

Influence of the layer orientation and the binder system on the mechanical behavior of titanium components manufactured by Metal Fused Filament Fabrication (MF³)

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ABSTRACT

Metal Fused Filament Fabrication offers a simple and cost-effective method to produce titanium components. However, multiple factors, including the binder system, contamination, and print parameters, have a significant impact on the physical and mechanical properties of the final parts. The present study investigates the utilization of the backbone polymers poly(methyl methacrylate) (PMMA) and poly(vinyl butyral) (PVB) in partially water-soluble binder systems. Two distinct debinding strategies were applied with the aim of increasing density while reducing contamination by oxygen and carbon in sintered Ti-6Al-4V components. The specimens were characterized by computed tomography, metallography, scanning electron microscopy, carrier gas hot extraction, and Raman spectroscopy. In addition, the effects of layer orientation and binder system on mechanical performance were evaluated by tensile testing. PMMA-based feedstocks yielded relative densities of 94–95 % combined with comparatively low oxygen and carbon contamination, resulting in ultimate tensile strengths of up to 870 MPa and elongations of up to 11 %. Nevertheless, print-induced defects led to pronounced scatter in the mechanical properties. In contrast, PVB-based systems achieved a high relative density of 98.4 % and an ultimate tensile strength of 900 MPa, but suffered from elevated oxygen and carbon contents, leading to limited ductility (elongation 4.3 %). The utilization of isopropyl alcohol in the debinding process to dissolve the poly(vinyl butyral) resulted in a slightly lower density of 97.5 %, but in excellent ultimate tensile strengths of 890 MPa and elongations up to 13.5 %. No significant differences were observed between the different layer orientations for samples produced with an optimized feedstock and without major print-induced defects. Overall, density, impurity content, and print-related defects were identified as the dominant factors governing the mechanical behavior of MF³-fabricated Ti-6Al-4V components.

1. Introduction

Metal additive manufacturing (AM) has become an increasingly popular production method due to its capability to quickly produce functional metal prototypes, ready-to-use parts, and small-scale-series. Additionally, AM enables the manufacture of complex geometries that are difficult or economically unfeasible to realize using conventional manufacturing techniques. It is widely adopted in industries characterized by high customization requirements and small batch sizes, such as

aerospace, medical, automotive, and energy applications. At present, the market dominance of AMs is largely attributed to well-established methodologies such as selective laser melting (SLM), electron beam melting (EBM), direct energy deposition (DED), and binder jetting (BJ) [1]. However, these AM technologies have several limitations, including a substantial capital expenditure, considerable energy consumption during operation, and the necessity for strict safety measures, particularly in powder-based AM processes. Especially the high energy input during the SLM, EBM, or DED process can result in alterations to the

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microstructure and high anisotropy of the printed parts [2–4], as well as changes to the microstructure and morphology of the unused powder, thereby limiting its recyclability [5].

In order to address these challenges, researchers and manufacturers have been developing new AM processes to produce metallic components in a more affordable and simple way. One such approach is Metal Fused Filament Fabrication (MF³), which combines principles of metal injection molding (MIM) and fused filament fabrication (FFF). MF³ offers several advantages, particularly for small-scale production, including low equipment costs and the possibility of fabricating hollow or complex internal structures [6,7]. A wide range of materials has already been processed successfully using MF³, such as 17-4 PH stainless steel [8–10], Cu [11], and WC-10Co [12]. However, only a limited number of studies address the processing of Ti-6Al-4V by MF³. Singh et al. reported the development of a flexible filament for the manufacturing of Ti-6Al-4V components [13], followed by printability studies [14], and a comprehensive analysis of factors influencing the properties of sintered parts [15]. Relative densities of up to 94 %, ultimate tensile strengths of 875 MPa, and elongations of 17 % were reported. However, the binder systems used were not disclosed due to confidentiality restrictions, limiting comparability and reproducibility. Shaik et al. investigated the manufacturing of maxillofacial implant prototypes [16]. The fabrication of complex components was accomplished through the utilization of support structures. However, the removal of support structures from uneven surfaces proved challenging. Additionally, the composition of the binder system was also not specified. Zhang et al. successfully manufactured Ti-6Al-4V components using a polyolefin-based binder system, though the relative density of the sintered samples was below 90 % [17]. A major limitation of MF³ remains the debinding and sintering process, which typically requires specialized solvent debinding systems and inert-gas furnaces, resulting in increased process complexity and cost. Partially water-soluble binder systems offer a promising alternative by reducing health and environmental hazards and lowering equipment requirements. Previous work demonstrated the feasibility of such binder systems, enabling the manufacturing of complex structures and relative densities exceeding 98 % [18,19]. Nevertheless, carbon contamination remained a critical challenge.

A prevailing challenge pertains to the mechanical properties of components fabricated by MF³, which are still inconsistent and often lower compared to those achieved by SLM or EBM [20–22]. The primary reason for this observation is the presence of a higher residual porosity after sintering [21,23]. Additionally, the surface roughness of the MF³ process is found to be inferior to that produced by SLM and EBM processes [24]. Another factor that appears to influence the mechanical properties is the build orientation during the printing process. Although the sintering process produces a homogeneous microstructure characterized by grains of equal size in all directions [25], [26–28] reported anisotropic tensile properties in 316L stainless steel and 17-4 PH. In the specimens printed with the layer direction oriented parallel to the tensile direction, the tensile properties exhibited increased strength in comparison with the specimens with the layer orientation positioned perpendicular to the tensile direction. According to Pellegrini et al., this issue is related to the printing parameters and the binder system, which can generate voids between the deposited layers [22]. The same behavior was observed with pure polymers printed by FFF [29,30]. A comprehensive review of the extant literature revealed no reports on Ti-6Al-4V in this regard. Another significant factor that can influence the mechanical properties is the presence of impurities. In particular, titanium and its alloys exhibit a high affinity for oxygen, nitrogen, and carbon, which leads to the formation of oxides, nitrides, and carbides, resulting in embrittled final components [31]. Therefore, it is crucial to completely remove the organic binder system during the debinding process as well as sintering in a vacuum or argon atmosphere. It is noteworthy that the majority of literature on the subject focuses exclusively on the influence of oxygen content on mechanical properties,

despite the fact that carbon, as the primary component of polymers, can exert a comparable effect. An additional noteworthy observation pertains to partially water-soluble (polar) binder systems. For these systems, the contamination with oxygen and carbon is slightly higher than for non-polar binder systems [32].

As previously mentioned, the existing literature offers limited insight into parts produced by MF³ with partially water-soluble binder systems, particularly concerning their impact on the mechanical properties of the sintered Ti-6Al-4V components. Therefore, the present study systematically investigates the influence of partially water-soluble binder systems and layer orientation on the mechanical behavior of Ti-6Al-4V components produced by MF³. The samples were manufactured using two distinct partially water-soluble feedstocks and three different layer orientations. In addition, two novel debinding strategies were implemented to mitigate defect formation and reduce oxygen and carbon contamination. Raman spectroscopy was employed to identify impurities, while tensile testing was conducted to evaluate mechanical performance as a function of binder system, debinding route, and build orientation. The quality of the components was assessed by comparing the properties to the specifications of medical titanium implants manufactured via metal injection molding (ASTM F-2885-17 [33]).

