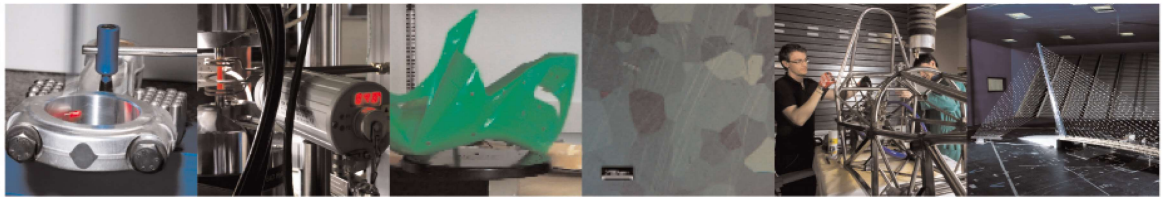




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## Rapid production of AZ91 Mg alloy by extrusion based additive manufacturing process

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1 **Rapid production of AZ91 Mg alloy by extrusion based additive manufacturing process**

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13

14 **Abstract**

15 AZ91 magnesium alloy parts were successfully produced using a novel extrusion-based additive  
16 manufacturing process. The green parts were built in two different orientations and subjected to  
17 debinding and sintering treatments. The as built alloy showed a heterogeneous microstructure made up  
18 of  $\alpha$  – Mg matrix,  $Al_8Mn_5$  second phase particles, MgO layers and  $Mg_{17}Al_{12}$  continuous precipitates. After  
19 solution treatment followed by aging,  $Mg_{17}Al_{12}$  discontinuous precipitates were observed. The sintered  
20 samples showed a yield strength and ultimate tensile strength of 79MPa and 207MPa, respectively, in  
21 the horizontal configuration. Analysis of the fracture surfaces revealed that a continuous network of  
22 magnesium oxide layer around the powder particles act as preferential path for crack propagation.

23

24 **Keywords**

25 Additive Manufacturing, Magnesium, AZ91, microstructure, DSC, electron microscopy.

26

## 27 Introduction

28 Extrusion based Additive Manufacturing (EAM) of metals is a relatively novel processing technique  
29 involving layer-by-layer deposition of feedstock material available in the form of pellets or filaments.  
30 The feedstock material is made of metal powder and polymeric binder. 3D printed parts are then  
31 processed through subsequent debinding and sintering steps, similar to those followed in powder  
32 injection molding [1] [2] [3]. The major advantage of this technique is the near net-shape processing in a  
33 single step, thus eliminating the need of machining. Another advantage is the ease of processing  
34 complex shapes and parts, which are extremely cumbersome to produce by conventional processing  
35 techniques [4].

36 Fused Deposition Modeling (FDM) is an additive manufacturing technique where filaments of a build  
37 material and a support material are extruded together layer-by-layer, according to a pre-programmed  
38 trajectory [5]. This technique is more commonly used to produce polymer products, however, several  
39 metallic products and ceramics have already been explored [6] [7]. To produce metallic or ceramic  
40 products by FDM, the feedstock is a mixture of a powder and polymeric binder. The binder provides  
41 adequate viscosity for extrusion while also acting as a support for the extrusion of the green part. The  
42 feedstock then passes through the extruder that plasticizes the material before finally passing out of the  
43 nozzle. Once the feedstock is deposited layer-by-layer, the green part undergoes debinding and  
44 sintering. This ensures good metallurgical bonding of the powder material [8]. A major advantage of  
45 FDM is that it is the most economical process available in the market [9].

46 Magnesium is the lightest structural element in use with a density of  $1.74 \text{ g/cm}^3$  [9]. In comparison, iron,  
47 the most used element for structural applications has a density of  $7.87 \text{ g/cm}^3$ , which is nearly five times  
48 heavier [9]. This could prove to be an economical choice for automotive and aerospace applications.  
49 Joost in [10] has documented that a 10% reduction in vehicle weight provides a 6–8% improvement in  
50 fuel economy [10]. Another application for Mg-alloys is the medical industry due to the high  
51 biocompatibility of this metal. Mg-Ca, Mg-Zn, Mg-Sr are suitable systems commonly used for such  
52 applications [11] [12].

53 Amongst the wide variety of available Magnesium alloys, the AZ91 is the most used for structural  
54 applications due to its superior castability, corrosion resistance and mechanical properties in  
55 comparison to other Mg alloys [13]. The enhanced strength is due to the microstructure, which consists  
56 of  $\alpha$ -Mg matrix and precipitates of  $\text{Mg}_{17}\text{Al}_{12}$  [14].

