

## Sintering of Mg and its Alloys under Hydrogen Atmospheres

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### Abstract

Ongoing investigations have highlighted that MIM of Mg shows high potential for mass production of small lightweight components as well as of degradable implants with complex geometry. However, prior research activities have shown that Mg reacts sensitively to atmosphere impurities like oxygen and specific thermal decomposition products of the used backbone polymers. Polyethylene based polymers reveal a negative influence on sintering of Mg while polypropylene based polymers behave uncritically. This work is highlighting that when hydrogen instead of argon atmosphere is used during sintering, the negative influence caused by carbon residuals at the particle boundaries can be prevented. Mg-0.9Ca elongation increased with a slight decrease in UTS revealing a strengthening effect of the carbon residuals at the particle boundaries. For pure Mg UTS could be increased from 7 MPa up to 80 MPa with elongation of 6% showing the positive effect of hydrogen on the sintering of Mg.

### Keywords:

Sintering, light alloys

### Introduction

Magnesium as the lightest of all conventional technical metallic materials has a great potential to be used in a wide range of applications such as automotive, consumer and aerospace [1, 2]. Another promising field for the use of magnesium is the biomedical sector where magnesium can be used as a biodegradable implant material to avoid second surgery for implant removal. Due to its excellent biocompatibility combined with its degradation products being essential elements in the human body magnesium is of high interest as an implant material. The mechanical properties of magnesium, especially the Young's modulus, match the properties of the human bone. This can prevent complications caused by mismatching of implant and bone stiffness (so called stress shielding effect). [3]

Metal injection moulding (MIM) possesses the potential to produce small and complex shaped parts in high quantities. Using AZ81, as an example, it could be shown that it is possible to produce magnesium parts that can compete with the conventional production techniques used for magnesium [4]. However, work is still required to fully understand the influence of all process parameters and for the introduction of a broad range of alloys.

The high affinity to oxygen and its stable oxide layer are the most critical properties of magnesium post sintering. High purity atmospheres and liquid phase sintering can be used to overcome this challenge [4, 5, 6]. When magnesium is introduced into the MIM process, the thermal decomposition of the used backbone polymer is another critical factor. Using polyethylene (PE) based backbone polymers revealed to have a strong sintering inhibiting effect while polypropylene (PP) based polymers do not show this inhibiting effect [7, 8, 9].

### Experimental

#### Sample Production

Three different alloys were produced using different backbone polymers. **Table 1** gives an overview of the powders used. Pure Mg, Mg-10Gd and AZ91 were used as elemental and pre alloyed powder, respectively. Mg-0.9Ca alloy was fabricated by mixing elemental Mg powder and a pre alloyed Ca rich Mg-Ca master alloy powder. Mg-5Gd samples were produced by blending the Mg-10Gd pre alloyed and the elemental Mg powder. **Table 2** gives an overview of the binder components used. Feedstock was produced using a powder loading of 64 vol.%. **Table 3** gives an overview of the processed alloys and backbone polymer compositions. Powder and binder components were weighed and heated in a glove box system with controlled argon atmosphere (Unilab, MBraun, Germany) followed by mixing in a planetary mixer (Thinky ARE-250, Japan). The resulting feedstock was homogenized by extrusion with the plasticizer unit of the injection moulding machine (Arburg Allrounder 320S, Germany) and granulated using a cutting mill (Wanner B08.10f, Germany). Tensile test specimens (dog bone shape, ISO 2740-B) were produced using the same injection moulding machine. After injection moulding the waxy

components were removed by solvent debinding in hexane at 40 °C for 900 min. (Lömi EBA50, Germany). Thermal debinding and sintering was performed using a hot wall furnace (MUT RRO 350-900, Germany). A labyrinth like crucible set up with Mg powder getter material as published in [4] was used. Thermal debinding was performed while heating from 380 °C to 500 °C with a heating rate of 0.5 K/min under vacuum while applying a purge gas flow of 0.8 l/min Ar (if not stated differently). Sintering atmosphere was introduced starting 550 °C. H<sub>2</sub> (purity 5.0) with a constant flow of 0.5 l/min at a pressure between 1200 mbar and 1250 mbar was applied as hydrogen sintering atmosphere. Ar (purity 5.0) was applied as reference atmosphere using the same conditions as with H<sub>2</sub>. A sintering temperature of 638 °C for 64 hours was chosen as a sintering temperature for pure Mg and Mg-0.9Ca while 607 °C for 4 hours was used for sintering of the AZ91 alloy and 632 °C for 4 hours for the Mg-Gd alloys.

