OPTIMIZATION OF SINTERING CONDITIONS FOR THE PREPARATION OF POROUS MAGNESIUM

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Abstract

In this paper we focused on the influence of sintering conditions; purity of argon atmosphere and sintering time namely, on microstructural and mechanical characteristics of porous magnesium prepared by powder metallurgy. An argon with technical purity (99.996 vol.%) and argon purified by a magnesium getter were used as the sintering atmospheres. The samples were sintered for different times (0, 3, 6, 12 and 24 h). Subsequently, microstructure, flexural and compressive behaviour were investigated in detail. The type of used atmosphere had no significant influence on the studied characteristics after sintering up to 6 h and the mechanical properties increased with longer sintering time. On the other hand, after sintering longer than 6 h, mechanical properties of the samples sintered under the purified atmosphere increased with longer sintering time, while the use of technical argon decreased mechanical properties significantly and slightly increased porosity. It was caused by oxidation, which took place after longer sintering times under the argon atmosphere with technical purity.

Keywords: Porous magnesium, powder metallurgy, sintering conditions, scaffolds

1.   INTRODUCTION

Magnesium based materials are used in many branches, such as aerospace, aircraft and automotive industry [1]; moreover, some of them are considered as suitable materials for the fabrication of biodegradable implants [2]. The demand for magnesium-based materials is large because of their low densities and appropriate mechanical properties [1]. For some construction applications (e. g. shock absorbers, mufflers, catalyst supports) open-cellular porous structures are demanded [3]. Recently, such porous materials have been investigated for the use in orthopaedics as load-bearing implants, called scaffolds. Due to its biocompatibility and biodegradability magnesium based materials seem to be very promising candidates for the fabrication of temporary scaffolds. Although many methods for the fabrication of open-cellular metallic materials are available, only a few of them are suitable for magnesium because of its high reactivity and low melting point. For example, commonly used methods, such as plaster casting and negative salt pattern molding, may lead to a contamination of the products, which is undesirable, especially for biomaterials. On the other hand, the melting methods, such as injection of an inert gas into the melt and "GASAR" process do not necessarily lead to an interconnected porous structure [4]. From these reasons, powder metallurgy using space-holder particles seems to be very suitable for fabricating of porous structures for implantology. This method consists in the preparation of a mixture containing a metallic powder and particles of a space-holder material. The mixture is compacted and subsequently the space-holder material is removed by leaching, or thermal decomposition. Thermal decomposition of space-holder particles have been preferred in a majority of available literature [4,5]. The leaching of space-holder particles may lead to a larger contamination because some particles can be hermetically enclosed and the leaching medium can react with the metal [4]. Urea and ammonium bicarbonate have been successfully used as the space-holder material for the preparation of porous magnesium. In our opinion, ammonium bicarbonate is more suitable because its decomposition takes place at temperatures up to 60 °C, while total decomposition of urea takes place at temperatures higher than melting point of magnesium [4]. It is probably the reason that contamination by carbon was observed by Zhuang et. al. when urea was used as space-holder material [5]. Despite the fact that many studies on preparation of porous magnesium by

powder metallurgy were performed and the influence of preparation conditions, such as compacting pressure, spacer amount of used and sintering temperature, on material properties was investigated [4,5,6], no systematic study on the influence of sintering time and atmosphere in not known to the best of our knowledge. Therefore we investigated the influence of these parameters on structural and mechanical characteristics of porous magnesium prepared by powder metallurgy using ammonium bicarbonate as a space-holder material.

