corrosion of Mg can accumulate in the surrounding tissues, hindering the bone tissue regeneration [5].

Over the last decade, a number of Mg-based alloys were studied and subject to animal trials including WE43, AE21 , AZ31B , AZ91 , Mg-Nd-Zn-Z [6], [7]. WE43 ($\text{Mg-Y}_{3.7\text{-}4.3\text{wt\%}}\text{-RE}_{2.4\text{-}4.4\text{wt\%}}\text{-Zr}_{0.4\text{wt\%}}$), is the only one that has been clinically approved: WE-based fracture fixation screws from Syntellix and WE43 vascular stents from Magnezix® received the CE certification in 2013 and 2016 respectively[3]. Nevertheless, WE43 still presents certain challenges and limitations. One limitation is the potential cytotoxicity associated with the presence of REEs. Although REEs have been shown to enhance the mechanical properties and corrosion resistance of Mg alloys, their release during degradation can lead to adverse biological effects. The cytotoxicity of REEs can hinder the biocompatibility of WE43 and raise concerns regarding its long-term safety and performance as a biomaterial[8]. Considering biological safety, the preferable alloying elements for Mg-based biomedical devices should be those that are either essential to the human body or naturally present in it. However, processing of such alloys may be challenging, particularly when using novel techniques such as additive manufacturing (AM).

Additive manufacturing techniques offer several advantages in fabricating Mg alloys, including the ability to produce complex geometries and the ability to produce patient specific implants. Furthermore, the high cooling rates generally associated with the AM process allow rapid solidification that limits composition segregation and coarse grains which can help improving the degradation properties. Powder Bed Fusion Laser Beam (PBF-LB) is one of the most investigated techniques for printing Mg alloys thanks to the low heat flux and the ability to obtain complex internal and external geometries[9]. Another significant advantage of PBF-LB is the reduction in material waste. Unlike subtractive manufacturing processes that involve cutting away excess material from a solid block, PBF-LB selectively melts the powder bed, minimizing material wastage.

Despite the challenges associated with Mg-based alloys, their unique advantages make them an attractive material of choice for biomedical applications. We aim to develop a novel Mg-based alloy suitable for PBF-LB that can overcome some of the downsides of the more commonly used alloys. This should have a controlled degradation rate and it should contain just highly biocompatible elements that do not negatively impact the surrounding tissues.

Deliverable Description

Deliverable 3.1 is a first step toward a new generation of Mg-based alloys for PBF-LB. The main focus was the selection of a tailored composition that could overcome the limitations of previously employed alloys like WE43. We aimed to include only highly biocompatible alloying elements, avoiding REEs, while also seeking to improve the degradation properties. The powder was then produced by an external company and the printability was demonstrated in a PBF-LB system.

Materials and methods

a. Selection of alloying elements

A bibliographic study was conducted in order to understand the effect of different alloying elements on the Mg matrix and select the most suitable candidate for the production of powder for the PBF-LB process. Computational thermodynamics based on the CALPHAD method was also used to predict which phases would form during the PBF-LB process.

We selected a family of alloys often referred to as ZX alloys containing Magnesium (Mg), Calcium (Ca), and Zinc (Zn). These alloys have received increased attention for their possible biomedical applications since all the constitutive elements are present in the human body, and this should guarantee a higher degree of biological safety [10]. ZX alloys still share some of the common challenges with other Mg-based alloys, especially the difficulties in having a controlled degradation rate. We aim to use some of the specific features of the PBF-LB process to improve this aspect while maintaining appropriate mechanical properties.

b. Powder production: Gas atomization

Gas atomization is a widely employed technique for the production of metal powders with controlled particle size and morphology. This process involves the conversion of liquid metal into fine droplets by subjecting it to high-pressure gas (e.g., Argon) streams (Figure 1). The liquid metal is typically poured through a nozzle then disintegrated into droplets by the gas flow. The gas impinges on the liquid metal stream, breaking it up into smaller droplets that solidify rapidly in flight due to the temperature difference with the cooling gas. The resulting metal powders exhibit spherical or near-spherical shapes, with a narrow size distribution. Gas atomization offers several advantages, including the ability to produce a wide range of metal powders, such as ferrous and non-ferrous alloys, refractory metals, and even reactive metals. Gas atomization also enables the production of powders with high purity and low oxygen content, as the process takes place using inert gas or under vacuum conditions. For this research, two selected powder compositions (Mg-Ca-Zn based) were gas atomized by Nanoval GmbH (Germany).

