

## Sintering of Aluminium and Magnesium Alloy Fiber Structures

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### Abstract

Due to their oxygen affinity, magnesium and aluminium alloys are difficult-to-sinter materials. Either mechanical destruction or the action of a liquid phase can be used to break up oxide layers and thus achieve the desired diffusion bonds between the individual particles. In the present work, a liquid phase sintering approach is used in conjunction with high-purity particulates and controlled processing conditions in order to achieve a porous sintered product. Appropriate sinter conditions were determined with the help of thermodynamic calculations using the PANDAT software package. As no organic or other auxiliary substances are required, it is possible to obtain high-purity, high-porosity (up to 90 %) parts with exclusively open porosity. Such parts may find application as degradable implants or, in the case of aluminium, as heat exchangers in phase change heat storage or adsorption cooling devices.

### Introduction

Extensive work has been carried out on sintered metal fiber structures at IFAM Dresden. Short metal fibers are made in an in-house manufacturing process by rapid solidification directly from the melt (crucible melt extraction). This allows for almost unlimited materials compositions and clean metallic surfaces without oxides or organic impurities which are frequently found in fibers made by mechanical manufacturing processes such as turning, shaving, or drawing. After manufacturing of the fibers, they are usually dry deposited and sintered to yield highly porous structures. More processing details can be found elsewhere [1, 2].

Due to the oxygen affinity of aluminium and magnesium alloys, it is nearly impossible to sinter the single fibers in the solid state. The presence of a liquid phase, however, locally destroys oxide layers and thus produces initial bridges in the fiber-to-fiber contacts, and also enhances the diffusion during sintering. Good results can be expected for amounts of approximately 20 vol-% of liquid phase [3]. Appropriate conditions for the heat treatment both with regard to the liquid phase content and phase formation can be theoretically determined prior to the experiments with the help of thermodynamic software. This approach is especially useful for systems with more than two elements, where phase diagrams are not readily available. Without the use of thermodynamic calculations, the time and effort required for the experimental work can become quite considerable.

This approach has been demonstrated successfully for the sintering of aluminium based fibers. The amount of liquid phase at a certain temperature was calculated for the system aluminium-copper-zinc and fibers of a suitable composition were made by melt extraction. Sintering was carried out successfully under the calculated conditions [3]. In subsequent work, the Zn was removed from the composition for corrosion reasons and AlCu5 fiber structures were produced for the manufacturing of heat exchangers for prototype adsorption cooling devices. Figure 1 shows such a demonstrator where 250 mm long strips of sintered Al fibers were brazed onto rectangular Al ducts.

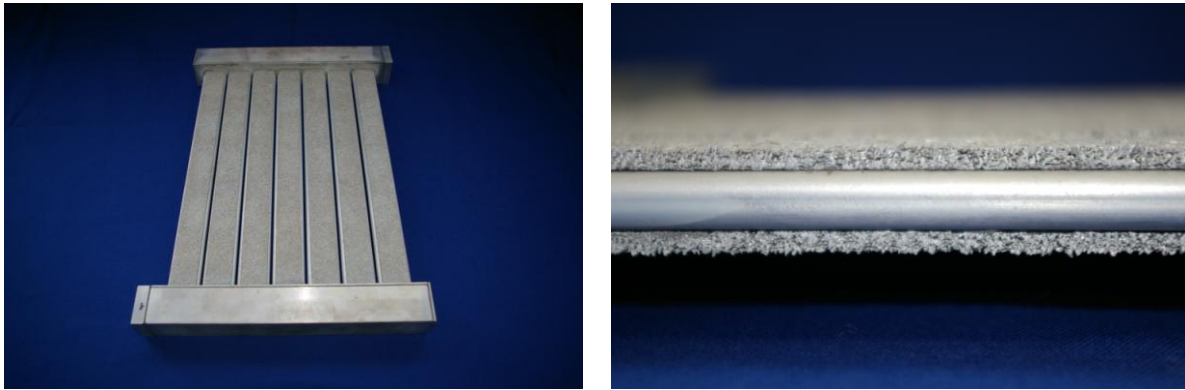


Figure 1: Heat exchanger for adsorption cooling device made from sintered AlCu5 fibre structures brazed onto aluminium ducts (Fraunhofer ISE and IFAM).

