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Selective Laser Melting of Magnesium and Magnesium Alloys

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Abstract

Selective Laser Melting (SLM) offers the possibility to create three dimensional parts by having full freedom of design. Therefore prototypes can be produced faster and conventionally manufactured parts can be shaped individually, including an optimized design regarding potential loads and parts weight. The manufacturing of biocompatible metals like 316L and TiAl6V4 is already industrially established. Because of the corrosive and mechanical properties of magnesium and the advantages of the SLM process, using magnesium is of great interest for manufacturing individual biodegradable implants. Recent investigations on SLM of magnesium have not led to successful operation so far. Due to the low vaporizing temperature, manufacturing non-porous and three dimensional parts from magnesium was not possible yet. Following a new strategy, using an industrial SLM system with an overpressure building chamber, investigations on SLM of magnesium are now carried out in order to overcome these difficulties and produce fully dense three dimensional parts.

Introduction

Additive manufacturing is an automated and repeating process where parts are built from layers. This enables the creation of three-dimensional parts with full freedom of design. The Selective Laser Melting (SLM) process is an additive manufacturing technique, which produces fully dense parts from metallic powder material. The 3-D part is first "sliced" into layers, which are manufactured in a two step process. Metal powder is deposited in the first step, and melted by laser radiation in the second step. Afterwards, the build-up platform is moved, and the process is repeated until the part is finished (see figure 1) [1].

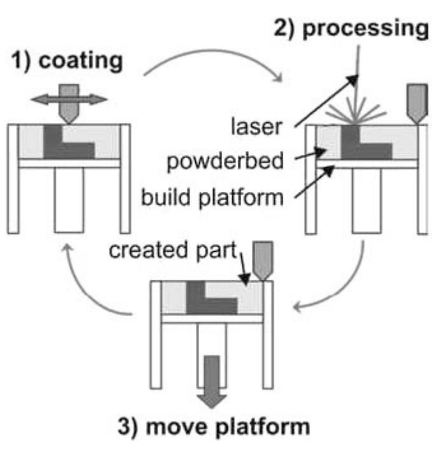

Figure 1. Sketch of an SLM process (according to [2])

The technology was originally used for manufacturing prototypes, and is also known as 'rapid prototyping'. Nowadays, further improvements on the process have been made so that prototypes, individual parts and small series can be produced faster [3], including an optimized design regarding potential loads and the part weight [4].

Since the Selective Laser Melting process is already established for implant materials like 316L stainless steel and TiAl6V4 [5], manufacturing individual implants for surgery is of high interest [3]. One of the future challenges is the manufacturing of biodegradable, biocompatible metal implants. These implants, e.g. for osteosynthesis applications or stents, must not be removed through additional surgery, after the healing process has taken place. Magnesium alloys are the preferred materials for producing such implants, because of their mechanical and corrosive properties.

Selective Laser Melting of magnesium alloys therefore offers the possibility to create complex shaped individual biodegradable implants for osteosynthesis. The great challenges are to establish magnesium alloys in the SLM process, and to control the degradation rate and the resulting mechanical integrity in the human body.

To accomplish this, a research project funded by the Deutsche Forschungsgemeinschaft (German Research Foundation, DFG) was launched in 2012, to manufacture biodegradable implants for cranial bone replacement using the SLM process. The main component of the future implant is a biodegradable scaffold made of magnesium alloys. A surrounding biodegradable polymeric coating made of poly(3-hydroxybutyrate) (P(3HB)) controls the degradation behaviour. Additionally, a titanium component can be added for long term stability (see figure 2). Before implanting the device, it is pre-vitalized with human cells, to support the growth of bone (on the implant). During the healing process, the magnesium scaffold degrades, and the growing bone closes the gap.