2.   EXPERIMENTAL

A purchased Mg powder (purity of 99.6 wt. %, mesh -100+200, Alfa Aesar) and NH_4HCO_3 powder (p.a. purity, 250-500 μm) were used as starting materials. The powders were manually blended into mixtures containing 10 vol.% of NH_4HCO_3, which was used as the space-holder. Hexane was added during blending to make a dough-like mixture. This was performed for better homogenization and to avoid segregation. Subsequently, pre-weighed mixtures were pressed into cylindrical green compacts (10 mm in diameter and 30 mm in length) at a pressure of 265 MPa using a LabTest 5.250SP1-VM universal loading machine. The green compacts were then subjected to a two-step procedure. First, the compacts were annealed for 4 h at 130 °C in a muffle furnace in air. During this step, the decomposition of ammonium bicarbonate and the evaporation of hexane occurred. Afterwards, sintering was performed at 550 °C in a tube furnace. The green compacts were sintered for 0, 3, 6, 12 and 24 h. The sintering process was performed under two types of flowing atmosphere at a flow rate of 0.1 l/min: 1. argon with technical purity (99.996 vol. %) and 2. argon purified by a 55-mm-thick layer of Mg chips (250-500 μm in size), which was placed around the sintered material and acted as a getter. After sintering, the average material porosity was determined from sample densities. The material mechanical properties were characterized by flexural and compression tests performed at room temperature. Samples 26 mm and 15 mm in length were used for flexural and compression testing, respectively. Five samples of each series were used for the flexural tests, and three samples of each series were used for the compression tests. The deformation rates during the flexural and compression tests were 0.5 mm·min^{-1} and 1 mm·min^{-1}, respectively. A LabTest 5.250SP1-VM universal loading machine was used for these tests. After flexural testing, the fracture surfaces were observed by a TESCAN VEGA-3 LMU scanning electron microscope (SEM). Metallographic cross-sections were also prepared and examined by SEM. Afterwards, the metallographic cross-sections were etched (2 g of picric acid, 10 ml of 99% acetic acid, 10 ml of water and 70 ml of ethanol) and the microstructures of the powder particles were observed using an Olympus PME 3 light metallographic microscope. The phase composition and elemental distributions were examined by X-ray diffraction using a PANalytical X´Pert PRO X-ray diffractometer equipped with a Cu anode (XRD) and a TESCAN VEGA-3 LMU SEM equipped with an Oxford Instruments INCA 350 EDX analyzer (SEM-EDX).

3.   RESULTS AND DISCUSSIONS

3.1   Microstructure and porosity

Fig. 1 shows microstructures of selected samples. There can be observed that two types of pores occurred in the microstructures of prepared samples. The "Type I" pores formed by the decomposition of space-holder and they copied the shape and size of the used particles of ammonium bicarbonate. The small "Type II" pores originated from imperfect compaction and expansion of enclosed gasses. If we compare samples sintered for 6 and 24 h, we can see in **Fig. 1** that the amount of the small "Type II" pores decreased after 24 h of sintering under the gettered atmosphere, while their amount was almost the same, or slightly higher after sintering for the same period under the unpurified atmosphere. This observation was confirmed by the measurements of sample densities and subsequent calculation of their porosities, which results are listed in **Table 1**.
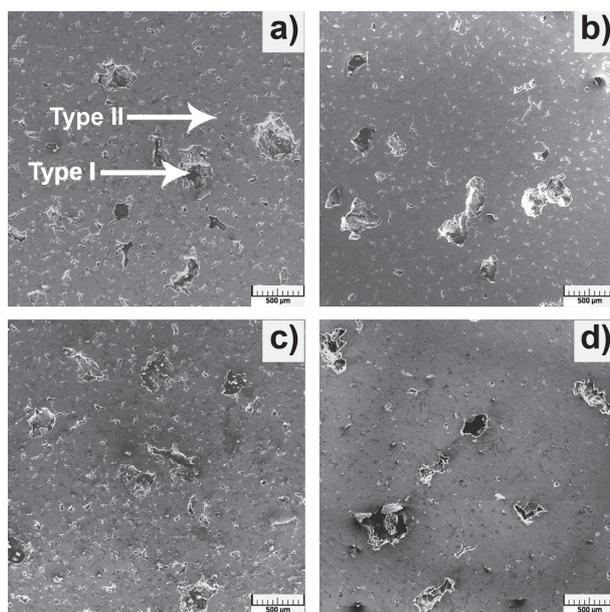
Fig. 1 SEM micrographs (SE detector) of sample cross-sections prepared under the following sintering conditions: a) technical argon for 6 h, b) technical argon for 24 h, c) gettered argon for 6 h and d) gettered argon for 24 h

Table 1 Porosities of the prepared samples

Atmosphere/sintering time	0 h	3 h	6 h	12 h	24 h
Technical argon	29 ± 2	28 ± 1	28 ± 2	29 ± 3	31 ± 4
Gettered argon	29 ± 2	28 ± 1	27 ± 2	25 ± 3	24 ± 2