2. Materials and methods

2.1. Material selection

A commercial Ti-6Al-4V powder (Grade 23, Tekna Advanced Materials Inc., Sherbrooke, Canada) with a density of 4.4 g/cm³, an average particle size (d_{50}) of 28.6 μ m and specific surface area of 0.15 m²/g was used. The carbon and oxygen contents were 0.008 wt% and 0.09 wt%, respectively [19]. Two binder systems from previous work were utilized [19]; the composition is shown in Table 1. The organic binder was composed of poly(methyl methacrylate) (PMMA Degalan G7E, Roehm GmbH, Darmstadt, Germany), poly(vinyl butyral) (PVB Mowital 30H, Kuraray Europe GmbH, Frankfurt, Germany), polyethylene glycol (PEG 8,000, C. Roth GmbH Co. KG, Karlsruhe, Germany) and acetyltributyl citrate (ATBC, Sigma Aldrich, St. Louis, USA). The solid load of both feedstocks was set to 60 vol%. The development and the rheological properties of both systems can be found in Ref. [19]. These two feedstock systems demonstrated varying properties with respect to relative density and contamination with carbon and oxygen. Composition A demonstrated an average relative density of approximately 95.3 %, while composition B exhibited a relative density of 99.5 %. However, analysis of the carbon and oxygen content in composition A via carrier gas hot extraction showed significantly lower values (0.18 wt% and 0.22 wt%, respectively) than those of composition B (0.94 wt% and 0.29 wt%, respectively), primarily due to insufficient pyrolysis of PVB without oxygen [19,34]. The target values for oxygen (0.20 wt%) and carbon (0.08 wt%) content are based on those for titanium implants and are specified in the standard ASTM F-2885-17 [33].

2.2. Sample preparation

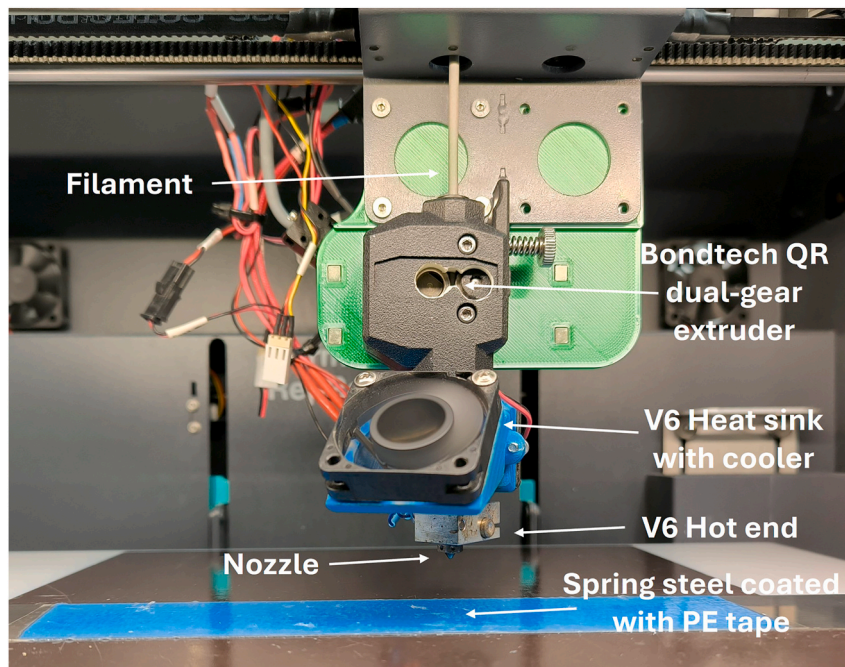
2.2.1. Filament preparation and fused filament fabrication

The titanium powder and the organic binder were thoroughly compounded in a mixer-kneader (W50-EHT, Brabender GmbH, Duisburg, Germany) at 160 °C (Composition B) and 170 °C (Composition A) for 2 h. The feedstocks were then pelletized using an impact mill (Granulator 1514, Rapid Germany, Kleinostheim, Germany), extruded to filaments with a diameter of 2.85 mm using a single screw extruder at 70 °C (Noztek pro HT, Noztek, Shoreham, UK), and wound onto a spool using a winder (Noztek Filament Winder 1.0, Noztek, Shoreham, UK). A commercial FFF printer (x350pro, German RepRap, Feldkirchen, Germany) was used for printing, but with slight modifications. The print head is depicted in Fig. 1. The original extruder was replaced by a Bondtech QR Extruder (Bondtech, Värnamo, Sweden) with Dual-Drive technology, as

Table 1

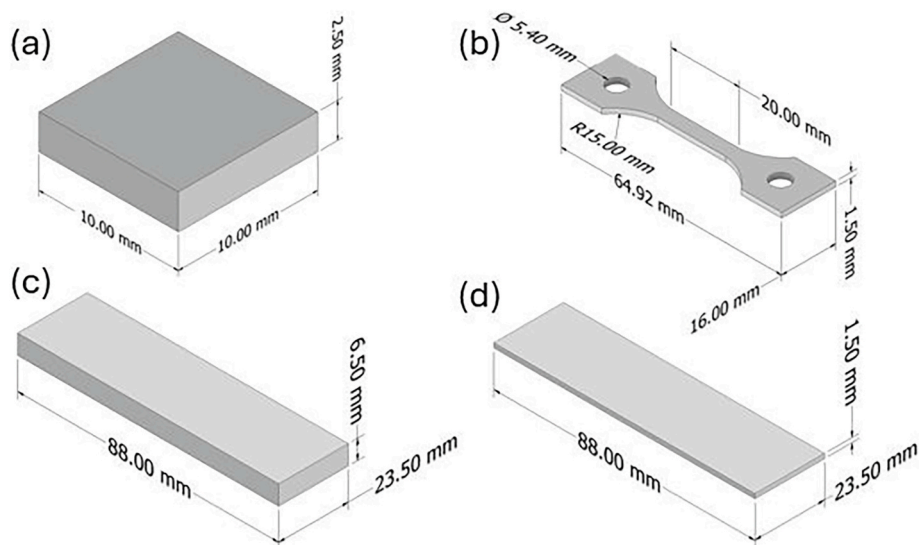
Binder composition of the filaments.

Composition	PMMA G7E		PVB 30H		PEG 8000		ATBC	
	(vol%)	(wt%)	(vol%)	(wt%)	(vol%)	(wt%)	(vol%)	(wt%)
A	40	40.4	0	0	45.9	47.1	14.1	12.5
B	25	25.5	25	23.6	44.3	45.9	5.7	5.0

**Fig. 1.** Modified FFF print head ×350 pro.

well as an E3D V6 Hotend for 2.85 mm filaments (E3D, Oxfordshire, UK). This extruder type offers superior precision and the ability to print with softer filaments. Additionally, the print bed was covered with spring steel coated with PE tape to enhance adhesion and improve the removal of printed parts. Ultimaker Cura (V 5.4.0) was used for slicing. A variety of test specimens were printed (Fig. 2). Small cuboidal samples (a) were used to evaluate the debinding behavior and for Raman

spectroscopy analysis. Tensile specimens (b), large cuboidal samples (c) (composition A), and flat large cuboidal samples (d) (composition B) were used for tensile testing. The rationale behind this approach is the debinding process, since it was not possible to achieve defect-free debinding for composition B for the cuboidal samples displayed in Fig. 2c. Consequently, the thickness was reduced. This is explained in detail in sections 2.2.3 and 3.1. To compensate for sintering shrinkage,

**Fig. 2.** Sketches with dimensions of the samples printed.

as previously investigated [32], the dimensions of the samples were increased by 15 % in the slicer.

The printing parameters are listed in Table 2. To investigate the impact of the orientation on the mechanical properties without the influence of the walls, the infill of the large cubes and the large flat cubes were printed in three different orientations (Fig. 3a–c). The tensile specimens were then cut from the cubes in the sintered state (see Section 2.2.3). The infill of the tensile specimens was printed in a single orientation, resulting in an infill orientation that is parallel to the wall within the measuring length (Fig. 3d). Due to the shape of the deposited strands [35], voids are generated between the strands during printing [36]. Several examples exist in literature of successful attempts to address this issue using infill density or a material flow rate of over 100 % to enhance the relative density of the final component [13,15,37]. Therefore, the infill density was set to 105 %.