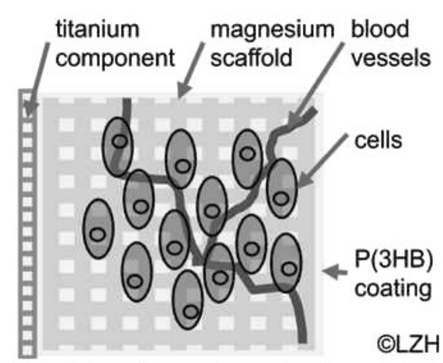

Figure 2. Pre-vitalized hybrid implant

State of the art

Several investigations on Selective Laser Melting of magnesium and magnesium alloys have been carried out during the last few years. In 2010, Ng et al. investigated Selective Laser Melting of magnesium to produce scaffolds for bone substitution. Using a miniature SLM system constructed at the Hong Kong Polytechnic

University, single tracks in a shielding gas atmosphere were built up at ambient pressure. For first trials, coarse particles with the size of 75 µm - 150 µm and spherical particles with the size of 5 µm - 45 µm were used, which only lead to satisfactory results. The produced structures showed sintered powder around the track [6]. In 2011 they investigated the SLM process with magnesium under different processing conditions, using the same setup as in 2010. Magnesium was processed using pulse mode and continuous wave mode. Continuous wave irradiation led to a disrupted surface with regular beads, whereas pulsed mode irradiation led to a smooth surface and flat surface morphology with pores within the tracks (see figure 3) [7]. Later they also discovered that an increase of the laser energy density resulted in a decrease of cooling rate, and therefore grain coarsening in the melted zone [8].

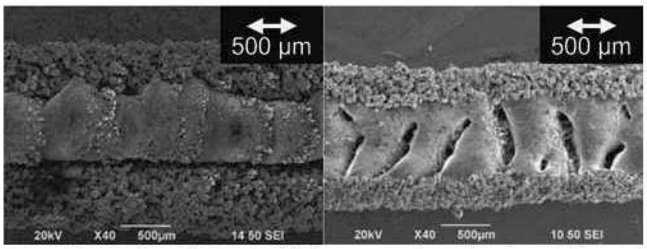

Figure 3. Laser melted magnesium tracks with continuous wave radiation (left) and pulsed mode laser radiation (right) (according to [7])

In 2011, Zhang et al. investigated Selective Laser Melting of a magnesium powder mixture containing 9 wt% of aluminum. Using an MCP Realizer 250 II^{SLM} (MCP HEK Tooling GmbH, Germany) machine with a process pressure of 7 Pa, structures with 82 % density were produced. During the experiments they observed balling phenomena (see figure 4) and powder evaporation, due to the low boiling point of magnesium using high energy densities [10].

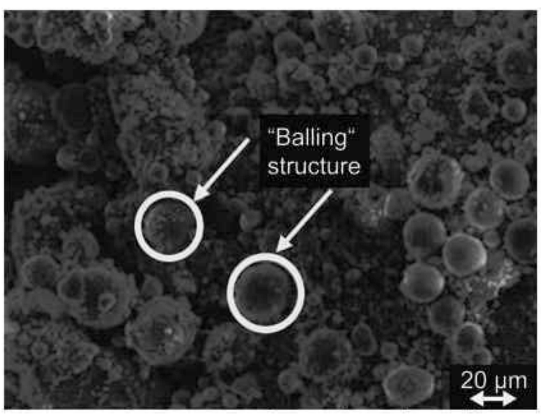

Figure 4. Microstructure of a sample surface of laser melted magnesium aluminum powder material (according to [10])

Materials and methods

One major problem is the low boiling point of magnesium of 1,093 °C, compared to the melting point of 650 °C and the low evaporation heat of 5.272 kJ/kg at ambient pressure [9]. Zhang et al. produced porous structures with a maximum density of 82 % by working at 7 Pa process pressure. Ng et al. had better results by working at an ambient pressure atmosphere. To overcome this problem, the boiling point has to be increased by working in an overpressure atmosphere. Another problem is the low dynamic viscosity of molten magnesium, which is 1.5 Pa·s, and therefore lower than molten titanium (2.2 Pa·s) and iron (6.93 Pa·s) [11] alloys which are well established in the SLM process [5]. Since the viscosity of the melt depends on the temperature [11], the viscosity decreases, due to high energy input during laser treatment. This can lead to problems regarding the track formation.