57 Processing of Mg alloys through conventional metal additive manufacturing processes, such as  
58 Selective Laser Melting (SLM), has a number of drawbacks and limitations [15]. Mg has an extremely  
59 high affinity towards oxygen, especially in the liquid phase. Magnesium powders are also prone to dust  
60 explosions and their handling and storage is a crucial step for the production of parts. AZ91D parts  
61 produced by SLM have also displayed poor ductility with a maximum elongation at fracture between  
62 1.24-1.83% [15]. EAM of magnesium powders, premixed with a polymeric binder, allows to avoid  
63 technological and safety risks associated with SLM. Previous studies concerning Metal Injection  
64 Moulding of magnesium have indicated two main challenges, the first regarding the binder that should  
65 not react with the powder and should be removable at rather low temperatures before sintering starts,  
66 the second regarding the sintering itself, which can be aided by liquid phase. The work of M. Wolff in ref.  
67 [16] reports the main issues related to sintering of Mg and the effect of Ca addition.

68 This study aims to investigate the microstructure and mechanical properties of Mg alloy AZ91 produced  
69 by EAM. The novel process is complementary to metal injection molding (MIM). While MIM is for mass  
70 production with high tooling costs but low part costs, EAM is adequate for prototypes, customized parts  
71 and small series production.

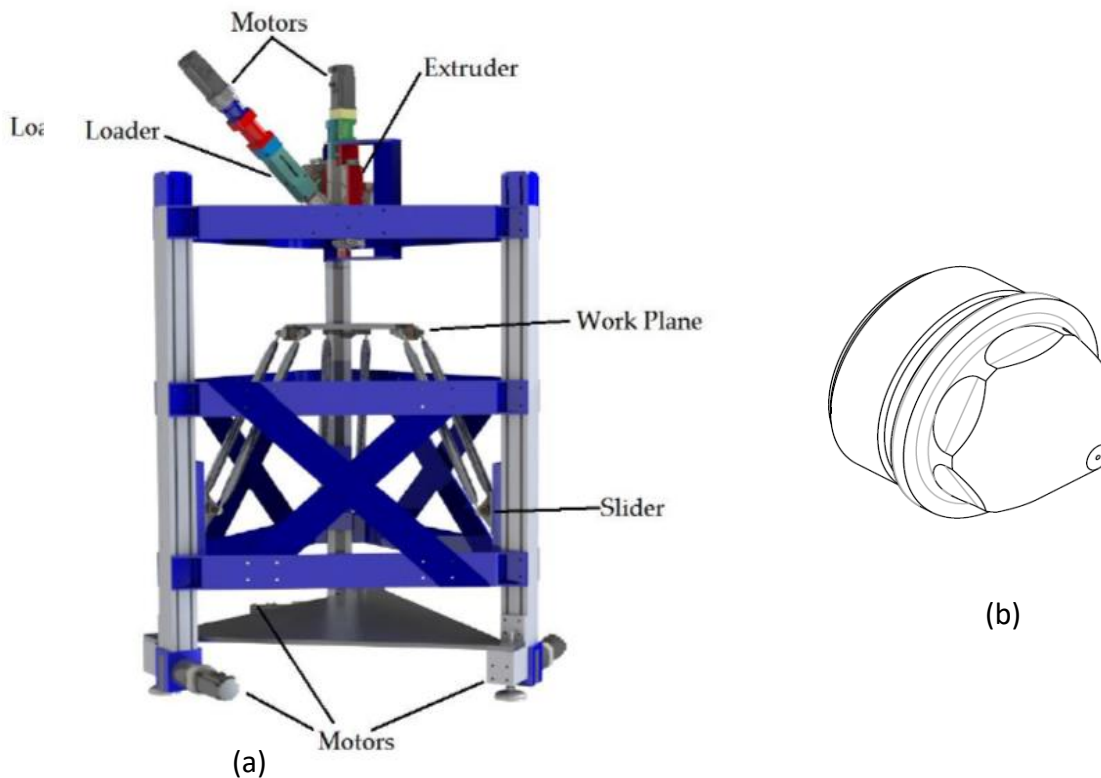
72 Microstructure of as sintered and heat treated parts are investigated by X-ray diffraction (XRD), Electron  
73 microscopy and thermal analysis. Mechanical behavior of sintered parts was evaluated by Vickers  
74 microhardness and tensile tests.

75

## 76 **Experimental Procedure**

77 The AZ91 alloy powder was produced by gas atomization at SFM SA in Martigny, CH. The powder particles  
78 have a maximum size smaller than 45  $\mu\text{m}$ . The feedstock (powder + binder mixture) was produced at  
79 Helmholtz-Zentrum Geesthacht in Germany. The feedstock has AZ91 alloy powder loaded at 64 vol% into  
80 polymeric binder.

