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Properties of sintered Mg alloys for biomedical applications

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Abstract In addition to the use as light weight construction material, magnesium alloys are also very suitable for future orthopaedic and traumatology applications. Common permanent implant materials such as titanium or stainless steel still suffer from stress shielding problems, causing bone resorption and implant loosening. In contrast, magnesium alloys provide elastic moduli and strengths matching those of cortical bone. In order to support osseointegration and vascularisation, an open porous surface structure of an Mg-implant is advantageous. The powder metallurgical processing route of Mg-alloys enables the generation of such parts. Powder blends with different sintering behaviour were produced via mixing pure Mg-powder with different Ca containing master alloy powders (MAP). As a result, sintering of these Mg alloy powders and blends became feasible. Sintered parts were investigated in view of shrinkage, porosity, grain size using SEM, EDX and XRD. In addition, compression tests were performed revealing ultimate compression strength up to 328 MPa, plastic compressibility of 22 % and compressive yield strength up to 90 MPa. Hence, the PM-route enables the production of parts with mechanical properties matching those of cortical bone.

Introduction

Today, magnesium is well known as a light weight construction material [1]. Recent studies have shown that magnesium alloys are also very suitable for future orthopaedic and traumatology applications [2-5]. Current permanent implant materials such as titanium or stainless steel still suffer from stress shielding problems, causing bone resorption and implant loosening. In contrast, magnesium alloys provide elastic moduli and strengths matching those of bone tissue [6]. Corrosion products of Mg, generated during biodegradation, support osteoconductivity [7]. In order to support also osseointegration and vascularisation, an open porous surface structure of Mg-implants is advantageous [4].

Mg-based implant material should be nearly dense in the interior in order to provide enough stiffness for load bearing applications. And it should provide an open porous surface area in order to support ingrowth of bone cells into the degrading implant. The powder metallurgical processing route of Mg-alloys enables the generation of such parts, nearly dense inside with an open porous surface structure. Powder blends with different sintering behaviour can be produced via blending pure Mg-powder with different master alloy powders (MAP) as well as powder fractions of varying size [8].

The major requirement for a successful sintering process was found to be the protection of the Mg-green parts from oxygen during the sintering process [8, 9]. The goal of sintering Mg alloys finally aims at the future processing of Mg-alloy powder by MIM (Metal Injection Moulding). This process would permit the near-net-shape manufacturing of small-sized and sophisticated biodegradable implants of specific design with high reproducibility. The process presented in this paper will enable the generation of magnesium alloy parts with ultimate compression strength (UCS) up to 328 MPa and 90 MPa compressive yield strength (CYS).

Experimental

Raw materials and powder blending: Table 1 lists all raw materials and powder blends. As a base material, a spherical commonly available gas atomized pure Mg powder, manufactured by SFM SA (Switzerland) was used (mat.-no. 1). The calcium containing master alloy powder (mat.-no.2) was also gas atomized and spherical, manufactured by ZFW GmbH (Germany).

mat.no.	powder fraction	spec. no.	raw material	blended materials	resulting powder blend
1	d<45µm		Mg	-	-
2	d<90 µm		Mg-7Ca	-	-
1+2	d<***45*** µm	MC/***45***	-	Mg (88 wt %) + Mg-7Ca (12 wt %) →	Mg-0.9Ca
3	-	cast	*Mg-0.9Ca*		

Table 1: List of raw materials and resulting powder blends

All powder handling, pressing and sintering took place under an argon atmosphere in a glove box system (Unilab, MBraun) in order to prevent the powder and green parts from picking up additional oxygen. The powder blending was performed by stirring the raw materials from Tab. 1 in a laboratory mortar for ten minutes. In order to avoid agglomeration, moisture- and oxygen-free C_6H_{12} was used as a milling agent.

Specimen preparation: Cylindrical compression test specimens of 8 mm in diameter and 12 mm in length were produced by double sided, axial pressing at surface pressure of 100 MPa in a manual press (Enerpac RC55, USA). Additional compression test specimens (mat.-no. 3) made of Mg-0.9Ca by investment cast were produced as a reference material.