Preliminary tests and results

In 2009, the first unpublished investigations on SLM of magnesium powder material were carried out with an SLM test setup at the LZH. The challenge of the low boiling point and evaporation heat was known at that time, so the SLM setup was equipped with a vacuum and overpressure process chamber and a pressure control valve (see figure 5). Rectangular, single layer magnesium samples with a size of 4.5 mm x 4.5 mm were manufactured in a 2 mm thick powder bed using a 50 W fiber laser. Pure spherical magnesium powder in grain size < 75 µm with 80 % < 45 µm provided by Tropag Oscar H. Ritter Nachf. GmbH Hamburg, Germany was used. In several tests, the effect of laser power, scanning speed, shielding gas and process atmosphere were investigated.

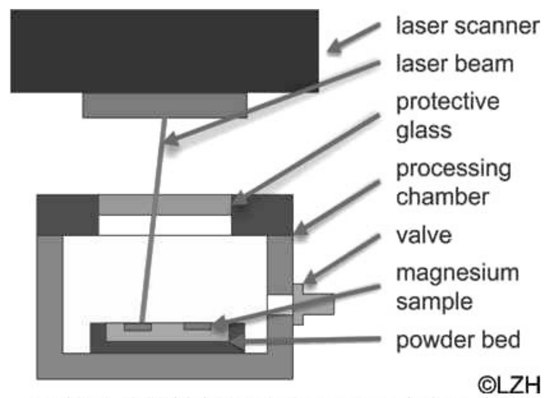

Figure 5. Sketch of an SLM machine with overpressure process chamber

Using the maximum feasible overpressure of 0.13 MPa (absolute pressure), stable structures of magnesium were manufactured (see figure 6). Processing under an argon atmosphere led to precipitation of process emissions on the protective glass, which could easily be removed. This effect could not be observed using a helium atmosphere.

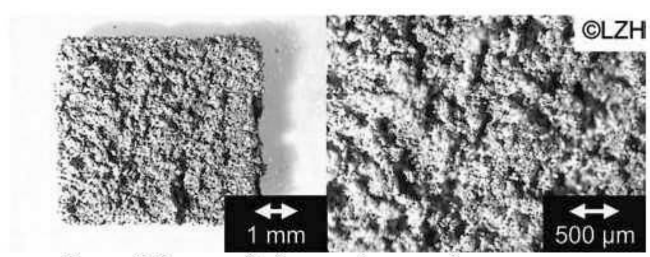

Figure 6. Laser melted magnesium sample

The preliminary results showed that it is possible to use magnesium powders in the SLM process. Nevertheless, a smooth surface with definite straight edges could not be achieved, due to the evaporation of the powder material. Therefore, the boiling point had to be increased by increasing the process pressure, and the process parameters had to be improved.

Concept for the SLM machine for magnesium processing

Consequently, a Selective Laser Melting Machine with an overpressure process chamber based on an SLM 125^{HL} was developed by SLM Solution GmbH, Lübeck, Germany in 2012, to produce magnesium parts using the SLM process. The build-up chamber is designed for an absolute pressure of 0.3 MPa, which increases the boiling point of magnesium of 127 °C compared to the investigations of Ng et al. 2010 and 2011, to a boiling temperature of 1,220 °C (see figure 7).

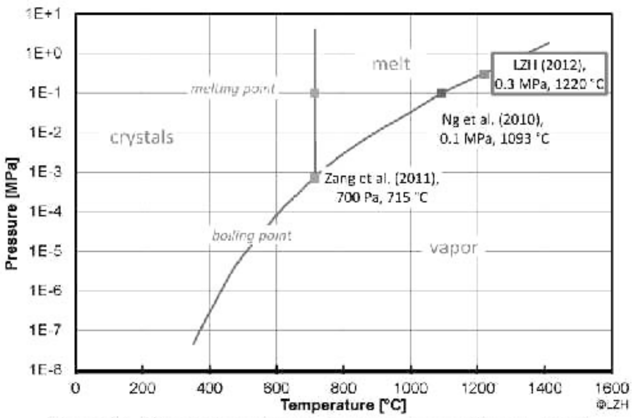

Figure 7. Magnesium phase diagram (according to [12])

For security reasons, the build-up platform is reduced to 50 mm x 50 mm and a maximum part height of 50 mm, in order to limit the maximum amount of magnesium powder to 500 g. To enable a Selective Laser Micro-Melting (SLµM) process which creates structures < 100 µm, the focus spot size is minimized to 70 µm.