81



82

83 *Figure 1: (a) Extrusion based additive manufacturing (EAM) machine with principle components (b)*  
84 *Nozzle used in this study  $\phi$  0.8 mm.*

85 The feedstock was 3D printed in form of rectangular bars by a specially developed EAM machine as  
86 shown in Figure 1 (a). Machine capabilities and operations were demonstrated in earlier works [2] [17].  
87 More information about binder composition can be found in ref. [18].

88 The work plane is free to move in directions X, Y and Z and it is governed by a 3-axes parallel kinematic  
89 system (Linear Delta) operated through three stepper motors as shown in Figure 1(a). The printing head  
90 is fixed and is composed by a feeder, where the pellets of feedstock are placed, a screw plasticizer and  
91 an injector piston. In the extruder system, the feedstock is loaded into the feeder and falls by gravity in a  
92 first loader chamber, which plasticizes the material, and is then injected in a second extruder chamber,  
93 which directly provides a molten feedstock to the nozzle for deposition on work plane. A PLC controls  
94 loading, printing and temperature at three different locations, including the exit nozzle. The input is  
95 given by loading a g-code file generated using the shareware Slic3r software.

96 12 bars (6 mm height, 60 mm length and 10 mm width) were printed in a “horizontal” configuration,  
97 laying on the face of dimensions 60 x 10 mm, and a “vertical” configuration, laying on the 60 x 6 mm  
98 face. The printing parameters, namely nozzle diameter of 0.8 mm, extrusion temperature of 150 °C and  
99 extrusion velocity of 7.5 mm/s were kept constant for all the experiments. The printing speed, i.e. the  
100 horizontal velocity of the printing table, was selected by setting an extrusion multiplier of 0.75, defined  
101 as the ratio between extrusion velocity and printing speed. In other words, with a printing speed of 10  
102 mm/s, the material flows out of the nozzle at an extrusion speed of 7.5 mm/s. The samples were 3d  
103 printed with a theoretical full density at the green state. However, it is well known that the EAM process  
104 always induces some porosity, i.e. leaves some empty space between adjacent tracks.

105 After the production of the green part, the solvent debinding was done using hexane. The final  
106 densification was achieved by sintering at 605 °C for 4 hours. Then, the as-sintered part was cooled in  
107 the furnace to room temperature. Further processing details can be found in [18].

108 The samples were cut and were subject to solution annealing at 415 °C for 16 h, followed by quenching  
109 in water. Rapid non-equilibrium heating has known to induce void formation by the melting of eutectic  
110 precipitates in Mg-Al alloys [19]. Therefore, samples were heated by linear ramp from 260 °C to 415 °C  
111 over a time period of 2 h according to the ASM Handbook Volume 4E [19].

112 The solution treated samples were further subjected to ageing treatment at 168°C for 16 h according to  
113 the ASM Handbook Volume 4E [19]. Microhardness measurements were carried out using the Future-  
114 Tech FM700 fitted with a Vickers indenter. Loads of 50 g and 500 g were used with a dwell time of 15s.

115 After the ageing treatments, all the samples were ground and polished using diamond paste. The  
116 microstructures of the samples were observed under an optical microscope (Nikon Eclipse LV150L) and  
117 Scanning Electron Microscopy (SEM) (Zeiss Evo 50 and Zeiss Gemini) equipped with EDX detector  
118 (Oxford Instruments model 7060). The samples were etched using a 2% Nital solution. To quantify the  
119 porosity, five images of the as sintered sample were analyzed using the ImageJ software. XRD analyses  
120 were carried out by Rigaku SmartLab SE. Diffractograms were analyzed by QualX software and COD  
121 database. Thermal analysis was carried out by Labsys TG-DSC by Setaram instruments. The samples with  
122 mass of about 40 mg were heated to a temperature of 700 °C at a rate of 20 °C/min, held there for 300  
123 s, and cooled to room temperature.