2.2.2. Debinding and sintering

The debinding process was conducted in a three-step process. Fig. 4 and Table 3 give an overview of the whole debinding process. (1) The printed green parts were first placed in demineralized water at 30 °C for 24–48 h, depending on the size of the samples, to remove the PEG and subsequently dried overnight in a vacuum drying furnace (Vacutherm VT 6130 P, Heraeus, Hanau, Germany) at 40 °C to remove residual water. (2a) Secondly, since the ATBC leads to defects during the thermal debinding step, it must be removed in a thermal pre-debinding (TPD) step in air at 250 °C. However, when used in combination with PVB, this can lead to a significant increase in contamination with carbon and oxygen [19]. Furthermore, inadequate pyrolysis of PVB without oxygen contributes to elevated carbon levels in the sintered component [34]. (2b) Therefore, the samples made of composition B were placed in isopropyl alcohol (IPA) at 25 °C to dissolve the PVB and the ATBC. For comparison, this debinding method was also evaluated for the PVB-free composition A. To assess binder loss, the samples were weighed after each of the initial two debinding steps. (3) Finally, thermal debinding was conducted prior to sintering in a metal sintering furnace (MUT Advanced Heating GmbH, Jena, Germany). The samples were heated to 550 °C in an argon atmosphere at a heating rate of 1.5 °C/min and then held for a duration of 1 h. The samples were subsequently sintered using a heating rate of 5 °C/min, a maximum temperature of 1350 °C, and a sintering time of 4 h. Both heat treatments were carried out under an argon atmosphere (purity > 99.999 vol%, ALPHAGAZ 1 Argon, Air Liquide, Düsseldorf, Germany) in the same furnace to prevent contamination from oxygen and nitrogen.

2.2.3. Post processing

To investigate the influence of the orientation of printed layers on the mechanical properties of the sintered parts, tensile specimens were cut from large cubes (composition A, three samples per cube) and flat cubes (composition B, one sample per cube) via electro-discharge machining (EDM).

Table 2

Overview of the printing parameters used for compositions A and B.

Parameter	Value
Temperature	170 °C (A), 200 °C (B)
Bed temperature	40 °C
Infill density	105 %
Infill pattern	Rectilinear
Infill overlap	0.4 mm
Layer height	0.2 mm
Nozzle size	0.8 mm
Number of walls	1
Printing speed	10 mm/s

2.3. Characterization of sintered samples

2.3.1. Physical and chemical properties

The density of the printed and sintered samples was measured using the Archimedes principle (Secura 225D-1S equipped with YDK 01, Sartorius Lab Instruments GmbH & Co. KG, Göttingen, Germany). The pycnometer (AccuPyc II 1340, Micromeritics Instr. Corp., Norcross, GA, USA) density of the Ti-6Al-4V powder was utilized as a reference point for the calculation of relative densities. A combustion analysis via Carrier Gas Hot Extraction (CS600 and TC600, LECO 176 Instruments GmbH, Mönchengladbach, Germany) was conducted to characterize the final carbon and oxygen content in the sintered parts.

The Raman experiments were carried out in a confocal Raman microscope (Renishaw plc, New Mills, UK) in backscattering geometry. This system was equipped with a frequency-doubled Nd-YAG laser (wavelength: 532 nm) and a Charge-Coupled Device (CCD) detector. The backscattered signal was collected through a 100× objective lens (working distance ~ 300 µm) and dispersed by a 2400 grooves per mm grating. The laser power density was kept below 0.5 mW/µm² to avoid heating effects and thermal damage of the investigated materials. This “safe” laser power density level was estimated according to the experimental procedures reported previously [38–40], to stay below the material's thermal damage threshold. The spectrometer was referenced to the transverse optical phonon of Si at 521 cm⁻¹. Spectra were recorded in the range between 100 cm⁻¹ and 2000 cm⁻¹.

2.3.2. Microstructure

Metallographic preparations were conducted using ATMBright 200 (ATMQness GmbH, Mammelzen, Germany), employing a corundum circular saw, subsequently followed by resin embedding using Opal 410 (also from ATMQness GmbH, Mammelzen, Germany). Following solidification, the specimens were ground with SiC sandpaper (granularity 320 and 800). The surface was subsequently polished with diamond paste (9 µm) and finished with a mixture of Eposil M (colloidal SiO₂, 0.06 µm) and a 10 % H₂O₂ solution on an ATM SAPHIR 350 polishing machine (ATM Qness GmbH, Mammelzen, Germany). The samples were etched with ammonium bifluoride for 12 s according to Weck. CT images for pore distribution and defect analysis were conducted on a GE phoenix v|tome|x s240 (General Electric, Boston, USA). CT images were taken with the following parameters: 120 kV, 100 µA, 100 ms exposure time, and 1600 images per rotation. Optical imaging was carried out using a Leica light microscope (Leica Microsystems GmbH, Wetzlar, Germany). SEM analyses were performed with a scanning electron microscope (XL 30 S, Philips, Amsterdam, The Netherlands) at an accelerating voltage of 12 kV. In addition, energy-dispersive X-ray spectroscopy (EDX) was performed to determine the chemical composition of the different phases.

2.3.3. Mechanical properties

The tensile tests were performed on an Instron 1185 universal testing machine (Instron GmbH, Darmstadt, Germany) as distance-controlled tests with a constant travel speed of 1 mm/min. Five tensile specimens were tested for each investigated variant. The samples were suspended using a fully gimbaled suspension to minimize the influence of bending on the samples. The forces occurring during the test were recorded using a 10 kN load cell installed in the test frame, and the specimen elongation was measured using an MTS displacement transducer (MTS Messtechnik Schaffhausen GmbH, Stein am Rhein, Switzerland) based on an initial length of 18.8 mm.

3. Results and discussion

3.1. Debinding

After 24 h (cubes and tensile specimens) and 48 h (large cubes) in water, most of the PEG was removed from the samples (Fig. 5a). As

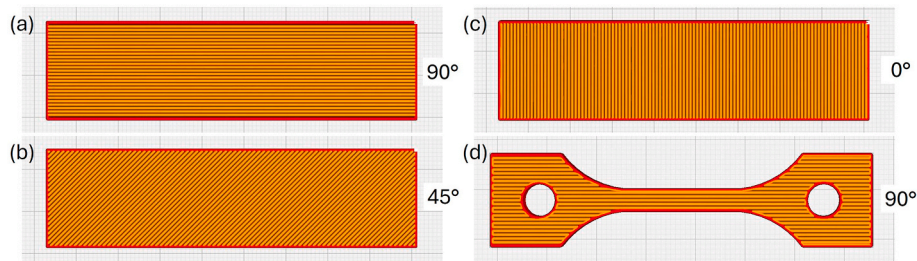


Fig. 3. Infill pattern and orientation of the (a-c) large/flat cubes and (d) the tensile specimens.

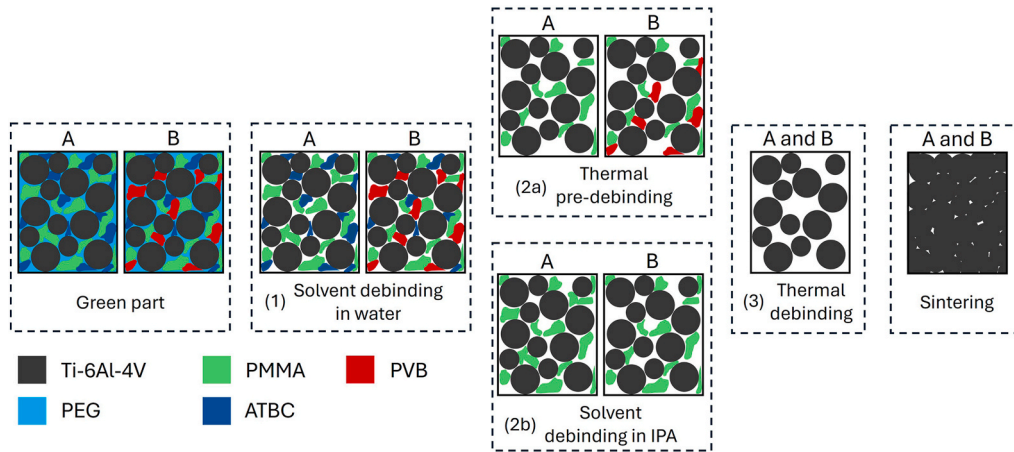


Fig. 4. Schematic overview of the two debinding routes investigated for feedstocks A and B, illustrating the progressive removal of the binder components during the debinding and sintering process. The numbered stages refer to the processing conditions given in Table 3.