**Table 1.** List of used powders.

Powder	Size	composition	Supplier
Mg	<45 µm	99.8 wt.% Mg	SFM SA, Switzerland
MgX5	<45 µm	5.3 wt.% Ca, Mg bal.	Casting: Helmholtz-Zentrum Geesthacht Atomisation: MSE Clausthal, Germany
AZ91	<45 µm	8.5 wt.% Al, 0.55 wt.% Zn, Mg bal.	SFM SA, Switzerland
Mg-10Gd	<65 µm	9.14 wt.% Gd, Mg bal.	Casting: Helmholtz-Zentrum Geesthacht Atomisation: MSE Clausthal, Germany
Mg Getter	Grit 0.06-0.3 mm	98.5 wt.% Mg	Merck KGaA, Germany

**Table 2.** List of used binder components.

Component	Abbreviation	Manufacturer
paraffin wax	PW	Merck
stearic acid	SA	Merck
polyethylene vinyl acetate	PE-EVA	LyondellBasell
polyethylene (low density)	PE	LyondellBasell
polypropylene ethylene copolymer	PPcoPE	Total

**Table 3.** List of processed compositions

Labelling	Powder	Binder System Composition
Mg PE-EVA	Mg	35 wt.% PE-EVA, 60 wt.% PW, 5%SA
Mg PE		35 wt.% PE, 60 wt.% PW, 5%SA
Mg PPcoPE		35 wt.% PPcoPE, 60 wt.% PW, 5%SA
Mg-0.9Ca PE-EVA	Mg+MgX5	35 wt.% PE-EVA, 60 wt.% PW, 5%SA
Mg-0.9Ca PE		35 wt.% PE, 60 wt.% PW, 5%SA
Mg-0.9Ca PPcoPE		35 wt.% PPcoPE, 60 wt.% PW, 5%SA
AZ91 PE	AZ91	35 wt.% PE, 60 wt.% PW, 5%SA
AZ91 PPcoPE		35 wt.% PPcoPE, 60 wt.% PW, 5%SA
Mg-10Gd	Mg-10Gd	35 wt.% PPcoPE, 60 wt.% PW, 5%SA
Mg-5Gd	Mg-10Gd+Mg	

### Material Characterisation

Geometrical data assessment was performed using a calliper (Mahr 16EX, Germany). Shrinkage  $S$  was calculated according to **Eq. 1** with  $L_g$  being the green length and  $L_s$  the sintered length. The tensile tests of dog bone-shaped test specimens took place on a universal materials testing machine (Schenck Trebel RM100, Germany) according to DIN EN ISO 6892-1:2009 B.

$$S = (L_s - L_g) / L_g \quad \text{Eq. 1}$$

The total carbon content of the samples was measured external (HuK Umweltlabor GmbH) using a Leco CS200 (LECO Instruments GmbH, Germany). Three measurements were performed on each sample by analysing around 500 mg sample weight per measurement. Analyses were performed according to DIN EN ISO 15350.