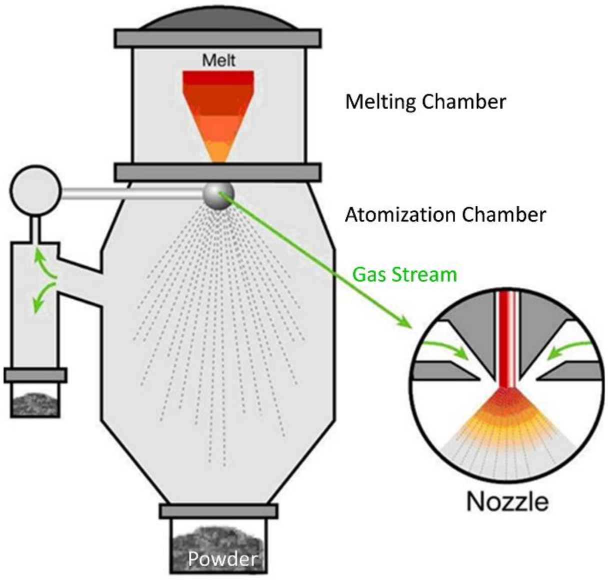

Figure 1. Schematic of the gas atomization process.[11]

c. Powder characterization

The produced powder was characterized prior to printing. Spreadability was measured using a modified TQC Sheen automatic film applicator as developed by Hulme C.N. et al.[12]. In this test a weighted amount of powder is spread in a layer with known dimensions (thickness) on a simulated build plate. The results are expressed in terms of apparent density, calculated from the difference in amount of powder on the plate and the amount of powder left in the spreading container.

The particle size distribution and shape of the powder (aspect ratio) was measured using dynamic image analysis on a Camsizer XT (Retsch GmbH). Finally, the powder particle morphology was examined using scanning electron microscopy (SEM).

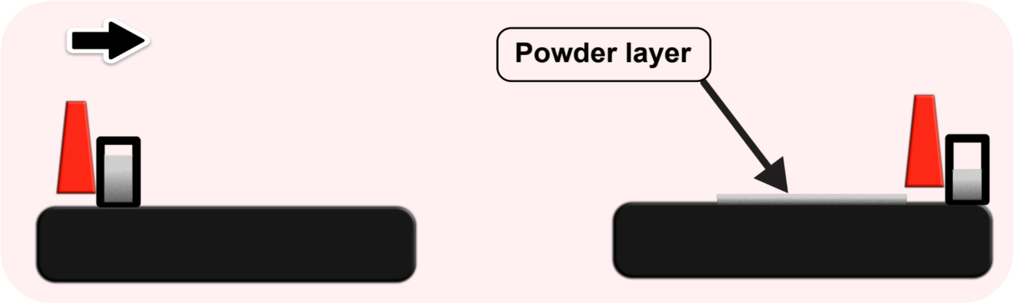

Figure 2. Schematic of the spreadability test performed with the TQC Sheen automatic film applicator.

d. Powder bed fusion laser beam (PBF-LB)

Powder Bed Fusion-Laser Beam utilizes a high-energy laser beam to selectively melt and fuse metal powder particles, layer by layer, to create complex three-dimensional objects. In PBF-LB, a thin layer of metal powder is evenly spread over a build platform, and a laser beam scans the powder layer according to the desired shape, melting and solidifying the powder particles to form a solidified layer. The build platform is then lowered, and a new layer of powder is spread on top of the previous layer. In this work, an Aconity MIDI PBF-LB system (Aconity 3D GmbH) equipped with a single laser was used to demonstrate the printability of the produced Mg-based powder. For these trials, both laser power and scan speed were varied, while hatch spacing, scan strategy and layer thickness were held constant.