Table 3
Overview of the debinding process.

Debinding step	Debinding type	Medium	Atmosphere	Heating rate	Temperature	Dwell time
1	solvent	water	-	-	30 °C	24 – 48 h
2a	thermal	-	air	0.2 °C/min	250 °C	4 h
2b	solvent	IPA	-	-	25 °C	24 – 96 h
3	thermal	-	argon	1.5 °C/min	550 °C	1 h

demonstrated in previous studies [18,19], composition A exhibits a substantially higher PEG loss compared to composition B. This is attributable to the higher proportion of PEG in binder system A, which reduces the barrier effect of the backbone polymer [41]. In addition, the presence of PVB in composition B impeded PEG removal due to hydrogen bonding between PEG and PVB chains. The debinding behavior in water was largely independent of sample geometry. Only tensile specimens of composition A exhibited a notably higher PEG loss, which is likely attributable to their large surface-to-volume ratio and the low barrier effect resulting from the high PEG content. As outlined in section 2.2.2, ATBC and PVB may result in defects and significant carbon contamination during the thermal debinding process. Therefore, PVB and ATBC were removed in a second debinding step using IPA. Fig. 5b compares the relative binder loss after 72 h in IPA to TPD, depending on the sample geometry. TPD resulted in the greatest binder loss, particularly for composition A, exceeding 85 %. The composition of sample B is likely distinct from that of sample A due to its higher ATBC and PMMA content. These components typically have a decomposition temperature lower than 250 °C (ATBC) or approximately 250 °C (PMMA) [19]. However, the binder removal with IPA is significantly higher for composition B than for A, primarily due to the solubility of PVB in alcohol. Exposure of composition A samples to IPA led to blister formation (Fig. 5c). Furthermore, cubes made of composition B exhibited cracks at the interface between the core and the peripheral regions

(Fig. 5d and e). However, this issue did not occur with the tensile specimens. Therefore, it is reasonable to conclude that this method is only applicable to samples thinner than 2 mm. This behavior is likely attributed to a differential swelling gradient established by the inward diffusion of IPA. During the initial stages of exposure, the solvent-swollen outer layers undergo volume expansion, while the unpenetrated core maintains its structural rigidity [42]. The resulting localized tensile stress concentration at the transition zone ultimately drives the initiation and growth of the observed cracks (Fig. 5d and e). For thinner samples, the penetration rate with IPA is sufficient to prevent the formation of a high concentration gradient. Consequently, to address this issue, large flat cubes were produced with composition B instead of large cubes (Fig. 2 in section 2.2.1). After 72 h, the binder removal exhibited comparable characteristics to the tensile specimens and the cubes. Fig. 5f illustrates the binder loss of samples made of composition B after different times in IPA. Binder removal increased steadily with IPA exposure time, but remained slower than PEG removal in water, despite the formation of initial porosity. Even after 24 h in water and 96 h in IPA, the theoretical soluble binder fraction of 74.6 % was not fully reached.

3.2. Sintering

The density of the sintered parts was influenced by the binder system

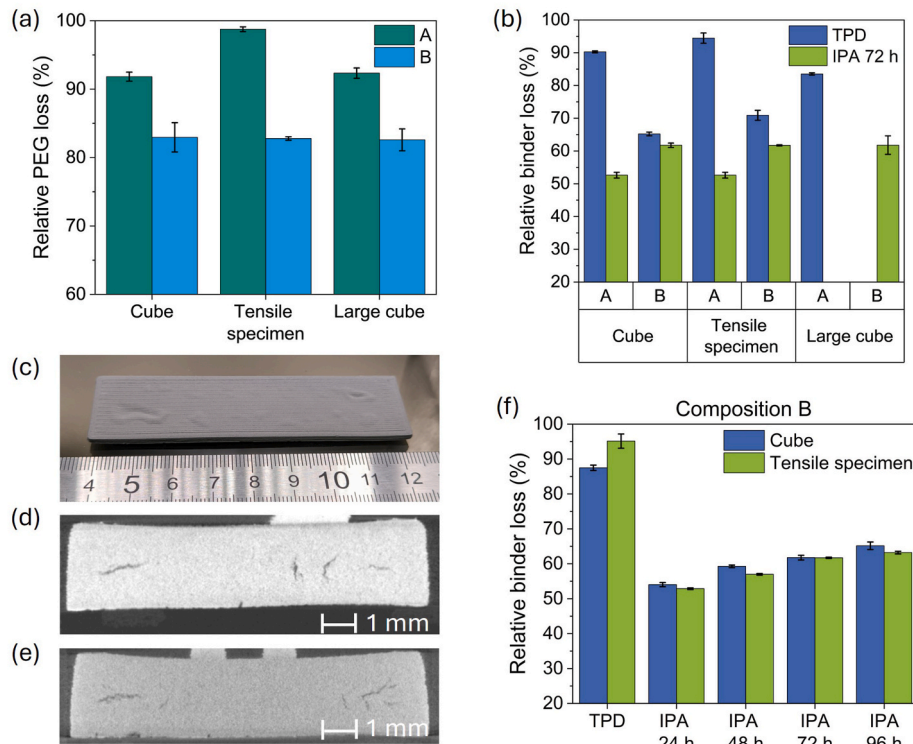


Fig. 5. Debinding behavior of composition A and B in (a) water as well as (b) in isopropyl alcohol (IPA) and through thermal pre-debinding (TPD); (c) blisters in samples made of composition A after treated with IPA; (d) and (e) CT-images of the cracks in parts with thickness > 2 mm after treated with IPA (composition B, 72 h) from 2 different sides; (f) Influence of the debinding time in IPA on the binder removed from the samples made of composition B.

and debinding method employed. Fig. 6a illustrates the relative density of samples made of both compositions. It is evident that none of the samples of composition A using TPD as the debinding method meet the relative density of 96 % standard outlined in ASTM F2885-17 [33]. While the cubes slightly exceed 95 %, the tensile specimens display values within the range of 94 and 95 %. Additionally, no significant differences were observed between the as-printed tensile specimens and those cut from the large cubes using EDM. The samples that were treated with IPA demonstrated densities below 90 %, as indicated by the presence of blisters that were generated during the debinding process. Further investigation of these samples was deemed unnecessary and thus not pursued. In comparison to the samples made of composition A, parts made of composition B and treated with IPA for 72 h showed significantly higher relative densities. In particular, the tensile specimens demonstrated values ranging from 97 to 97.5 %. However, the cubes with a lower surface to volume ratio exhibited notably lower densities due to the presence of cracks in the center of the samples

induced by the IPA. This was observed for all cubes that were treated with IPA, independent of the debinding time (Fig. 6b, blue bars). By using TPD as the debinding method, the highest densities were achieved. This behavior is likely attributable to the high carbon content within the sample, which appears to act as a sintering aid. Carbon induces a localized reduction of titanium dioxide (TiO_2) at the particle surfaces, thereby enhancing interparticle contact. In addition, the possible formation of titanium carbide (TiC) at grain boundaries suppresses grain growth, maintaining short diffusion distances necessary for pore elimination. The formation of TiC is investigated in Section 3.3 and Section 3.4. As PVB removal progresses by increasing debinding time, the density decreases. This is due to PVB acting as the primary source of carbon contamination. However, the amount of ATBC and PVB removed from the samples, which were treated with IPA for 24 and 48 h, was not sufficient to achieve a defect-free debinding process. Consequently, cracks and blisters were present. The higher surface-to-volume ratio of the tensile specimens prevented the formation of blisters for the tensile