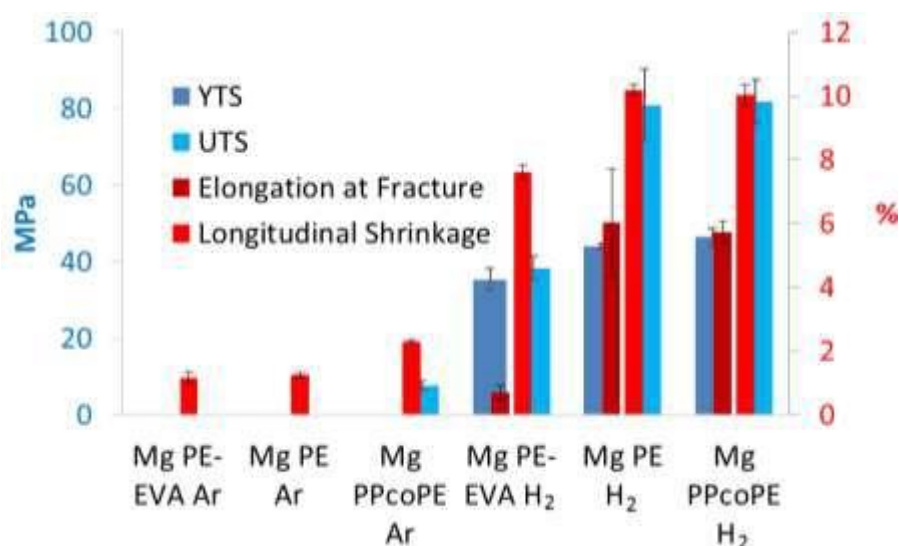
### Results and Discussion

**Figure 1** displays the mechanical properties of pure Mg processed with different backbone polymers sintered under Ar and H<sub>2</sub>. When comparing the samples sintered under Ar it is obvious that the samples processed with the PPcoPE show the highest longitudinal shrinkage revealing that this polymer has the

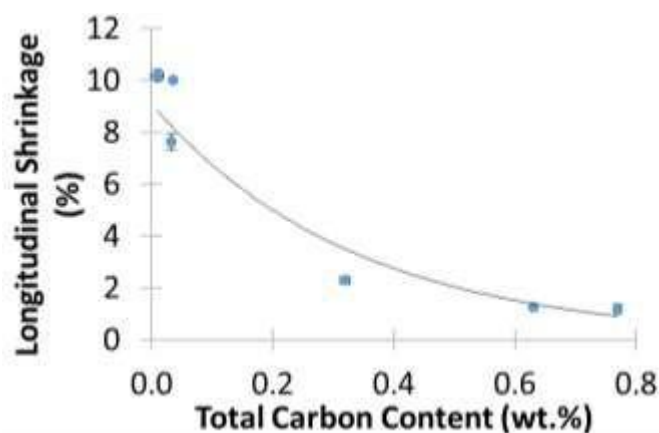
lowest sintering inhibiting effect. The PPcoPE samples were the only ones of the samples sintered under Ar that had strength high enough to handle and measure the samples without premature breaking of the samples. However, even then the ultimate tensile strength (UTS) of only 20 MPa is very low. When H<sub>2</sub> is used as sintering atmosphere the shrinkage as well as the mechanical properties increase drastically. Both, shrinkage and mechanical properties of the samples processed with PPcoPE and PE are comparable. This indicates that the negative influence of PE based polymers on the sintering of Mg is not apparent when H<sub>2</sub> is used instead of Ar. The lower shrinkage and mechanical properties of the PE-EVA samples are caused by the fact that these samples formed blisters during the thermal debinding because the debinding was not optimised for this backbone polymer.

**Figure 2** shows the longitudinal shrinkage of the pure Mg samples displayed over their total carbon content. The samples can be divided in two groups: one group with low shrinkage and high carbon content and one with low carbon content and high shrinkage. The low carbon content group was sintered using H<sub>2</sub> while the high carbon content group contains the samples sintered under Ar. A relation between total carbon content and longitudinal shrinkage can be observed. A higher carbon content results in lower shrinkage. These results show that the sintering inhibiting effect is caused by carbon residuals from the backbone polymer. Moreover, it can be stated that the carbon residuals from the thermal debinding of the backbone polymer can be removed when H<sub>2</sub> is used as sintering atmosphere.

It is assumed that during sintering the removal of carbon is taking place by hydrogenation forming methane according to the equilibrium reaction **Eq. 2** [10]. The hydrogenation of carbon during the sintering of FeCuC components at around 600 °C was also reported by Quadbeck *et al.* [11].