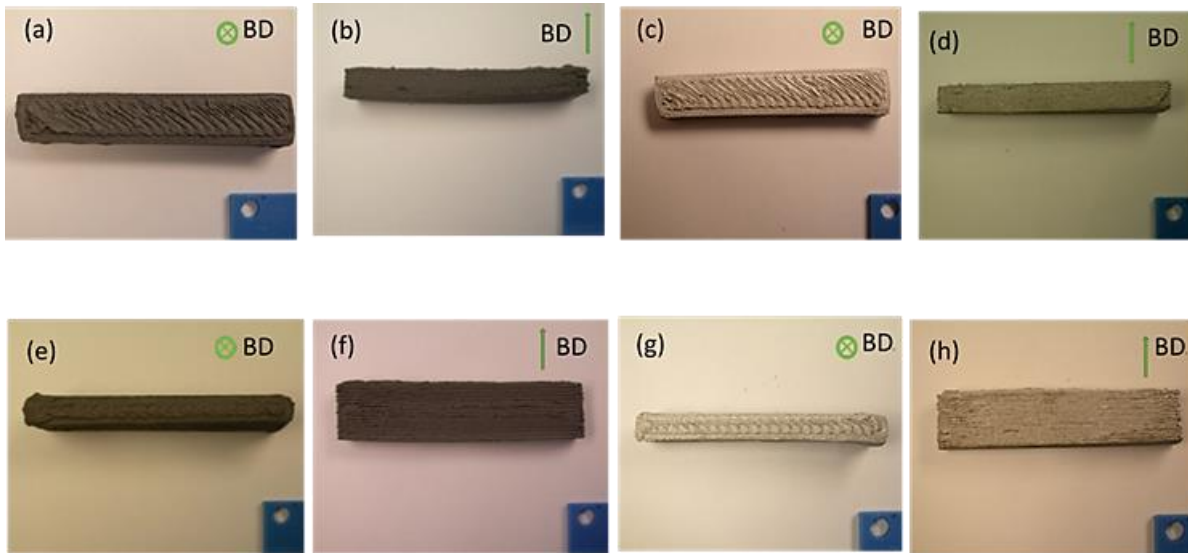
124 Three tensile tests were carried out on as-sintered and peak-aged samples. Standard specimens were  
125 milled with with gauge length of 25 mm, thickness of 3 mm and width of 6 mm according to the ASTM  
126 standard E8/E8M. The tensile test was conducted on an MTS Alliance RT/100 3.7 at a deformation rate  
127 of 1 mm/min.

128

## 129 Results and Discussions

130 The AZ91 samples were successfully prepared using extrusion based additive manufacturing process.  
131 Both the vertical and horizontal builds were produced and sintered according to the procedure reported  
132 in the experimental section. The green parts are illustrated in Figure 2 (a) (b) (e) and (f). The samples  
133 prepared do not have any coarse defects under visual examination at their outer surface, except for the  
134 inherent waviness due to the overlap between adjacent 3d printed tracks. The as sintered samples are  
135 shown in figure 2(c) (d) (g) and (h). The shiny surface implies that the sintering has been successful. The  
136 layers were distinctly visible on the lateral surfaces, whereas extrusion tracks were noticeable on the top  
137 surfaces.

138



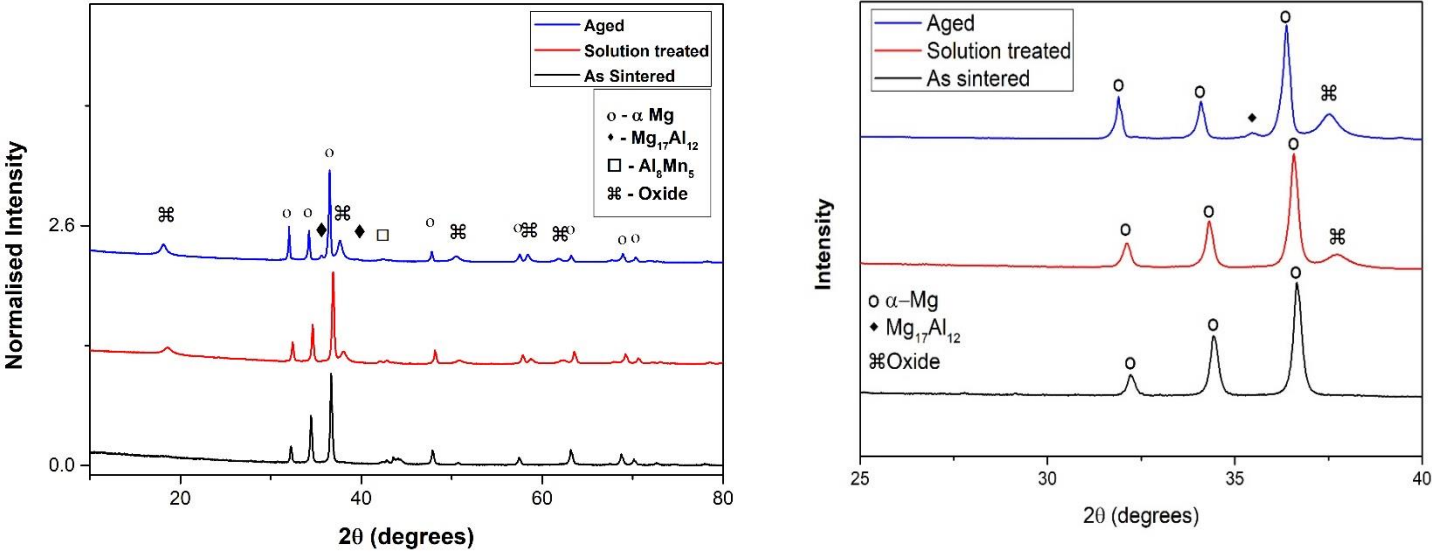
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140 *Figure 2: (a),(b),(e),(f) as built (green) specimens and (c) (d) (g) (h) as sintered specimens*