All samples were prepared from the mixtures with the same composition; although, their porosities slightly differed. Whereas the porosities were approximately the same after sintering up to 6 h independently on the atmosphere, after longer sintering times the porosity decreased with a prolonged sintering under the purified atmosphere and increased under the argon with technical purity. As will be shown later, the increase of porosity under the technical argon was caused by an extended oxidation, while under the gettered atmosphere the oxidation was limited and consequently the small "Type II" pores partially annihilated due to diffusion processes, which were enhanced under the gettered atmosphere. The oxides could also fall off which increased the measured porosity.

XRD patterns shown in **Fig. 2** proved that an extended oxidation took place under the unpurified atmosphere after sintering longer than 6 h, while the oxidation was suppressed under the gettered argon atmosphere. These results were also confirmed by EDX measurement (shown in **Fig. 3**), which proved that the oxidation took place only at the surfaces of magnesium particles. The oxide layers after sintering longer than 6 h were significantly thicker in the case of samples sintered under the unpurified argon atmosphere.
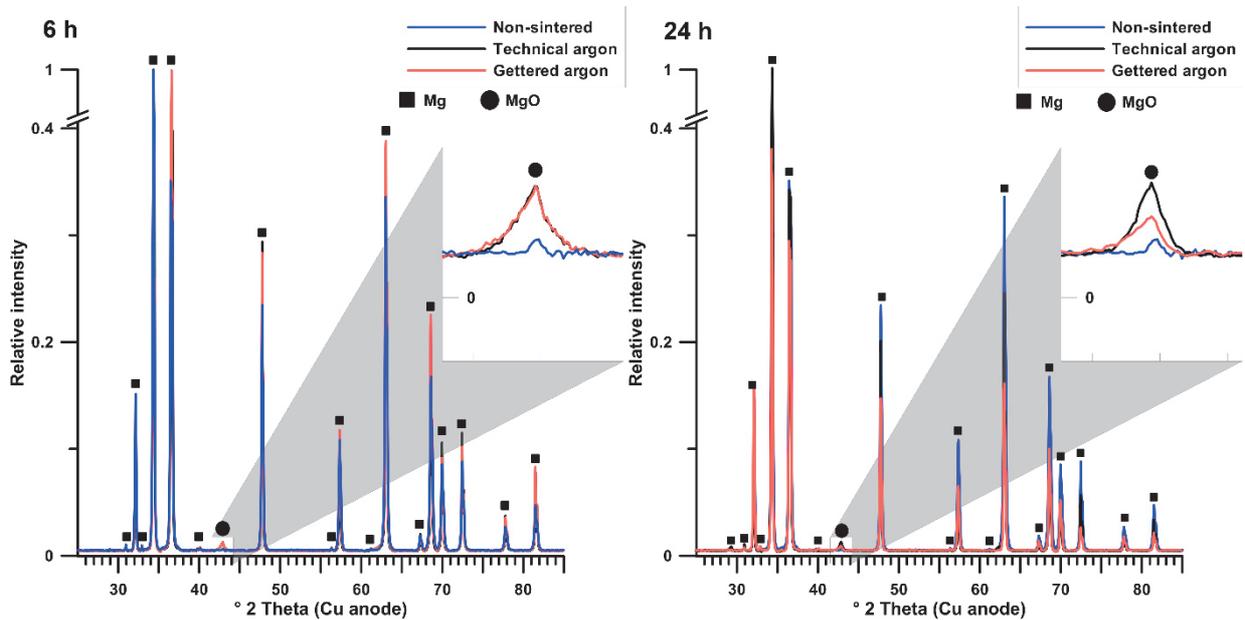
Fig.2 XRD patterns of the non-sintered sample and samples sintered 6 h (left) and 24 h (right)