### Determination of alloy composition and sintering conditions for Mg based systems

Magnesium has a long history with regard to its use as degradable implant material [4]. However, the manufacturing routes for porous implants employed so far showed several shortcomings, the most important being a limited amount of porosity and residues of space holder materials. Sintered fiber structures made from very pure Mg alloy fibers may overcome such limitations as they do not use any space holders and can be manufactured in a wide range of porosities. The alloy compositions were chosen because of their biocompatibility and adjustable corrosivity. The use of Mg alloys as implant requires a good understanding of the sintering conditions in order to produce good bonds between the single fibers for obtaining rigid, mechanically stable structures. The System Mg-Y-Ca is a good candidate for this purpose because a broad range of liquid phases forms in the Mg rich corner of the two binary phases Mg-Y and Mg-Ca. As the intermetallic phases are known to be prone to heavy corrosion in biological surroundings, the degradation rate should be tailored by adjusting the amount of intermetallic phase as well as its grain size and distribution by applying a suitable heat treatment procedure after sintering. The required experimental effort to find optimum solutions for these tasks can be considerably reduced by performing thermodynamic calculations before actually carrying out any experiments. For this purpose, the software package PANDAT 8.1 in conjunction with the PANDAT Mg database was used [5, 6].

Selected results of the calculations are shown in the partial phase diagram in Figure 2 for a constant yttrium content of 2.6 wt-% and increasing calcium content. The composition was chosen because calcium is widely used in this composition range [7, 8] and it can be used as a representative example for the use of the approach of liquid phase sintering for these systems. Above a calcium content of about 0.6 wt-%, the phase diagram shows no significant changes, which is also visible in the partial ternary phase diagram in Figure 3. Solidification calculations were carried out for the composition MgY<sub>2.6</sub>Ca<sub>1.6</sub> and for comparison also with MgY<sub>2.6</sub>Ca<sub>0.6</sub>, with the compositions and temperatures at the tie lines also being noted in Figure 2. The calculated phase fractions between 400 and 700 °C for this composition are shown in Figure 4 in more detail. With decreasing temperature, the fraction of liquid phase decreases whilst Mg precipitates as primary phase. At 514 °C, additional Mg<sub>2</sub>Ca appears by way of an eutectic reaction. With regard to the subsequent experiments, the amount of solid phase can be estimated to reach about 2 wt-% Mg<sub>2</sub>Ca at a temperature of 514 °C. This amount can be adjusted by a homogenisation heat treatment at lower temperatures, which can also be deduced from the phase diagram in Figure 2.

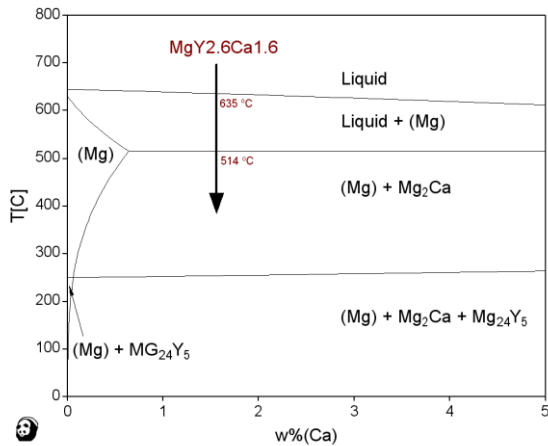


Figure 2: Calculated partial Mg-Y-Ca phase diagram for a constant yttrium content of 2.6 wt-%.