141

142 The XRD diffractograms of the as sintered, solution treated and aged samples are shown in Figure 3. In  
143 the as-sintered alloy, three sets of peaks were observed. The most intense peaks were identified as the  
144 main reflections of the  $\alpha$ -Mg, which is the matrix phase of the alloy. Peaks related to  $Al_8Mn_5$  and  
145  $MgAlFeO_4$  phases were also identified. Peaks corresponding to  $Mg_{17}Al_{12}$  in the as sintered sample were  
146 also expected. Indeed,  $Mg_{17}Al_{12}$  precipitates might form on cooling from the sintering temperature.  
147 However, no peaks related to such phase were detected. This does not exclude their presence in the as  
148 sintered samples, since their content could be lower than the minimum fraction that can be detected by  
149 XRD analysis. After the solution treatment, there is a subsequent increase in the intensities of the oxide

150 peaks. The isothermal aging results in the formation of  $Mg_{17}Al_{12}$  precipitates. The peak intensity was  
 151 observed to be very small with respect to that of  $\alpha$ -Mg. These results are in accordance with the work  
 152 conducted by Mondet et al [20], where AZ91 alloys were prepared by Spark Plasma Sintering (SPS).

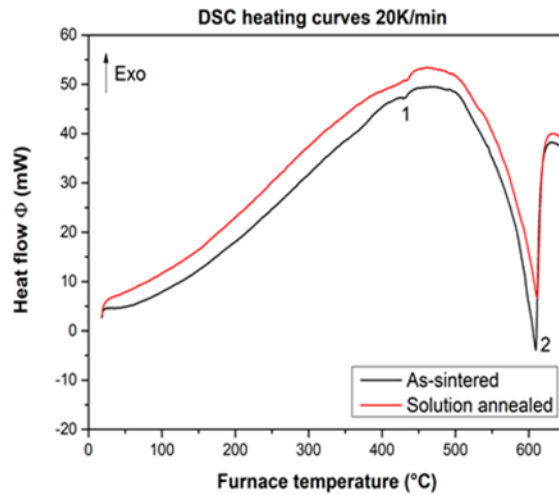


153 *Figure 3: XRD patterns of AZ91 after different heat treatments*

154

155 DSC curves of as sintered and solution treated samples are shown in Figure 4. On heating, two peaks  
 156 were observed. These are marked as 1 and 2 in Figure 4. Both the as sintered and the solution treated  
 157 samples had similar heating curves, and the same set of peaks were observed. At around 430 °C, the  
 158 first peak is observed. This corresponds to the melting of the eutectic product  $Mg_{17}Al_{12}$  [21]. The second  
 159 peak was observed at approximately 610 °C, which corresponds to melting of  $\alpha$ -Mg. Although an  
 160 endothermic peak was expected for dissolution and precipitation of  $Mg_{17}Al_{12}$ , it was not observed. The  
 161 observations, however, are consistent with the studies conducted by Ohno et al [21]. The melting of the  
 162 eutectic is at around 430 °C is crucial, as it could possibly induce porosity during annealing. From this  
 163 curve is also evident that the sintering of samples at 605 °C occurred in the semi-solid state.