We also investigated grain coarsening during sintering. We found out that the starting magnesium powder contained grains with a diameter of approximately 13 µm. The grain size slightly increased to approximately 15 µm after compaction and the first step of heat treatment (130 °C, 4 h). Whereas a significant grain coarsening was observed after 3 h of sintering when the grain size was approximately 45 µm, longer sintering times did not lead to any significant grain growth and a grain size of approximately 48 µm was observed after 24 h of sintering. No influence of atmosphere type on grain coarsening was observed.
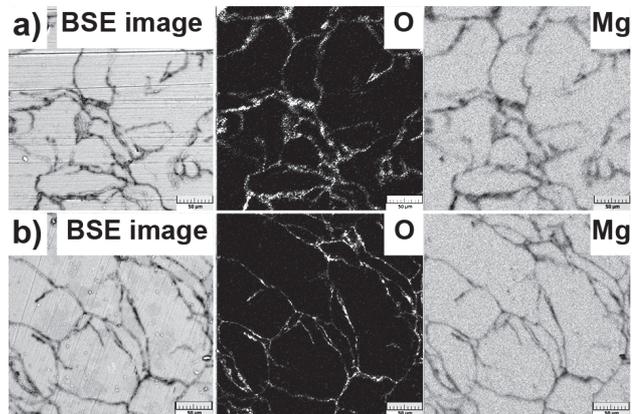

Fig. 3 X-ray elemental distribution of the sample sintered 24 h under the unpurified argon (a) and gettered (b) atmosphere

3.2 Mechanical properties

Fig. 4 shows selected stress-strain curves obtained by the flexural and compressive tests. Values of important mechanical characteristics obtained from these curves are listed in **Table 2**.
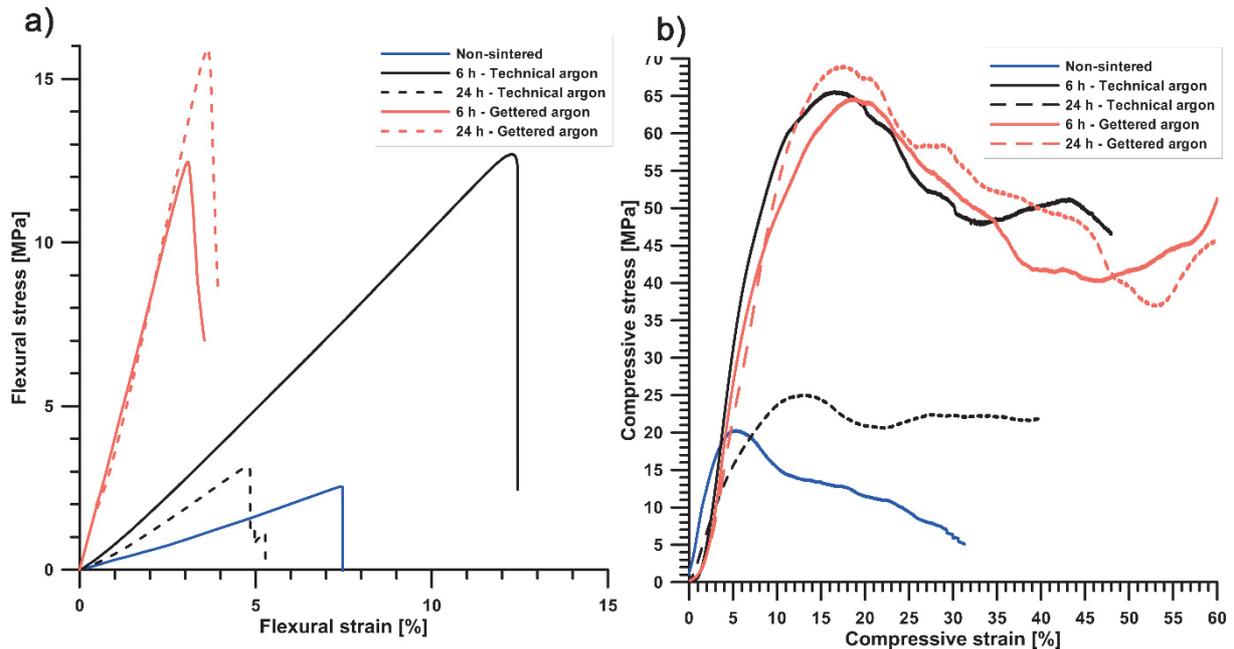
Fig. 4 Flexural (a) and compressive (b) stress-strain curves of selected samples