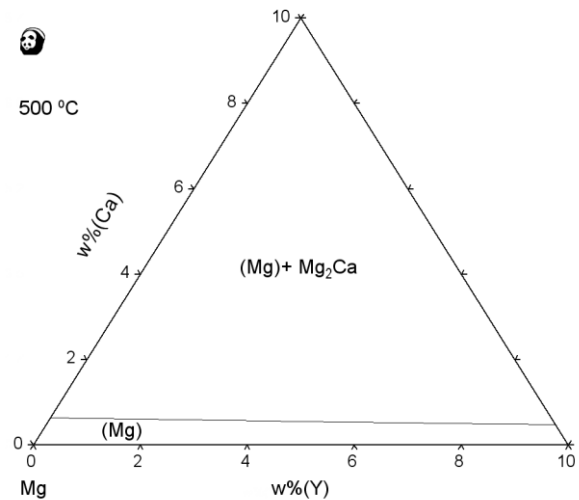


Figure 3: Calculated partial phase diagram of the Mg corner of the Mg-Y-Ca system at 500 °C. Only the phases (Mg) and  $Mg_2Ca$  are present in this area at 500 °C.

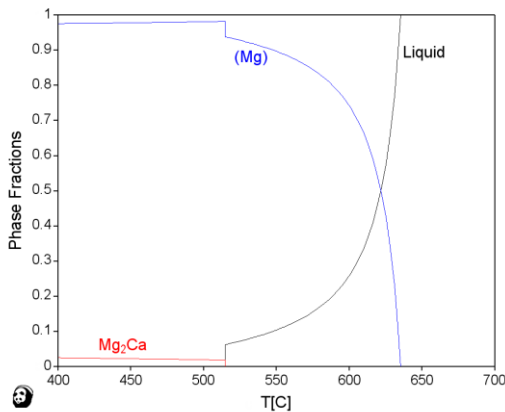


Figure 4: Calculated phase fraction of the composition  $MgY_{2.6}Ca_{1.6}$  between 400 and 700 °C. The solid phase fractions below complete solidification show only little variation.

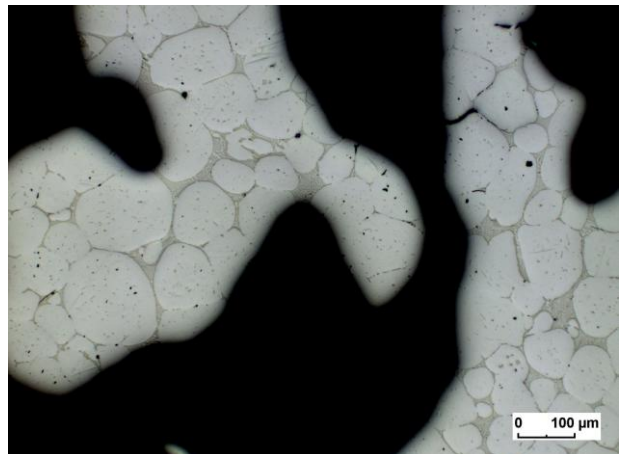


Figure 5: Optical micrograph of a solidified  $MgY_{2.6}Ca_{1.6}$  fiber structure. The liquid phase sintering leads to excellent fiber bonds.

In Figure 5, a cross section of the sintered fiber structure of  $MgY_{2.6}Ca_{1.6}$  shows the consistency of the calculation with the real system. The predicted primary precipitation of Mg and the eutectic microstructure of Mg and  $Mg_2Ca$  are clearly visible.

Due to the rapid cooling during fiber manufacturing, it can be assumed that real solidification from the liquid phase differs from the calculations in Figure 2 to 3 due to the fact that in rapid cooling the diffusion in solid state is blocked. This is taken into account by solidification calculations with blocked diffusion (Scheil model). It is expected, that due to the relative short heating time up to the sintering temperature, the microstructure will almost completely remain in the metastable state and will not change to the stable phases, because of the relative slow diffusion in the solid state. Therefore it is assumed, that the amount of liquid phase is close to the values of the calculation with blocked diffusion. The results for the two compositions under consideration show significant differences with respect to the

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calculated solidification temperatures and should yield a better representation of the actual sintering conditions (Table 1).