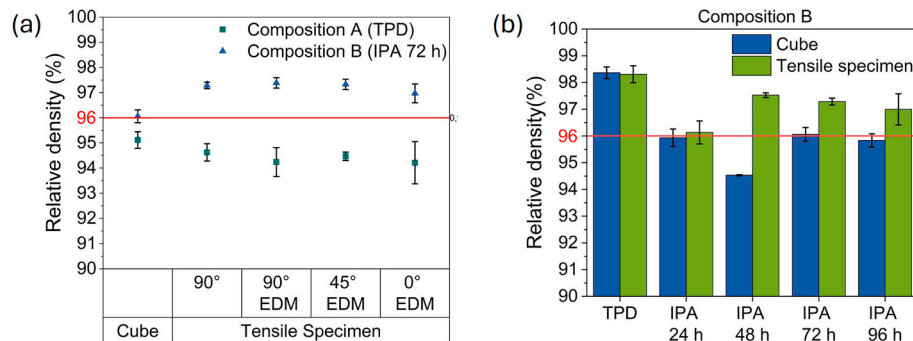


Fig. 6. Relative density of the parts after sintering. (a) parts made of composition A and B by using TPD and IPA 72 h, and (b) parts made of composition B by using TPD and IPA. The red marked values are derived from standard ASTM F-2885-17. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

specimens that were debinded in IPA for 48 h.

3.3. Element analysis

As shown in Fig. 7a, the amount of carbon and oxygen left in the samples after sintering depends on the binder system and debinding method used. Samples of composition A exhibited the lowest carbon contents, particularly when IPA was applied. However, given that this debinding method resulted in defects in the samples, it is not viable. The combination of IPA and composition B also led to a significant reduction in carbon content, primarily due to the removal of PVB before thermal debinding. Notably, combination B with IPA exhibited the lowest values for oxygen. Therefore, it is reasonable to conclude that higher concentrations of PMMA and ATBC result in increased contamination with oxygen. The highest values for carbon and oxygen were observed for composition B in combination with TPD. Fig. 7b shows the carbon and oxygen contents of parts made of composition B depending on the debinding time in IPA. While the oxygen content remains roughly on the same level, the carbon content decreases the longer the samples were in IPA. However, even after 96 h in IPA, the carbon content in the sintered samples is significantly higher than in the titanium powder utilized (0.21 wt% to 0.08 wt%), which is mainly due to the insufficient removal of PVB. For medical implants, the maximum permissible oxygen and carbon concentrations are 0.2 wt% and 0.08 wt%, respectively [33]. The carbon content is slightly higher than the values reported in the standard and literature [13,43]. However, a comparison with other binder systems is difficult, as the carbon content is seldom analyzed. The standard for oxygen is met or only marginally exceeded, despite the significant presence of oxygen atoms in the polymers of the water-soluble binder systems. The values for the oxygen content are comparable to those of traditional non-polar binder systems and are sometimes superior [13,43–45].

In order to ascertain the form in which the impurities were present, one sample each of composition A and composition B (thermal pre-binded) was examined using Raman spectroscopy. Fig. 8 shows the Raman spectra from 100 to 2000 cm^{-1} . TiO_2 , the principal agent responsible for the increase in oxygen content, is visible in the spectrum. The increase in carbon can be attributed to hydrocarbons (C-C) and elemental carbon (D, G modes). As previously mentioned, the insufficient pyrolysis of the binder components in the argon atmosphere, especially PVB is the primary cause of this observation. For this reason, the presence of elemental carbon is barely visible on the micro-Raman mappings of composition A. Furthermore, the micro-Raman mappings indicate that the impurities are almost homogeneously distributed over a large area.

At a higher magnification level of 100 $\times$, additional impurity forms become visible. Apart from the hydrocarbons, the presence of TiC has been detected in every area investigated for composition A (Fig. 9a–c). However, elemental carbon (D, G modes) was not detected. Without the insufficient pyrolysis of PVB, elemental carbon generation is minimal.

This is a continuation of the findings at lower magnification. Additionally, trace amounts of the sinter base yttria (Y_2O_3) are present in parts of the sample. Hydrocarbons, TiC and Y_2O_3 were also found in every area screened for composition B (Fig. 9d–e). Furthermore, elemental carbon (D, G modes) was detected in some areas. Notably, the impurities are not distributed evenly at this magnification, whether for composition A or composition B. This is likely attributable to the size of the titanium powder particles and the distribution of the binder. The former metal particles are nearly pure, while the area between the particles (the area adjacent to the new grain boundaries) contains polymer residues. Additional Raman spectra and micro-Raman mappings of more areas can be found in the [supplementary material \(S1 and S2\)](#).

3.4. Microstructure

The microstructure of the cross sections of the sintered small cubes was analyzed using light optical microscopic analysis and SEM. For composition A (TPD), optical micrographs (Fig. 10a) and backscattered electron (BSE) images (Fig. 10b) obtained after Weck etching reveal the characteristic lamellar ($\alpha+\beta$) microstructure of Ti-6Al-4V. The α/β distribution was 90.9 % to 9.1 %, which is close to the theoretical value of 91 % to 9 % [46]. The α -colonies exhibit widths of approximately 5–15 μm and lengths of up to 100 μm . As the samples demonstrated the lowest relative densities (95 %), large pores are also apparent and are a result of the sintering process. These observations align with the microstructure described in literature [13,16]. In contrast, the number and size of the pores decrease for the sample made of composition B with TPD (Fig. 10c). In addition, the sample showed shorter and more diffused α -colonies. This is likely attributable to the high carbon content of 0.94 wt%, which resulted in a more inhomogeneous nucleation of the α -phase within the β -phase. BSE images revealed the presence of carbon and its compounds in the form of granular phases, with a proportion of 6.9 % (Fig. 10d). EDX analysis confirmed the presence of titanium and carbon in these granular phases. These findings are consistent with the results from Raman spectroscopy, which revealed the presence of TiC, elemental carbon, and hydrocarbons. As this phase is only observed in samples of composition B, it is likely the result of insufficient pyrolysis of PVB during thermal debinding. Since carbon was also detected in the other phases, it is reasonable to conclude that these carbon-rich granular phases are likely composed of TiC. Due to the high proportion of TiC, and because carbon and oxygen stabilize the α phase, the proportion of the β phase declined to 6.8 %. After a 24 h debinding period in IPA, a substantial decrease of the TiC proportion is apparent (2.5 %), along with an increase in the length of the α -colonies (Fig. 10e–f). However, the number of pores increased due to the lower relative density. After 48 h, a further decline in the number of the TiC phases is observed (S3). At 72 h in IPA, the lower proportion of TiC (1.6 %) results in a further increase in the length of the α -colonies (Fig. 10g). Moreover, there is a tendency for the TiC phases to form lines (Fig. 10h). These TiC lines extend across grains and are not confined to grain boundaries. This

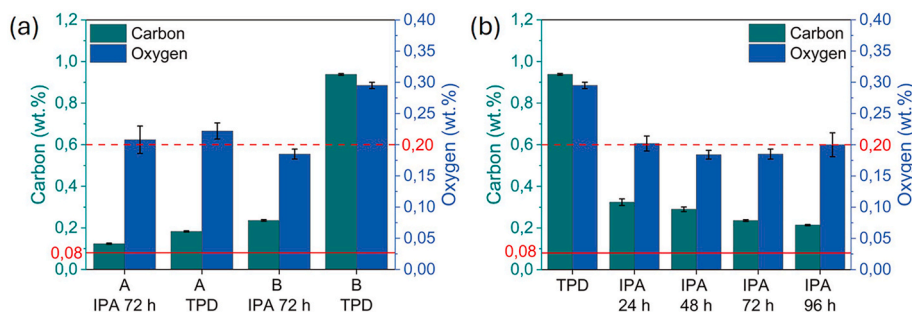


Fig. 7. Carbon and oxygen content of (a) composition A and B with different debinding strategies and (b) composition B with different debinding times in isopropyl alcohol (IPA). The red marked values are derived from standard ASTM F-2885-17. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

