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In vitro biodegradation testing of Mg-alloy EZK400 and manufacturing of implant prototypes using PM (powder metallurgy) methods

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ABSTRACT

The study is focussing towards Metal Injection Moulding (MIM) of Mg-alloys for biomedical implant applications. Especially the influence of the sintering processing necessary for the consolidation of the finished part is in focus of this study. In doing so, the chosen high strength EZK400 Mg-alloy powder material was sintered using different sintering support bottom plate materials to evaluate the possibility of iron impurity pick up during sintering. It can be shown that iron pick up took place from the steel bottom plate into the specimen. Despite the fact that a separating boron nitrite (BN) barrier layer was used and the Mg-Fe phase diagram is not predicting any significant solubility to each other. As a result of this study a new bottom plate material not harming the sintering and the biodegradation performance of the as sintered material, namely a carbon plate material, was found.

1. Introduction

Biodegradable Mg-alloys are showing increasing interest regarding biomedical and orthopaedic implant applications. The biodegradable and biocompatible new material hold mechanical properties comparable to those of human cortical bone [1–4]. Currently, first commercial implant applications are launched into the market [5]. These implants are made by extrusion of high strength Mg-alloy powders. However, the production process involves high effort and many individual machining steps to generate the finished part. Metal Injection Moulding (MIM) and Additive Manufacturing (AM) are alternative powder metallurgical production routes for both, mass production and manufacturing of individual single parts. MIM is an economic near net shape prototyping technique for small sized and complex shaped parts in high numbers. For the production of green parts via MIM, a feedstock blend made of spherical Mg-alloy powder and different polymer binder components as shown in Fig. 1 is needed. The shaping of the parts takes place via injection moulding of the semifluid or plasticised feedstock into a mould.

Applying AM techniques, especially the Fused Filament Fabrication (FFF) or Fused Deposition Modelling (FDM), the same feedstock blend shown in Fig. 1 can be used for the shaping of individual single parts without use of a mould. The 3D printing techniques require feedstock granules (see Fig. 1) or feedstock filament. The consolidation of the final metal parts take place via sintering. The detailed processing about sintering of Mg and MIM of Mg is described in detail in Refs. [6–11]. EZK400 tensile test specimen according to ISO 2740-B and different implant screw demonstrator parts could be successfully produced by MIM as shown in Figs. 1 and 2b. The assessment of mechanical properties of the as sintered EZK400 implant prototypes and test specimen is described in detail in Ref. [12]. The tensile test of the dogbone shape MIM EZK400 specimen illustrated an ultimate tensile strength (UTS) of 164 MPa, tensile yield strength (YS) of 123 MPa and elongation at fracture of 3.4% [12]. Moreover, the binder-free press and sinter (P + S) parts, also used in the framework of this study for the

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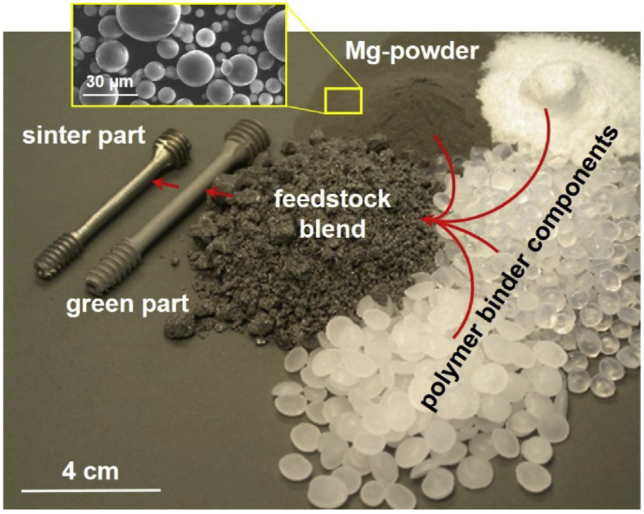

Fig. 1. Mg-powder, polymer components, feedstock and implant screw demonstrator part in green and sintered condition made by MIM of Mg-alloy at Helmholtz-Zentrum Geesthacht.

biodegradation testing, obtain an UTS of 188 MPa, 122 MPa yield strength and 5% elongation at fracture [12]. However, this study is more focused on assessment of the biodegradation performance of the EZK 400 material. Biodegradable magnesium alloy parts for biomedical applications only tolerate limited amounts of impurities in the final part. Next to the existing impurity level of the used raw material the impurity uptake during processing is of high importance. Hence, the study focusses on the effect of impurity uptake during sintering of the Mg-Nd-Gd-Zr-Zn-alloy powder (EZK400) and the resulting effect on its biodegradation performance. Especially the influence of different sintering crucible bottom plate materials, necessary for the positioning of the green parts in the sintering furnace, on the degradation rate will be investigated within this study. This study demonstrated that both, good mechanical properties and biodegradation performance of the sintered Mg-material could be achieved.

2. Materials and methods

2.1. Powder, feedstock

The test specimen and implant screw demonstrator part production took place using a commercially available spherical gas atomised Mg-2.6Nd-1.3Gd-0.5Zr-0.3Zn-alloy powder, following up referred to as EZK400 (product name: MAP+21, Magnesium Elektron, UK). The particle size distribution was 20 µm–45 µm.

The feedstock blend as shown in Fig. 1, necessary for the MIM-process, was prepared using following polymer binder components: 60 wt% paraffin wax, 35 wt% polypropylene copolymer and 5 wt% stearic acid. The powder loading of the feedstock was 64 vol %. The blending of the feedstock components was performed in a planetary mixer (Thinky ARE-250 planetary mixer, Japan), applying 160 °C and 500 G acceleration. To avoid the uptake of additional oxygen during processing the powder handling took place under argon atmosphere in a glovebox system (Unilab, MBraun, Germany). The feedstock blend was granulated using a cutting mill (Wanner B08.10F, Germany).

2.2. MIM-specimen preparation

The manufacturing of dogbone shape tensile test specimen according ISO 2740-B and implant screw demonstrator parts as shown in Figs. 1 and 2 took place using an injection moulding machine (Arburg Allrounder 320S) at up to 1500 bar injection pressure, 65 °C mould temperature and 135 °C feedstock temperature.

2.3. Debinding

To get rid of the waxy binder components and the stearic acid solvent debinding in a hexane bath (45 °C, 10–15 h) took place after the injection moulding process step (Lömi EBA50/2006, Germany). The thermal debinding of the polypropylene copolymer took place in a combined debinding and sintering hot wall furnace (RRO 350–900, MUT, Jena, Germany) using argon 6.0 as a protective gas.

2.4. Binder-free specimen preparation

To avoid any additional influences of binder components or binder residuals on the biodegradation test, binder free specimens produced by P + S were used for the biodegradation test procedure. In doing so, the EZK400 powder was directly filled into a die plate with cylindrical cavity. Cylindrical specimen with 11 mm in diameter and approximately 12–16 mm in high were produced using die plate, stamper, punching tool and a manual mode press (Enerpac RC 55, USA) as shown in Fig. 3a. The applied surface pressure was 100 MPa. The cylindrical specimens were placed in the sintering furnace using a BN coated sintering support bottom plate made of unalloyed steel as shown in Fig. 3b.

Fig. 2. a dogbone shape tensile test specimen [12] in: green condition (after injection moulding of the plasticised feedstock granules)- sintered condition (right side). b: suture anchor implant screw demonstrator parts made by MIM of EZK400 powder material in the green and sintered condition. Design: ConMed, USA.