164



165

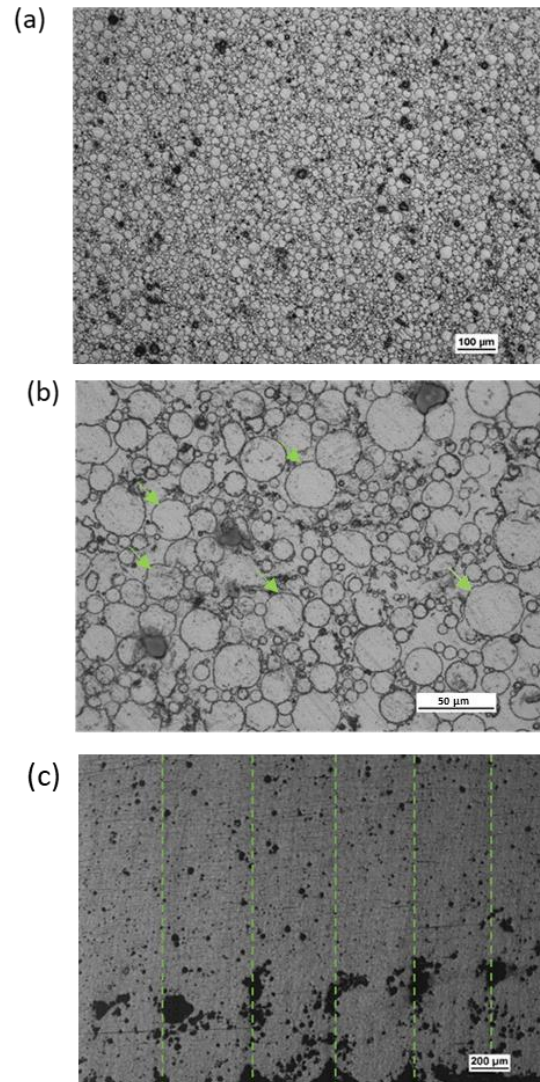
166

*Figure 4 DSC curves of the as sintered and the solution treated samples*

167

168 The optical micrographs of the as-sintered sample are shown in Figure 5. The overall microstructure  
 169 consists of a continuous matrix with spherical particles and dark spots embedded in the matrix, as  
 170 shown in Figure 5 (a). The spherical particles are the sintered particles of AZ91. The dark borders are  
 171 presumed to be Mg oxides (pointed out by arrows in the micrograph of Figure 5 (b)) inherit from the  
 172 feedstock powder. The black spots in the microstructures are identified to be pores. The total porosity  
 173 of the as sintered sample was calculated as  $5 \pm 2$  %. There is an increased pores concentration at  
 174 boundaries between layers as shown in Figure 5 (c), due to printing defects. The density of the material  
 175 in the central part of the specimens was of 98.8 %” Even if the sintering occurred in the semi-solid state,  
 176 the large pores could not be closed.

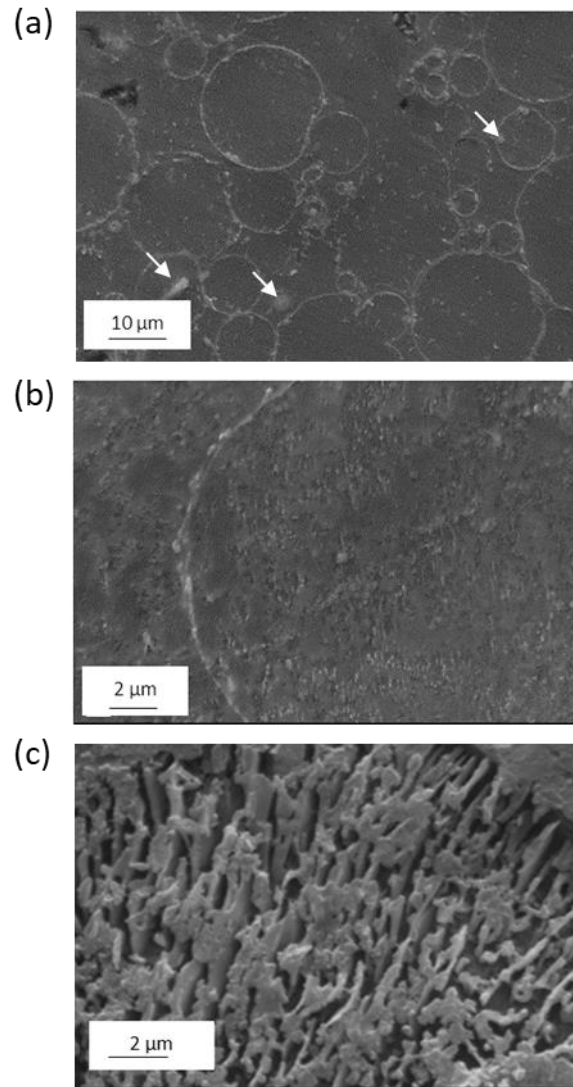




177

178 *Figure 5: Optical micrographs of the as sintered sample depicting (a) the overall matrix, (b) oxides*  
 179 *around the sintered particles, some representative oxide layers are pointed by white arrows and (c)*  
 180 *increased porosity at layer boundaries in the edge regions. Interfaces between adjacent layers are*  
 181 *highlighted with dash lines.*

182 Figure 6 (a) and (b) show the SEM microstructures of the as sintered sample. The EDS results confirmed  
 183 the presence of oxygen in the regions with bright contrast surrounding the sintered powder particles.  
 184 Second phases that are rich in Al and Mn are noticeable within the matrix (see for instance the particle  
 185 pointed out by the arrows in Figure 6 (a)). They are supposed to be  $Al_8Mn_5$  precipitates, in agreement  
 186 with XRD results and with [22]. Furthermore, at higher magnifications, tiny white needles are visible, as  
 187 shown in Figure 6 (b). These needles are consistent with the continuous precipitate morphology of  
 188  $Mg_{17}Al_{12}$  which is illustrated in the study of Braszczyńska et al [23]. After solution treatment and aging at  
 189  $168\text{ }^\circ\text{C}$  discontinuous precipitates are noticeable in the microstructure as illustrated in the micrograph of  
 190 Figure 6 (c). Braszczyńska et al [23] observed similar precipitates after aging at  $150\text{ }^\circ\text{C}$  for 16h in AZ91  
 191 produced by permanent mould casting.