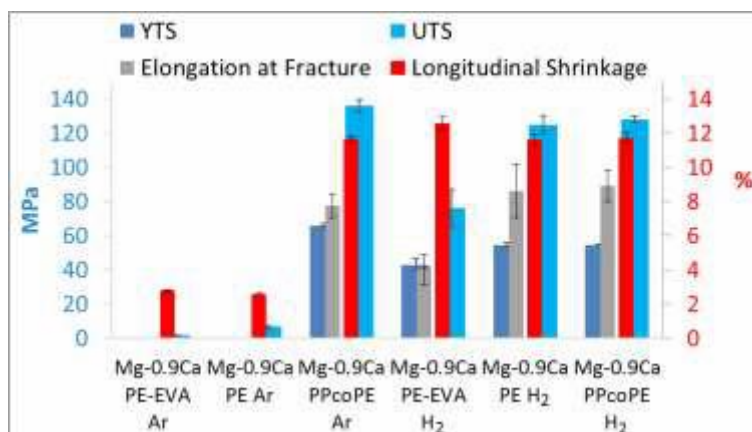
**Figure 1.** Mechanical properties and longitudinal shrinkage of pure Mg samples processed using different backbone polymers sintered under Ar or H<sub>2</sub>.



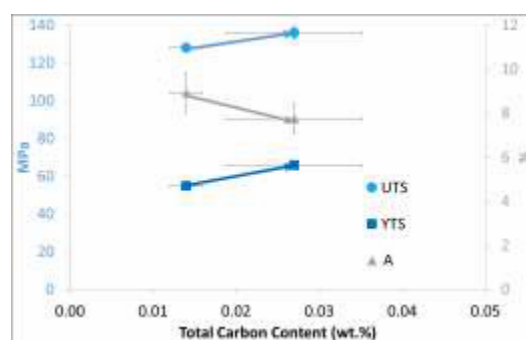
**Figure 2.** Longitudinal shrinkage VS total carbon content of pure Mg samples processed with different backbone polymers sintered under Ar and H<sub>2</sub> atmosphere.

**Figure 3** displays the longitudinal shrinkage and the mechanical properties of the Mg-0.9Ca samples processed using different backbone polymers. It seems when compared to the pure Mg results shown

in **Figure 1** that Mg-0.9Ca is less sensitive to the residuals of the backbone polymers. However, also with Mg-0.9Ca it is apparent that PE based polymers have a strong negative influence on the sintering results. When sintered under H<sub>2</sub> the mechanical properties as well as the longitudinal shrinkage of all sample sets are comparable. Using PPcoPE as a backbone polymer reveals comparable results as when sintered under H<sub>2</sub> showing that this polymer is suitable to be used as a backbone polymer. When comparing the mechanical results of the PPcoPE samples sintered under Ar and H<sub>2</sub> together with their total carbon contents a strengthening effect can be assumed as shown in **Figure 4**. The lower carbon content corresponds to the samples sintered under H<sub>2</sub>. It can be seen that yield strength (YTS) as well as the UTS increase with a slight increase of the carbon content while the elongation at fracture decrease. This leads to the assumption that carbon residuals at the former powder particle boundaries acting as slip barriers lead to a strengthening effect. Magnesium does not have solubility for carbon and does not form stable carbides [12, 13, 14, 15]. Hence, carbon residuals will remain at the former particle boundaries acting as precipitates that can enhance the strength.



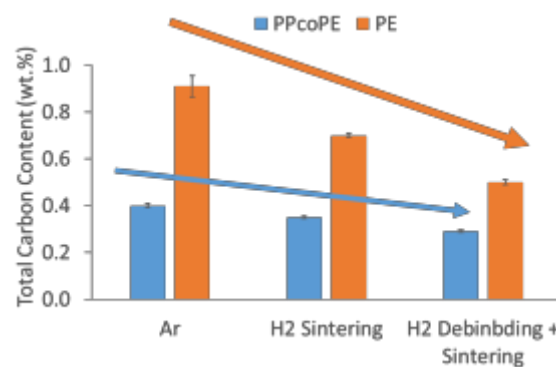
**Figure 3.** Mechanical properties and longitudinal shrinkage of Mg-0.9Ca samples processed with different backbone polymers sintered under Ar and H<sub>2</sub>.



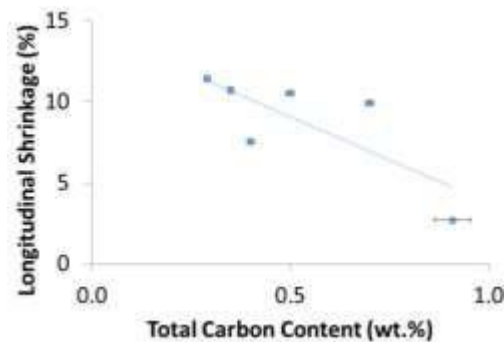
**Figure 4.** Mechanical Properties of Mg-0.9Ca with different total carbon content produced by sintering under Ar or H<sub>2</sub> atmosphere.