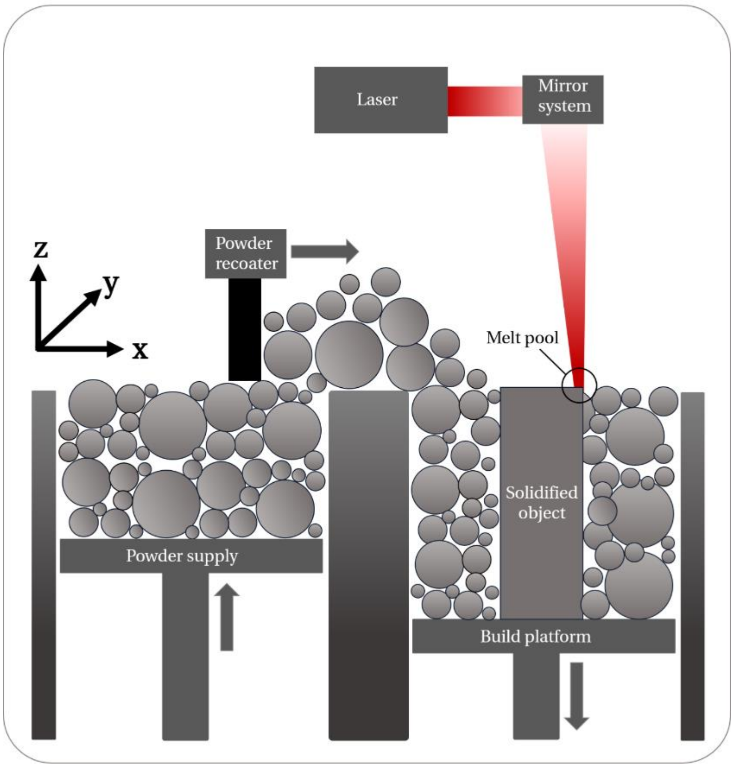

Figure 3. Schematic of the PBF-LB process.[13]

Results

The powder characterization showed properties close to commercially available WE43 Mg alloy powder used as reference. The measured powder size distribution for the new powders was symmetric and narrow (Figure 4) and ranged from 15-70 µm, demonstrating suitability for the PBF-LB process. Moreover, the aspect ratio was very close to one, indicating a high degree of sphericity (Figure 5). The powder also demonstrated good spreadability and the ability to form a high-density layer (Figure 6). The layer formed had a density more than 1.4 times higher than WE43 tested under the same conditions. Composition 2 showed a higher variability in the spreadability results possibly indicating a less homogenous powder, but that could also be related to the high variability associated with this test [11]. Overall these are promising results as being able to spread into a uniform and dense thin layer of powder is crucial for the final part properties with a direct impact on the printed part density[14]. Finally, SEM analysis (Figure 7) confirmed sphericity of the powder particles, while also demonstrating overall good quality with minimal presence of satellites and agglomerates.