There is obvious in **Fig. 4a** that flexural behavior was strongly influenced by the type of atmosphere. Samples sintered under the gettered atmosphere possessed higher modulus of elasticity then those prepared under the unpurified argon. Sintering time played an important role on flexural strength, while the influence of sintering time on modulus of elasticity was not so strong in comparison with the influence of sintering atmosphere. Whereas samples sintered under the unpurified atmosphere reached their maximum ultimate flexural strength (UFS) after 6 h of sintering and their UFS decreased after longer sintering due to the oxidation; UFS increased with longer sintering under the gettered atmosphere. Compressive behavior (**Fig. 4b**) trended similar like the flexural one; however, modulus of elasticity was approximately the same for all samples independently on sintering conditions. All data obtained by the compressive test (compressive yield strength-CYS and ultimate compressive strength-UCS) are listed in **Table 2**.

Table 2 Mechanical properties of the prepared samples

	Sintering time/ Atmosphere	0 h	3 h	6 h	12 h	24 h
UFS	Purified	3.2	9.0	12.4	15.1	15.4
[MPa]	Unpurified	3.2	5.0	12.7	5.1	3.4
CYS	Purified	14.1	28.2	32.5	40.1	53.4
[MPa]	Unpurified	14.1	23.7	38.9	33.0	12.8
UCS	Purified	20.3	51.1	64.7	66.8	69.0
[MPa]	Unpurified	20.3	32.0	65.6	57.1	25.0

Because the grain size of all sintered samples was approximately the same, we can suppose that the differences in mechanical behavior were only caused by the diffusion connection of particular magnesium particles. Therefore, we investigated fracture surfaces after the flexural tests. As can be seen in **Fig. 5** showing fracture surfaces of selected samples, traces of plastic deformation were observed on fracture surfaces of samples sintered 24 h under the gettered atmosphere. On the other hand, we observed oxides on fracture surfaces after the same sintering time under the unpurified atmosphere. After 6 h of sintering the fracture surfaces were very similar independently on the sintering atmosphere.
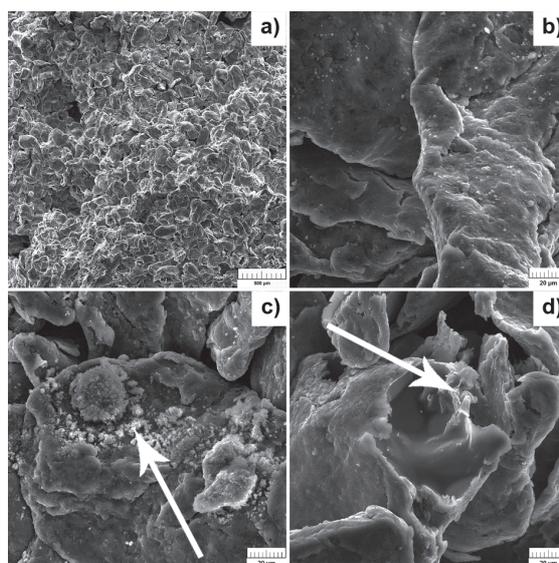
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Fig. 5 Fracture surfaces of samples after flexural testing under the following sintering conditions: technical argon for 6 h - overview (a), technical argon for 6 h - detail (b), technical argon for 24 h (c) and purified argon for 24 h (d). The white arrow in **Fig. 8**c denotes oxide particles. In **Fig. 8**d, the arrow indicates traces of plastic deformation

CONCLUSIONS

In this work we successfully prepared magnesium samples with average porosities 24-31 vol.% depending on sintering conditions. The samples exhibited enhanced mechanical properties in comparison with non-metallic porous biomaterials used in implantology; moreover, their mechanical properties were similar to those of human cancelous bone. Prolongation of the sintering time under the purified argon atmosphere leads to a larger annihilation of pores originated from imperfect compaction and enhances mechanical properties. Sintering under the unpurified atmosphere longer than 6 h, on the other hand, causes an extended oxidation on particle surfaces and deteriorates mechanical properties as a consequence. Our research also showed that purifying of the argon atmosphere is necessary to avoid oxidation and enhance mechanical properties when sintering time exceeds 6 h.

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