Focus of future investigations

First, the investigations will focus on the effects of key process parameters like laser power, scan speed and scan strategy as well as the process atmosphere and process pressure. A first parameter set for manufacturing scaffolds needs to be identified.

Second, the evolving microstructure has to be investigated. As Ng et al. showed in 2011, the SLM process can be used to adjust the grain size in the material according to the process parameters [8]. Since the grain size has an important effect on the mechanical and chemical properties, it can be adjusted according to the requirements [9].

Magnesium alloy selection

Initially, the behavior of magnesium in the SLM process will be investigated using spherical magnesium powder ATOULTRA 325 with a grain size of 10 µm - 45 µm provided by SFM SA, Matigny, Switzerland (see figure 8). Since pure magnesium leads to an increase of the pH-value during *in* vivo and *in* vitro degradation, it is not suitable as an implant material [13].

Since no biodegradable magnesium implant is available on the market [2], and since no magnesium alloy has approval as a biodegradable implant material, several magnesium alloys will be investigated for the intended purpose.

Figure 8. Magnesium powder ATOULTRA 325 (SFM SA)

As a first magnesium alloy for the required scaffolds, a magnesium alloy containing 0.8 % calcium will be used, since the amount of alloying elements is small. This MgCa0.8 alloy showed good biocompatibility for an osteosynthesis implant in *in vivo* test, but insufficient initial mechanical strength [14]. Since low mechanical stability is required, it is suitable as an implant material for the hybrid implants.

Later, further magnesium alloys will be established in the SLM process. Since the final hybrid implant will be an osteosynthesis implant closely meshed with blood vessels, it cannot be compared with the osteosynthesis implants investigated in the various publications. Several alloys showing good results regarding biocompatibility, degradation and mechanical stability in vascular, abdominal and osteosynthesis applications have to be taken into account.

The WZ21 magnesium alloy containing biocompatible alloying and rare earth elements showed good biocompatibility, and slow and homogenous degradation in the abdominal cavity of miniature pigs [15], and stable mechanical integrity in the femora of rats [16].

The WE43 alloy containing yttrium, rhenium and zirconium is the best alloy for biodegradable stent manufacturing. Results from using this alloy as an osteosynthesis implant material are varied. Krause et al. observed unpredictable and inhomogeneous degradation behavior in 2010 [14], whereas Castellani et al. observed high implant stability and good osseo-integration in 2010 [17].

Last, the metallic glass $Mg_{60}Zn_{35}Ca_5$ containing 60 % magnesium, 35 % zinc and 5 % calcium will be investigated. It showed less hydrogen evolution than other alloys, and a good biocompatibility in the abdominal wall of domestic pigs [18].

Conclusion

Biodegradable implants can have a significant impact on the future of osteosynthesis applications. Magnesium alloys, which have been thoroughly investigated by several research groups in recent years, are the preferred material for manufacturing such implants, because of the load bearing properties, compared to biodegradable polymers. Selective Laser Melting of magnesium alloys can be used to create individual complex shaped biodegradable implants.

Recent investigations on Selective Laser Melting of magnesium and magnesium alloys did not lead to the desired success, due to the low boiling point of the materials. Porous structures and single tracks with adhering powder particles were manufactured, and it was not possible to create three-dimensional parts. In a new approach, an industrial SLM machine setup equipped with an overpressure working chamber up to 0.3 MPa was developed to increase the boiling point up to 1,220 °C. Previous investigations at the LZH showed that using SLM in an overpressure atmosphere can result in improved sample properties.