Composition	Solidification		Liquid Fraction		Phase Fraction Mg after solidification [%]
	Model	Start [°C]	0.2 [°C]	0.15 [°C]	Mg [%]
MgY2.6Ca1.6	Scheil	635	577	550	97
MgY2.6Ca1.6	Equilibr.	635	588	572	98
MgY2.6Ca0.6	Scheil	641	Eutectic reaction at 41 % liquid phase		98
MgY2.6Ca0.6	Equilibr.	641	553	546	100

The results show clearly that the phase fractions are strongly dependent of the heat treatment and the composition. The calculations of table 1 show also, that a calcium content greater than 0.6 wt-% is necessary, because the large amount of liquid phase of 41 % at 0.6 wt% calcium would causes the sample losing its shape. For the fiber structure manufacturing, sintering temperatures were thus chosen to be in the range of 570 to 590 °C in order to obtain the desired amount of liquid phase. DTA measurements of fibers of the composition MgY2.6Ca1.6 verified the calculated melting point of 635 °C.

### Sample manufacturing and characterization

Melt extraction was used to produce short MgY4 and MgY2.6Ca1.6 fibers with a mean equivalent circular diameter of 220 µm and a mean length of 7.3 mm. A typical cross section of a MgY2.6Ca1.6 fiber is shown in Figure 6. The fibers were deposited homogenously onto an inert substrate and subjected to heat treatment at the calculated sintering temperatures. The heating was performed with 10 K/min, while the cooling was done with 2 K/min. The heat treatment was performed in a quartz tube furnace in pure Argon. The overall porosity of the MgY4 and MgY2.6Ca1.6 fiber structures after sintering measured by weighing and taking the geometric dimensions amounted to 61 to 70 %. A sintered MgY4 fiber structure is shown in Figure 7.



Figure 6: Etched micrograph of a cross section of a MgY2.6Ca1.6 fiber with a mean equivalent circular cross section diameter of 220 µm. The solidification started on the lower side of the fiber.

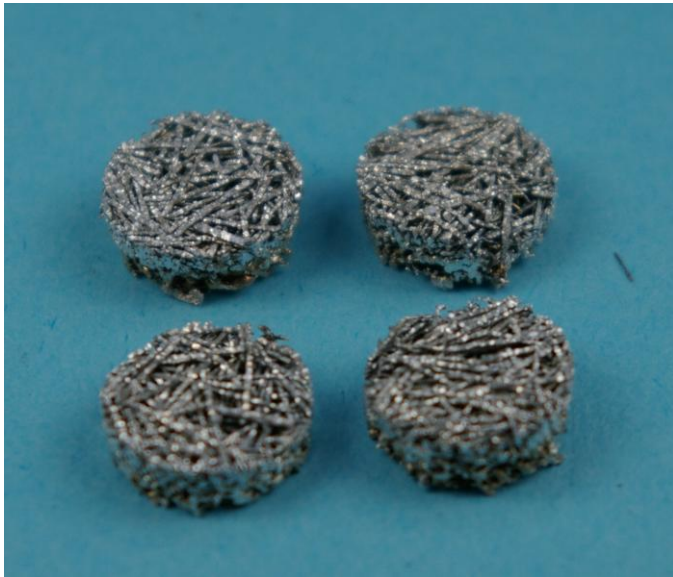


Figure 7: Top view of a sintered MgY<sub>2.6</sub>Ca<sub>1.6</sub> fiber structure with 61 % total porosity.

Only one deposited fiber sample of composition MgY<sub>2.6</sub>Ca<sub>1.6</sub> was taken to heat treatment. The sintering temperature was set to 580 °C based on the results of the calculations shown in Figure 4 and Table 1. The chosen temperature turned out to be slightly too high since the structure became too soft, resulting in a comparable low porosity. Nevertheless the inter-fiber bonds were excellent.