Processing and sintering: Sintering of all specimens was performed under high purity Argon (Ar 6.0) at atmospheric pressure using a sintering temperature of T_s=630 °C in a hot wall furnace (XRetort, Xerion, Germany). The chosen sintering time was 64 h [8, 9]. After sintering, a solution heat treatment was performed on an extra set of specimens, as well as on the investment cast reference material. The temperature range of the annealing was 515 °C for 16 h, followed by rapid cooling in water. The temperature ranges of sintering and heat treatment (T_S and T_{T4}) are marked in the phase diagrams for Mg-Ca, as shown in Fig. 2.

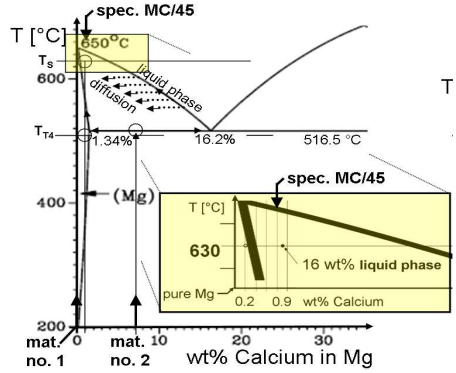

Figure 2: Detail of the phase diagram Mg-Ca [10]

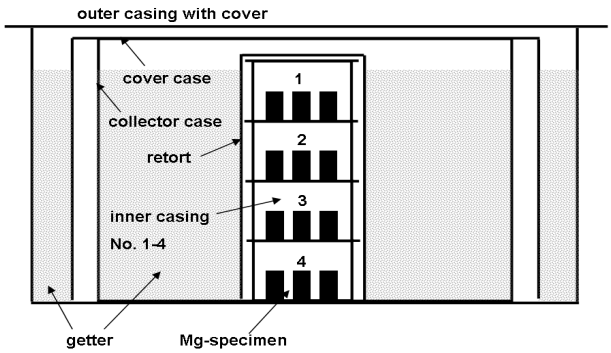

Figure 3: specimen placement and sinter crucible configuration

A liquid Ca-rich phase exists above the eutectic temperature of Mg-Ca (Fig. 2). This mechanism of liquid phase sintering is shown in detail in [9]. At sintering temperature T_s, a small amount of permanent liquid Ca-rich phase remains (see magnificated area of Fig. 2). Figure 2 can be used to demonstrate schematically how diffusion in the binary alloys occurs. By means of the subsequent heat treatment at T_{T4} = 515 °C, complete solution of Ca in Mg should be possible for the chosen alloy compositions.

The annealing box consisted of an outer casing made of molybdenum and inner casing, collector- and cover case made of unalloyed steel. An irregular shaped pure Mg powder (Ecka Granules, Austria) was used as oxygen getter inside the outer casing and the inner collector casing. All specimens were placed inside the inner casing at positions one to four as shown in Figure 3.

Mechanical tests, analysis and characterisation: Light microscopy (Olympus PGM3) and Photoshop software was used to further investigate the porosity. The microstructure and the surface of the powders, greenparts and sinterparts were investigated using SEM and EDX (DSM 962, Zeiss). XRD was used to identify different phases. Compression tests were performed on a Schenck Trebel RM100 universal testing machine (strain rate 0.2 mm/min).

Results and Discussion

Figure 4a shows the microstructure of specimen MC/45 after sintering. The remaining porosity was 3 vol. %. The magnified area of Fig. 4a indicates a bright phase at the boundaries of former powder particles (see arrows). This secondary phase occurred due to the presence of around 16 wt % Ca-rich liquid phase during sintering at 630 °C (see also Fig. 2a, magnificated area). XRD analysis could identify this secondary phase as the brittle intermetallic phase Mg_2Ca (see arrows in Fig. 4a). Although the primary use of calcium was to promote successful sintering, the element also led to solid solution and precipitation strengthening of the material. This was implemented via a subsequent solid solution heat treatment at 515 °C, close to the eutectic temperature. The equilibrium content of 0.9 wt % calcium in the Mg-alloy should be fully in solution into the magnesium matrix after this heat-treatment. Figure 4b shows the microstructure of specimen MC/45 after performing such a heat treatment (+HT).