In order to establish the SLM process for magnesium powder materials, the parameters have to be extensively investigated, to prevent evaporation and a further decrease of the viscosity due to high energy input. As recent investigations have shown, the energy input also changes the induced cooling rate, and therefore the evolving grain sizes in the SLM part. This offers the possibility to adjust the mechanical and chemical properties, which depend on the grain size.

Taking all these issues into account, the SLM process in an overpressure atmosphere is a challenging, but promising way to successfully generated scaffolds made of different magnesium alloys for the production of new hybrid implants for cranial bone replacement.

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References

1. Andreas Gebhardt, *Understanding Additive Manufacturing* (Munich: Carl Hanser Verlag GmbH & Co. KG, 2012), 31-63

2. M. Gieseke et al., “Additive Manufacturing of Drug Delivery Systems,” *46th annual conference of the German Society for Biomedical Engineering (BMT 2012)*, 2012, 425-428.

3. Ian Gibson, David W. Rosen, and Brent Stucker, *Additive Manufacturing Technologies* (New York Heidelberg Dotrecht London: Springer, 2010), 1-12, 385-399

4. Claus Emmelmann, and André Goeke “Laser freeform fabrication of aircraft components” *Proceedings of the 2nd Internation Workshop on Aircraft System Technologies* (Aachen: Shaker, 2009), 243-248

5. SLM Solutions GmbH, “Discover the variety” (company homepage SLM Solutions GmbH, Lübeck, Germany, http://www.slm-solutions.com/cms/upload/pdf/120923_SLM_Materialien.pdf, 09/26/2012)

6. C.C. Ng et al., “Layer manufacturing of magnesium and its alloy structures for future applications,” *Virtual and Physical Prototyping*, 5 (2010), 13-19

7. C.C. Ng et al.,“ Fabrication of magnesium using selective laser melting technique,” *Rapid Prototyping Journal*, 17 (2011), 479-490

8. C.C. Ng. et al., “Microstructure and mechanical properties of selective laser melted magnesium,” *Applied Surface Science*, 257 (2011), 7447-7454

9. Catrin Kammer, *Magnesium Taschenbuch* (Düsseldorf: Aluminium-Verlag Marketing & Kommunikation GmbH, 2000), 642-649

10. B. Zhang et al., “Effects of processing parameters on properties of selective laser melting Mg–9%Al powder mixture,” *Materials & Design*, 34 (2011) , 753 – 758

11. Herbert Pfeifer, *Taschenbuch industrielle Wärmetechnik: Grundlagen, Berechnungen* (Essen: Verfahren Vulkan-Verlag, 2007) 139-140

12. Stephan Hasse, *Gießerei Lexikon* (Berlin: Fachverlag Schiele & Schön GmbH, 2007, 19) 207

13. K. Lips et al., “Elektrochemische Korrosionsuntersuchungen an Magnesiumlegierungen AZ91: Beschreibung kritischer Parameter und deren Einfluss auf die Angriffsmechanismen auf NRC-Proben,“ *Materials and Corrosion*, 55 (2004), 5-17

14. Krause et al., “Degradation behavior and mechanical properties of magnesium implants in rabbit tibiae,” *Journal of Material Science*, 45 (2010), 624-632

15. A.C. Hänzi et al., “On the in vitro and in vivo degradation performance and biological response of new biodegradable Mg-Y-Zn alloys,” *Acta Biomaterialia*, 6 (2010), 1824-1833

16. T. Kraus et al., “Magnesium alloys for temporary implants in osteosynthesis: In vivo studies of their degradation and interaction with bone,” *Acta Biomaterialia*, 8 (2010), 1230-1238

17. C. Castellani et al. “Bone-implant interface strength and osseointegration: Biodegradable magnesium alloy versus standard titanium control,” *Acta Biomaterialia*, 7 (2010), 432-440

18. B. Zberg et al., “MgZnCa glasses without clinically oberservable hydrogen evolution for biodegradable implants,” *Nature Materials*, 8 (2010), 887-891