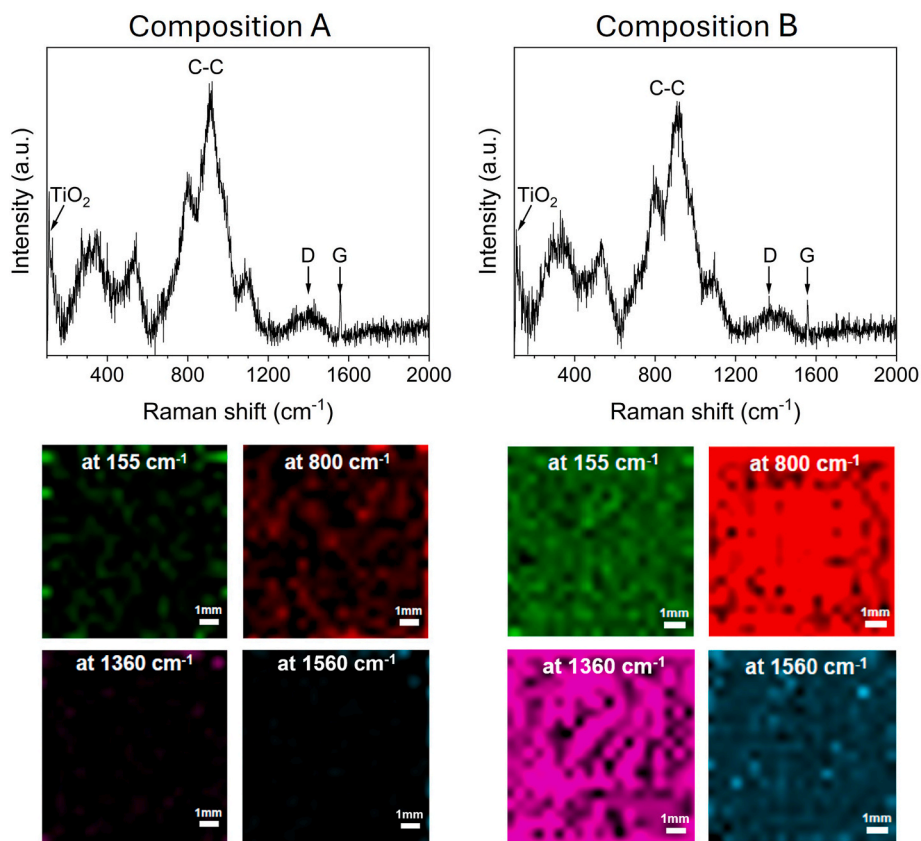


Fig. 8. Raman spectrum of samples made with composition A (TPD) and composition B (TPD) and micro-Raman mappings at 155 cm^{-1} , 800 cm^{-1} , 1360 cm^{-1} , and 1560 cm^{-1} .

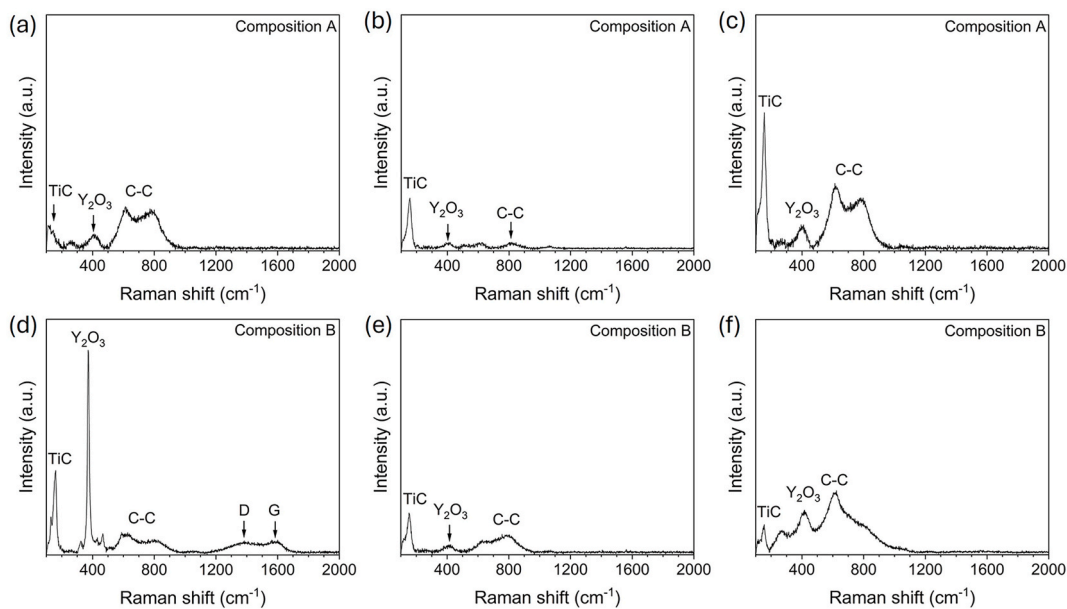


Fig. 9. Raman spectra of a sample made with composition A (TPD) and composition B (TPD) at each of three different positions, viewed at a higher magnification level of $100\times$.

behavior becomes more evident at 96 h in IPA (S4).

3.5. Tensile tests

The ultimate tensile strength (UTS) and the elongation to failure of

the samples made of composition A are displayed in Fig. 11a. To enhance the assessment, the values for UTS and elongation described in ASTM F2885-17 [33] have been included and highlighted in red. The UTS values required are 780 MPa without hot isostatic pressing (HIP) and 900 MPa with HIP, along with 10 % for elongation in both cases. The