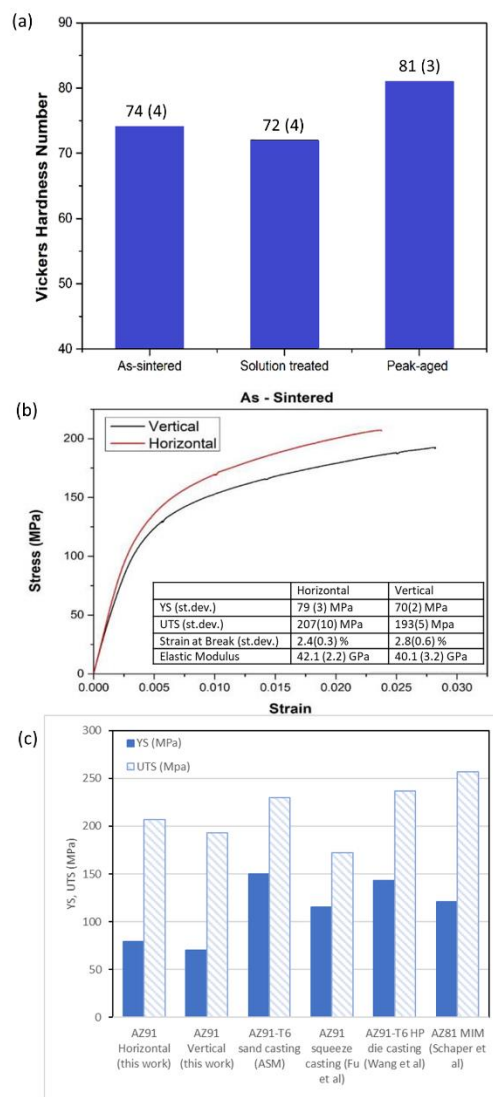
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194 *Figure 6: SEM micrographs of the as sintered specimen at (a) low and (b) high magnification and (c)*  
 195 *discontinuous precipitation after ageing.*

196 The Vickers hardness of the as sintered, solution treated and aged alloys are summarized in Figure 7 (a).  
 197 The hardness of the as sintered alloy slightly decreases after solution treatment. After the ageing  
 198 treatment, the alloy hardens due to precipitation of continuous  $Mg_{17}Al_{12}$ . The maximum hardness  
 199 achieved is 81 HV. Hardness values of aged sample are consistent with those measured by by Celotto et  
 200 al in cast AZ91E alloy aged at 150 °C and 200 °C [24].

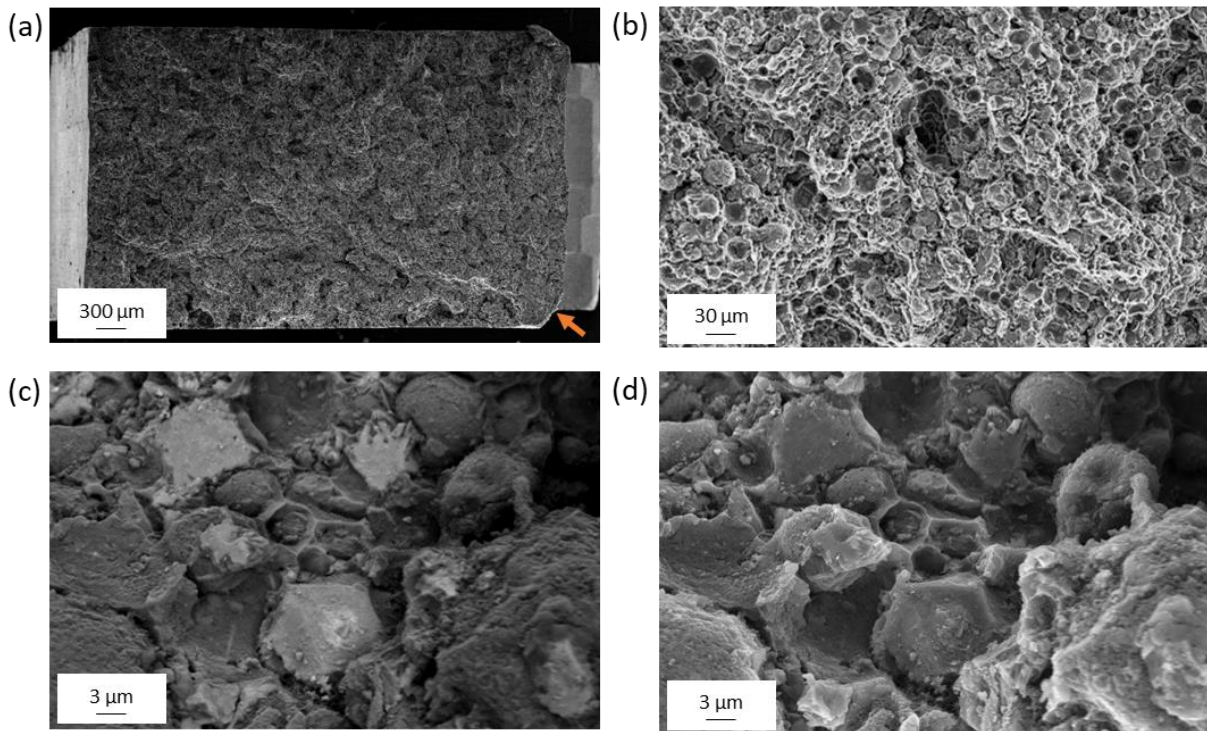
201 Tensile tests were performed on flat dogbone as sintered specimens, representative curves are reported  
 202 in Figure 7 (b). The samples had a yield strength of 79 MPa in the horizontal build and 70 MPa in the  
 203 vertical build. The ultimate tensile strength (UTS) was 207 MPa for the horizontal build and 193 MPa for  
 204 the vertical build. The difference in strengths in build orientations is attributed to the different  
 205 distribution of pores in the two samples, that are mainly concentrated at layer boundaries. Both