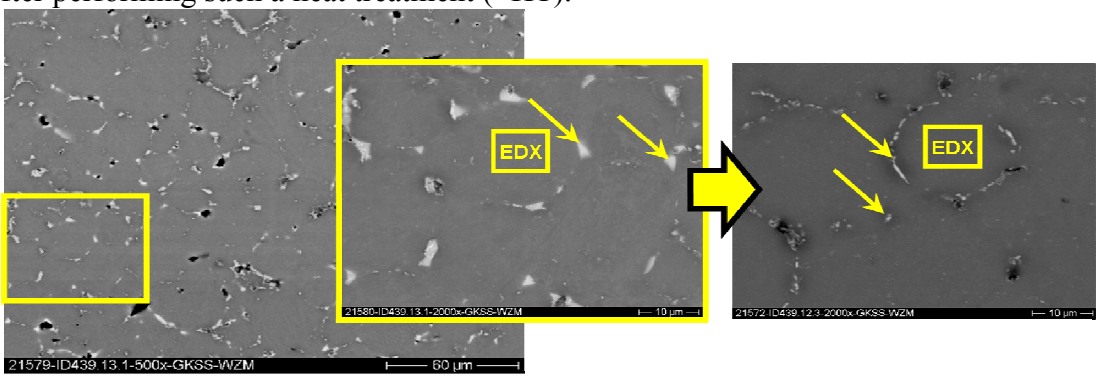

Figure 4a: Mg-0.9Ca (specimen MC/45) as sintered 4b: With subsequent heat treatment

It can be observed that the amount of secondary phase is considerably reduced after the heat treatment. EDX-analyses were performed at the centres of prior Mg-alloy particles (see squares in Fig. 4a and 4b). It was found that the specimen MC/45 (as sintered) had a lower Ca-content (0.15 wt %) in the alpha-matrix than specimen MC/45 (+HT) (0.42 wt %). Additional XRD-analysis on specimen MC/45 (+HT) as shown in figure 4b could not detect Mg_2Ca within the bounds of the limit of detection. Other than Mg, only MgO and CaO could be detected. Further EDX-analysis indicated an increase of oxygen in the secondary phases in comparison to the Mg matrix. This is due to the fact that the Mg raw materials have an oxide layer on its surface. This oxide layer was probably destabilised or reduced by the Ca rich phase during the sintering at 630 °C. The annealing led to a full solution of calcium in the magnesium matrix. Only the stable oxides remain at the boundaries of former particles.

In Fig. 5, the mechanical properties of MC/45 are shown in the as sintered condition in comparison to those of a subsequently heat-treated (+HT) condition. In addition, the mechanical properties of Mg-0.9Ca made by investment casting (+HT) and cortical bone are given. The full solution of calcium in the Mg-matrix of MC/45 (+HT) results in a marked increase of UCS and CYS. The residual porosity could be reduced marginally from 3 vol. % to 2.8 vol. %. The properties of specimens MC/45 (+HT) are similar to those of cortical bone. MC/45 (+HT) has enough stiffness and strength to serve as a bone implant material. The Young's modulus was within a similar range to that of bone.

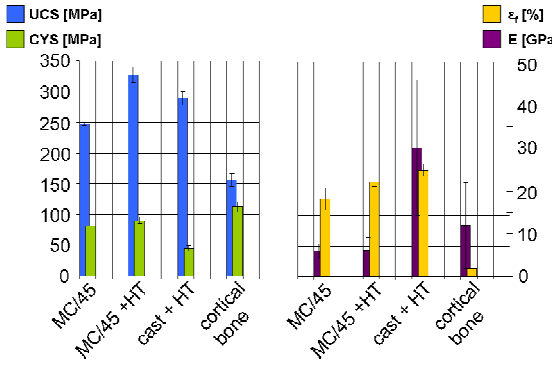

Fig 5: mechanical properties of Mg-0.9Ca (specimen MC/45 with and without heat treatment) in comparison to investment cast (+HT) and cortical bone [2, 6]

Summary

A new Mg-based material that should withstand loads similar to those experienced by bone has been developed by PM-route. By blending elemental and master alloy powders, the manufacturing of nearly dense Mg-alloy parts with material properties matching those of cortical bone was possible. Hence, sintering constitutes a new manufacturing route for the production of Mg-alloy parts and implants, respectively. The reduction of secondary phases in the microstructure by subsequent heat treatment increased the mechanical properties up to 328 MPa UCS and 90 MPa CYS. The exposition of additional tensile tests could not be integrated within the range of this study. A full solution of secondary phases could not be obtained because of stable oxides that remained at the grain boundaries.

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