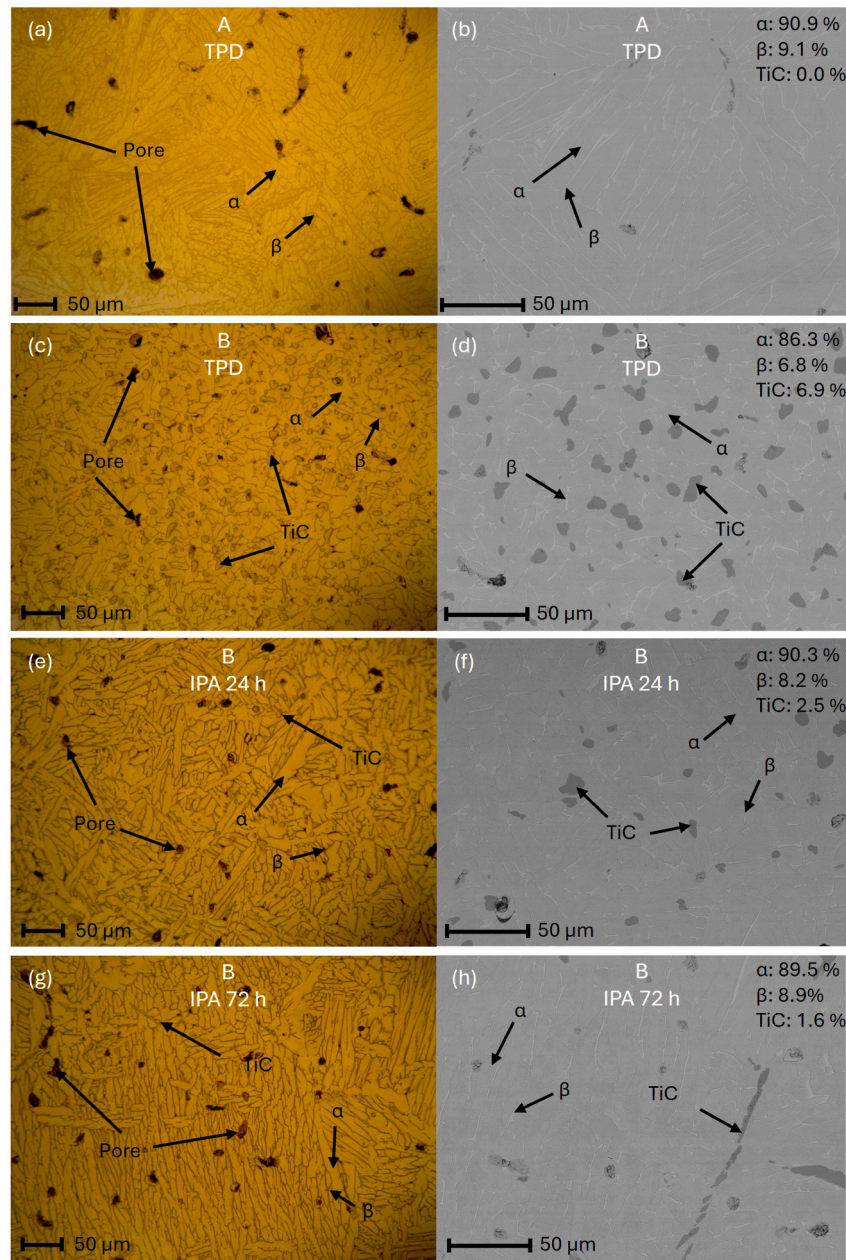


Fig. 10. Microstructure of the cross section of the small cubic samples depending on the debinding method; (a) optical image and (b) BSE image of composition A (TPD), (c) optical image and (d) BSE image of composition B (TPD), (e) optical image and (f) BSE image of composition B (IPA 24 h), (g) optical image and (h) BSE image of composition B (IPA 72 h). The optical images are magnified 32 $\times$, while the BSE images are magnified 500 $\times$. The α / β /TiC distribution was determined based on the area proportions. The samples were etched with ammonium bifluoride for 12 s according to Weck.

ultimate tensile strength (UTS) of the specimens with a 90° orientation consistently exceeded the required threshold of 780 MPa. This was observed in both the as-printed samples and those machined from large cubes via EDM. However, the as-printed samples showed significantly lower UTS values. This observation is probably related to the elevated surface roughness of parts produced by FFF [8]. In contrast to the strength, neither specimen type consistently achieved the specified 10 % elongation, with both demonstrating comparable results accompanied by high standard deviations. Analysis of the specimens machined from the large cubes highlights the influence of layer orientation. Specifically, both the 45° and 0° orientations exhibited inferior tensile strength and elongation. The results are consistent with the findings reported in the literature, which indicates that 90° demonstrated optimal UTS and elongation values, while 0° exhibited the poorest performance [23,47].

However, this behavior always strongly depends on the printing and sintering step. Pores related to printing have been identified along the strands and between the layers of samples made entirely of polymers, as well as in green bodies [48,49]. If the pores are sufficiently large, they may not fully disappear during the sintering process [12,50].

However, these regularly distributed pores along the deposited strands were not visible in the microstructure. The mechanical properties can also be influenced by pores induced by the printing process itself. These include temporary interruptions in material flow caused by nozzle clogging or underextrusion resulting from irregular filament diameters or feeding issues, such as filament grinding. As illustrated in Fig. 11b, the latter mechanism was predominant here. All cubes exhibited distinct pores along the deposited strands; however, these pores were limited to specific areas of the samples. These defects are the

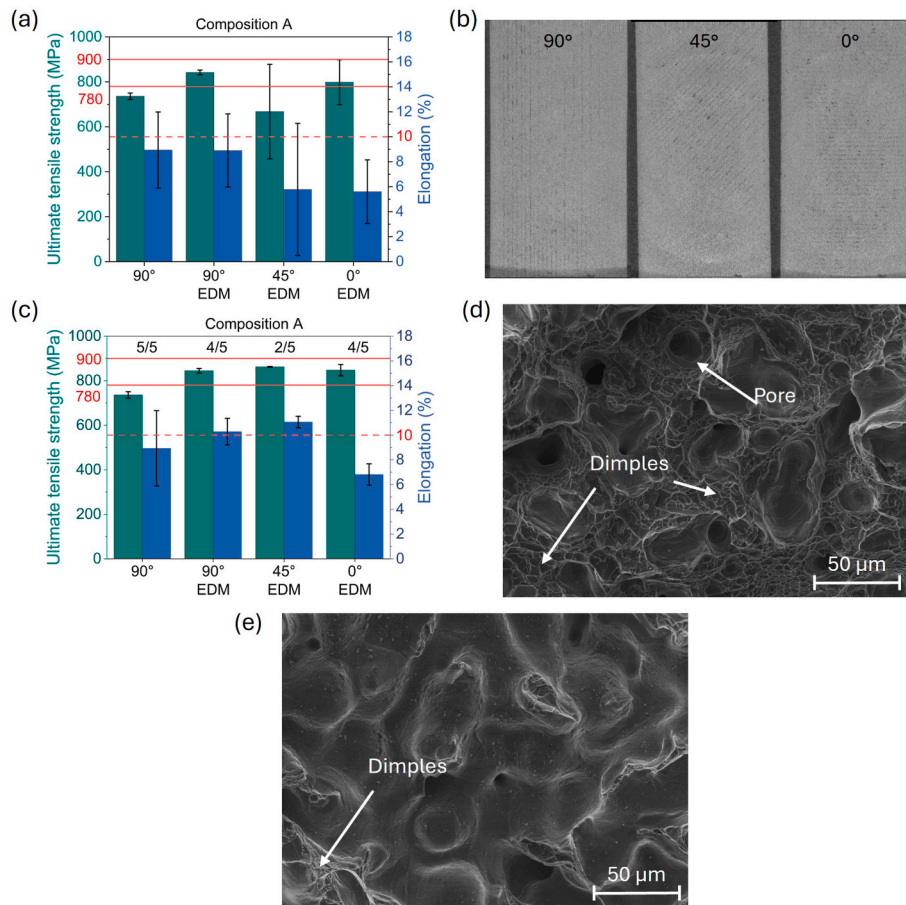


Fig. 11. (a) Ultimate tensile strength and elongation of tensile specimens made of composition A and infill orientation (TPD), (b) CT-images of print related defects in the large cubic samples made of composition A, and (c) ultimate tensile strength and elongation of tensile specimens made of composition A and infill orientation (TPD) without the non-valid specimens. The samples cut by EDM of the large cuboidal samples (Fig. 2c) are marked with EDM. Five tensile specimens were tested for each variant. The numbers indicate how many tensile specimens were valid. The red marked values are derived from standard ASTM F-2885-17. SEM image of the fracture surface of (d) a valid tested tensile specimen (45°) and (e) a non-valid tensile specimen (45°). The SEM images are magnified 500×. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cause of the anisotropic behavior observed across the different layer orientations. When the strands are aligned parallel to the loading axis, load transfer can still occur. Conversely, at layer orientations of 45° and 0°, stress concentration at the inter-strand pores can lead to premature failure, as the load cannot be effectively transferred to adjacent strands. These localized defects also account for the high statistical deviations in UTS and elongation, as they were restricted to particular regions of the large cubes. Specimens without these defects demonstrated excellent mechanical performance. Consequently, because these major print-induced defects misrepresent the material capabilities, and to demonstrate the true potential of the feedstock, specimens exhibiting an elongation below 1 % were classified as non-valid and excluded from Fig. 11c. In comparison to Fig. 11a, the UTS of all machined specimens was distinctly above the required 780 MPa. However, only the specimens with an orientation of 90° and 45° achieved the target 10 % elongation, whereas the 0° specimens exhibited values between 6 % and 8 %. Therefore, it is reasonable to conclude that the layer orientation exerts influence on the elongation, at least for the samples made of composition A.

Fig. 11d shows the fracture surface of a valid tensile specimen with a layer orientation of 45°, which was examined by SEM. The surface is characterized by a homogeneous distribution of fine dimples over the entire fracture area, which is indicative of a ductile fracture mechanism. In addition, isolated residual pores originating from the sintering process can be observed. Comparable fracture characteristics were identified for specimens with all investigated layer orientations. In contrast,

the fracture surfaces of non-valid tensile specimens exhibit markedly different features, as illustrated in Fig. 11e. A limited number of dimples are present, while large regions of the fracture surface resemble the typical morphology of a sintered component. This observation suggests that the previously described print-induced porosity may have hindered effective interlayer and interstrand bonding, thereby preventing proper coalescence and leading to premature failure.