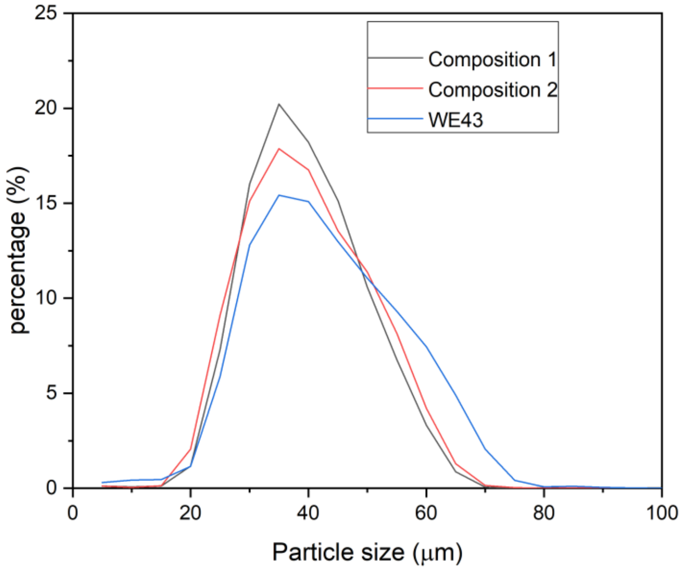

Figure 4. Powder size distribution for two compositions of a novel Mg-based powder compared to WE43. Measured using dynamic image analysis on a Camsizer XT (Retsch GmbH).

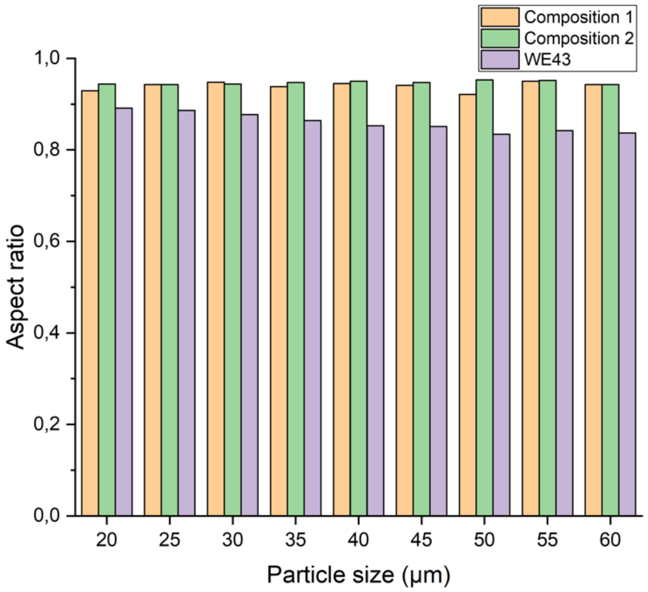

Figure 5. New Mg-based powder (composition 1 and 2) aspect ratio for different particle sizes compared to WE43 powder. Measured using dynamic image analysis on a Camsizer XT (Retsch GmbH).

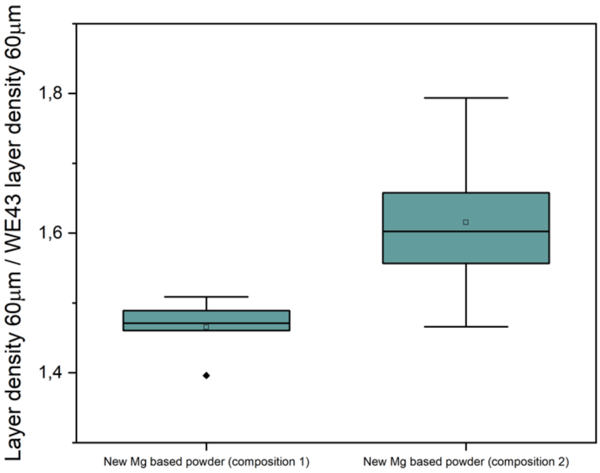

Figure 6. Spreadability results expressed as a ratio with WE43 layer density for a 60µm layer and 500mm/s speed. The test was performed using a modified TQC Sheen automatic film applicator and repeated 5 times.