Sintering at 630 °C gave good results for MgY<sub>4</sub> fiber structures. Metallurgical cross sections reveal excellent inter-fiber bonds in all cases (Figures 8 and 9). The SEM image in Figure 8 show some precipitations at the inter-fiber bonds which were investigated via EDX measurements. The two measurement locations in the bonds (Figure 9, denoted with 1 and 2) showed an increased Y concentration of up to 30 % which is much higher than the average concentration in the fiber of 3.5 % (location 3). This is most likely a mixture of Mg and Mg<sub>24</sub>Y<sub>5</sub> from an eutectic solidification of the remaining liquid at 73.2 wt-% Mg, which was expected from the binary phase diagram and the calculations with blocked diffusion (not shown here).

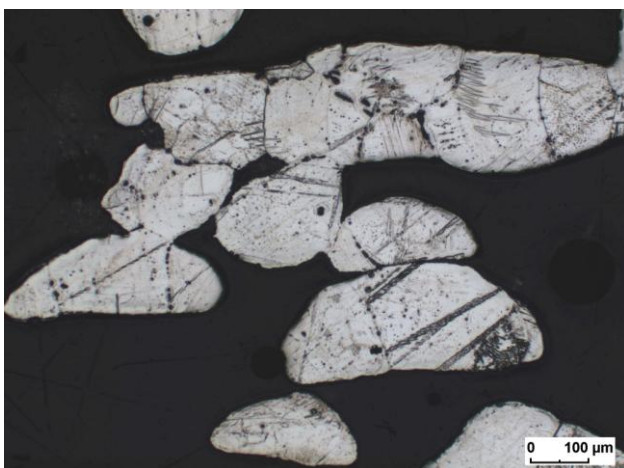


Figure 8: Optical micrograph of an etched cross section of a sintered MgY<sub>4</sub> fiber structure.



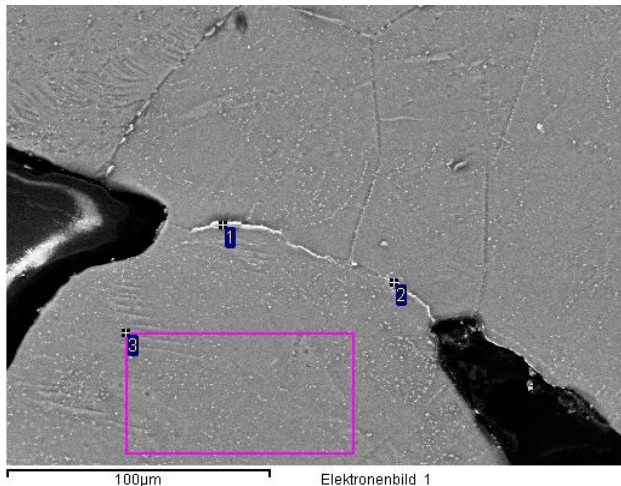


Figure 9: SEM image of an MgY4 fiber bond. The microstructure shows bright areas in the bond corresponding to Y-rich precipitations. The EDX measurements are explained in the text.

### Conclusions

It was demonstrated successfully that rigid fiber structures can be prepared with the same approach both from Al and Mg alloys when a sufficient amount of liquid phase is present during sintering. The resulting porosity in this work was around 70 %, but in other works rigid structures were also done with to 90 % without the help of space holders. Thermodynamic calculations were used in order to pre-determine the conditions for the heat treatment. Thus, the required experimental effort could be reduced substantially. The calculations also predict the phase fraction and phase formation during solidification. This was shown experimentally with the successful liquid phase sintering of the fibers with the specific composition, which would have been not possible without a correct calculation. They proved to be a useful tool for reducing the experimental effort and help to optimize alloy compositions and sintering conditions. The resulting structures may find application in heat exchangers and degradable implants.

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