206 samples show similar elongation at fracture, namely 2.4% and 2.8%, respectively. In a study conducted  
 207 by Schaper et al, AZ81 based feedstock was used to prepare samples using MIM. In that case, the  
 208 material showed YS of 121 MPa and UTS of 257 MPa in the as sintered state [18]. In comparison, sand  
 209 cast AZ91 has a yield strength of 150 MPa and a tensile strength of 230 MPa. A comparative illustration  
 210 is depicted in figure 7 (c), in which literature results of AZ91 produced by squeeze casting and high  
 211 pressure die casting are also reported [25,26,27]. The differences in strength among samples produced  
 212 using different methods could be due mainly to the different porosity levels and size and distribution of  
 213 second phases. Tensile tests were also conducted on the peak aged specimens, but the material showed  
 214 a brittle behavior and failed in the elastic regime, thus the results are not shown in this paper.



215  
 216 *Figure 7 (a) Hardness results of 3D printed AZ91 in as sintered, solution treated and aged conditions; (b)*  
 217 *representative tensile curves of as sintered samples; (c) comparison of YS and UTS for AZ91 processed*  
 218 *with different techniques [25,26,27].*

219 SEM micrograph of Figure 8 shows the fracture surface of the as sintered AZ91 specimen. The crack has  
 220 initiated on the surface of the dog bone specimen, close to the edge indicated by the arrow in the SEM  
 221 image of Figure 8 (a). The fracture propagated along the oxide layer boundaries, indeed spherical  
 222 particles and “cups” are well noticeable at higher magnifications. The cups are formed by the  
 223 magnesium oxides after the spherical particles were displaced by the applied load. The SEM images in  
 224 backscattered electron mode reveal large white polyhedrons rich in Al and Mn, therefore consistent  
 225 with  $Al_8Mn_5$  precipitates that broke in cleavage mode, suggesting that crack propagation has also taken  
 226 place through such precipitates.



227  
 228 *Figure 8: Fracture surfaces of as sintered sample at (a) 50x, (b) 500x, (c) BSE image at 5000x and (d) SE*  
 229 *image at 5000x*

230

## 231 Conclusions

232 The AZ91 alloy was successfully produced using an EAM technique. The XRD diffractograms showed  
 233 three sets of peaks in the as sintered and the solution treated samples. These peaks were identified as  $\alpha$   
 234 – Mg,  $Al_8Mn_5$  and MgO. After T6 treatment, peaks of  $Mg_{17}Al_{12}$  were also observed.

235 The alloy has a heterogeneous microstructure with a matrix  $\alpha$  – Mg phase,  $Al_8Mn_5$  and continuous  
 236 precipitates of  $Mg_{17}Al_{12}$  in the as sintered and solution treated states. After the aging treatment,  
 237 discontinuous precipitates of  $Mg_{17}Al_{12}$  were observed.

238 The sintered samples exhibited a yield strength and UTS of 79 MPa and 207 MPa, respectively, in the  
 239 horizontal configuration and 70 MPa and 193 MPa, respectively, in the vertical configuration.

240 Analysis of the fracture surface revealed that there is a continuous network of magnesium oxide layer  
241 around the powder particles. This acted as preferential path for crack propagation.

242

### 243 **Acknowledgements**

244 The Helmholtz-Zentrum Geesthacht, where feedstock preparation, debinding and sintering was carried  
245 out by co-author J. Schaper, is highly acknowledged.

246

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