**Figure 5** displays the total carbon content of AZ91 samples processed with PE as well as with PPcoPE backbone polymer sintered under Ar and H<sub>2</sub>. An additional set of samples was also treated with H<sub>2</sub> instead of Ar during the thermal debinding step. It can be seen that the total carbon content of PPcoPE samples is in all cases lower compared to the PE samples. When PE is used as backbone polymer the carbon content can be significantly reduced when H<sub>2</sub> is used as sintering atmosphere. Using H<sub>2</sub> during the thermal debinding step can further reduce the carbon content. PPcoPE processed samples already have a low carbon content when sintered under Ar. Sintering these samples under H<sub>2</sub> can further decrease the carbon content.

**Figure 6** displays the total carbon content of the AZ91 samples in correlation with their longitudinal shrinkage. A linear correlation between shrinkage and carbon content can be assumed. The higher the total carbon the lower is the sintering activity displayed as longitudinal shrinkage.

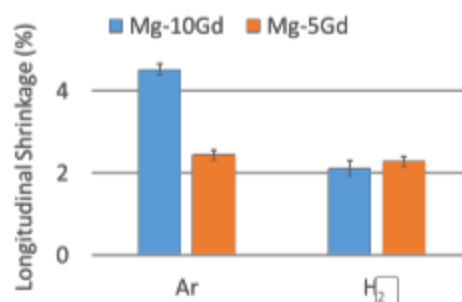


**Figure 5.** Total carbon content of AZ91 PPcoPE and PE processed samples sintered Ar (thermal debinding with Ar), sintered under H<sub>2</sub> (thermal debinding with Ar) and sintered under H<sub>2</sub> (thermal debinding with H<sub>2</sub>).



**Figure 6.** Longitudinal Shrinkage VS total carbon content of AZ91 samples processed with PE as well as PPcoPE backbone polymer sintered under Ar as well as H<sub>2</sub> atmosphere.

**Figure 7** displays the longitudinal shrinkage of Mg-10Gd and Mg5-Gd sintered under Ar and H<sub>2</sub>. It can be seen that the shrinkage of the Mg-10Gd samples decreased significantly when sintered under H<sub>2</sub>. For Mg-5Gd the decrease is smaller. This shows that sintering under H<sub>2</sub> atmosphere cannot be used for all alloys. Gd and other rare earth elements are reported to form hydrides when used as alloying elements in Mg [16]. Therefore, it can be concluded that alloy systems that contain hydride-forming elements might not be suitable to be sintered using H<sub>2</sub> atmospheres. A further understanding of the hydration process and a possible dehydration might help to improve the sintering of these alloys using H<sub>2</sub> atmospheres.



**Figure 7.** Longitudinal shrinkage of Mg-10Gd and Mg-5Gd samples sintered using Ar and H<sub>2</sub> atmosphere.

### Conclusions and Outlook

It could be proven that H<sub>2</sub> has a positive effect on the sintering results of Mg. It is shown that PE based polymers have a strong sintering inhibiting effect when compared to PP based polymers sintered under Ar atmosphere. Furthermore, it could be shown that for pure Mg as well as for Mg-0.9Ca sintering under H<sub>2</sub> atmosphere has a positive effect on the sintering results when compared to Ar sintering atmosphere. This effect could be attributed back to a removal of carbon residuals of the thermal decomposition of the backbone polymer. Using this effect even samples processed with PE backbone polymers resulted in sufficient sintering activity and mechanical properties showing that the sintering inhibiting effect of the PE thermal decomposition products can be reversed when H<sub>2</sub> is used as sintering atmosphere. Furthermore, a strengthening effect of carbon residuals is assumed for Mg-0.9Ca samples processed with a PP based backbone polymer.

However, sintering under H<sub>2</sub> atmospheres seems not to be possible for all Mg alloys as it could be shown for Mg-Gd alloys which are reported to form hydrides.

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