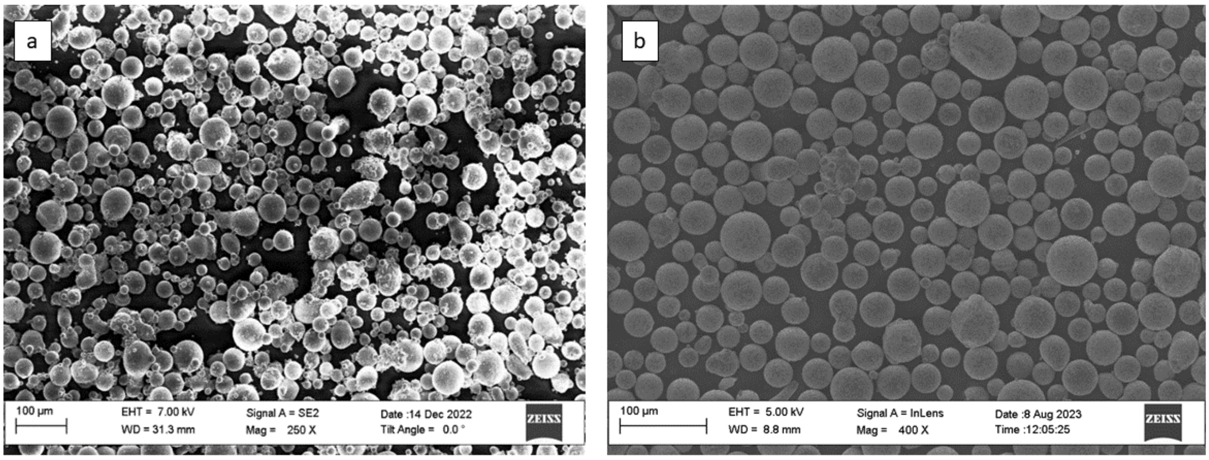

Figure 7. SEM Image of the new Mg-based powder for composition 1 (a) and composition 2 (b).

The first PBF-LB printing trials showed promising results. Cube-shaped samples with dimensions of 10*10*6 mm were successfully printed on a Mg alloy build plate using Composition 1(Figure 8). Nevertheless, the samples still presented visible defects (Figure 8). Delamination was observed in close proximity to the build plate indicating the presence of high residual stresses that could be resulting from an interaction with the build plate itself. The preliminary microscopy analysis (Figure 8

(B)) also clearly shows pores and cracks and the overall quality of the print is still not comparable to the reference WE43.

As a result, ongoing work is focused on further optimisation of processing parameters, including laser power, scan speed and hatch spacing. The goal is to produce samples with high density (i.e., > 99%), and mechanical and degradative properties suitable for biomedical applications.

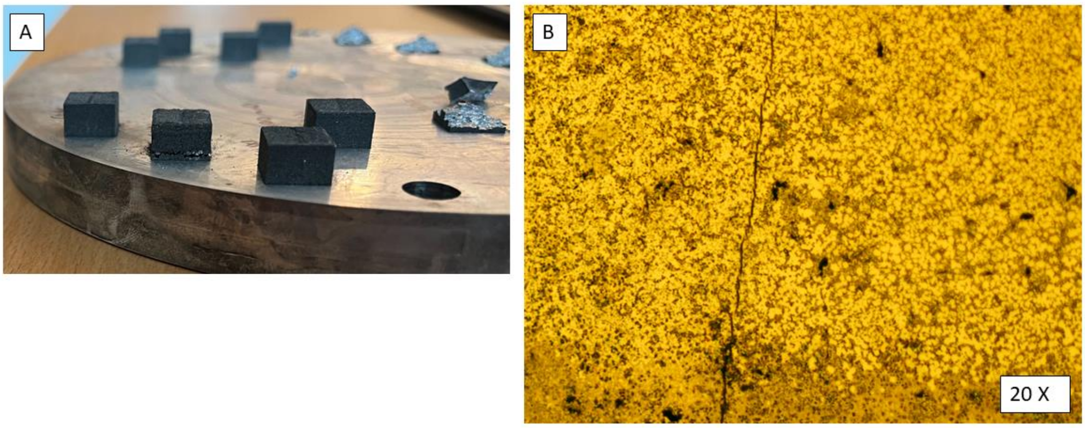

Figure 8. Results of preliminary printing trial for the novel Mg-based powder (composition 1). Some of the printed sample (A) and an optical microscopy image (20x) showing cracks and delamination. Printed in an Aconity MIDI PBF-LB system (Aconity 3D GmbH).

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