Samples made of composition B demonstrated superior values for UTS and elongation when compared to those made of composition A (Fig. 12a). This is primarily attributable to the higher density of composition B, which is approximately three percentage points higher (97 % to 94 %). The slightly elevated carbon content of composition B seems to have negligible influence on the elongation, in comparison with the influence of the density. Regarding the UTS, all samples met the standard of 780 MPa. Tensile specimens cut from the flat cubes nearly attain 900 MPa, a threshold exclusively necessary for components that undergo densification via hot isostatic pressing. As with the samples made of composition A, the as-printed samples again demonstrated inferior values for UTS and elongation compared to the samples cut from the cubes. This is likely attributable to the higher surface roughness of the as-printed parts. In contrast to the tensile specimens made of composition A, no remarkable difference can be observed between the different layer orientations. This suggests that the print-related pores between the strands and layers may become negligible when using an optimized binder system.

The influence of the debinding method, and thus the carbon content

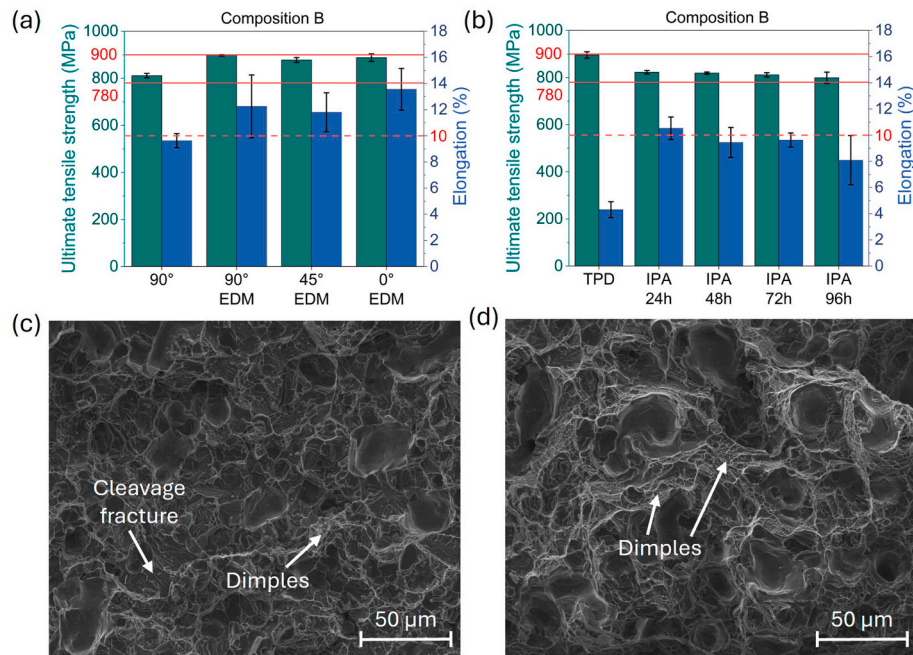


Fig. 12. Ultimate tensile strength and elongation of tensile specimens made of composition B depending on (a) infill orientation (IPA 72 h) and (b) debinding method. The samples cut by EDM of the flat cuboidal samples (Fig. 2d) are marked with EDM. The orientation of the as-printed tensile specimens (Fig. 2b) was 90°. Five tensile specimens were tested for each variant. The red marked values are derived from standard ASTM F-2885-17. SEM image of the fracture surface of (c) a tensile specimen debinded by TPD and (d) a tensile specimen debinded by IPA 72 h. The SEM images are magnified 500 $\times$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and the density, on the mechanical properties is displayed in Fig. 12b. The highest density (98.3 %), but also the highest carbon (and oxygen) content, is induced by thermal pre-debinding (TPD). As observed in the microstructure section, the carbon in form of TiC is evenly dispersed throughout the sample and created short and diffused α -colonies. Furthermore, the significant mismatch in Young's modulus between the Ti-6Al-4V matrix and the TiC particles induces substantial stress concentrations at their interfaces. Consequently, interfacial debonding occurs between the particles and the matrix, initiating micro-crack formation. This results in embrittlement of the samples, leading to a high UTS of nearly 900 MPa and a low elongation of 4.3 %. According to Ref. [51], the impact of the impurities on the mechanical properties can be calculated by the oxygen equivalent $O_{eq} = O + 0.75C$, indicating that the influence of oxygen is slightly higher than that of carbon. Table 4 presents the calculated oxygen equivalent, contingent on the debinding method utilized. The employment of IPA in the debinding process results in a lower value of O_{eq} , which decreases with increasing time in IPA. In addition, the α -colonies exhibited an increase in size. Consequently, the UTS decreases. Surprisingly, the elongation also decreases. This finding contradicts the observations reported in Ref. [51], where a pronounced decrease in ductility was noted over an O_{eq} value of 0.4 wt%. Therefore, factors such as density and defects also exert a substantial influence on the mechanical properties. Despite exhibiting the lowest values in density (96.1 %), the samples that were in IPA for 24 h are the only

components that meet the standard of 10 % elongation. However, the low density is a result of blisters in the heads of the tensile specimens. The gauge length did not exhibit any defects. Therefore, the result must be interpreted with caution. The decline in the specimens exposed to IPA for 96 h can be attributed to a single specimen that exhibited a relatively low density of 95.8 %, compared to the other samples in this group (97.2–97.5 %). Consequently, it also showed the lowest elongation, at 4.9 %. Excluding this specimen, the elongation increases to approximately 9 %. This behavior is most likely due to a printing-induced defect and can be regarded as a statistical outlier.

An analysis of the fracture surfaces of tensile specimens debinded using the two different debinding approaches, TPD and solvent debinding with IPA, reveals subtle differences (Fig. 12c and d). Specimens subjected to TPD, which exhibited lower elongation at break, show a reduced density of dimples compared to those debinded using IPA. Moreover, localized regions exhibiting cleavage fractures suggest the occurrence of a partially non-ductile fracture mechanism.

A comparison with the results of other extrusion-based AM technologies was only possible to a limited extent, since only three publications addressed the mechanical properties of the manufactured Ti-6Al-4V parts. In all of the publications, binder systems were used, in which organic solvents were required for solvent debinding. The findings of Singh et al. [13,15] demonstrated a substantial variability in UTS (500–900 MPa) and elongation (1–17 %), predominantly influenced by density and the presence of carbon and oxygen after sintering. An increase in density is accompanied by an increase in UTS and elongation. In contrast to the findings of the present study and those reported in the literature on metal injection molding [31,52], the UTS of the samples decreased with increasing oxygen content. The highest values recorded in the third publication were 720 MPa for UTS and 9 % for elongation, which is notably lower than the results obtained in this study [53]. The prevailing SLM process demonstrated higher UTS values (960–1300 MPa), while the elongation exhibited inferior outcomes compared to MF³ (1–10 %) [54–56]. The process of SLM results in the formation of a particularly fine lamellar microstructure, a consequence

Table 4

Influence of the debinding method on the tensile specimens of composition B, regarding the contamination with carbon, oxygen, and the calculated oxygen equivalent.

Debinding method	C (wt%)	O (wt%)	O_{eq} (wt%)
TPD	0.94	0.30	1.00
IPA 24 h	0.32	0.20	0.44
IPA 48 h	0.29	0.18	0.40
IPA 72 h	0.24	0.19	0.36
IPA 96 h	0.21	0.20	0.36

of the rapid cooling that occurs during the fabrication process. Additionally, the presence of residual stress further reduces elongation.

4. Conclusion and outlook

The present study investigated the influence of binder system, debinding strategy, impurity content, and layer orientation on the physical, chemical, and mechanical properties of Ti-6Al-4V components manufactured by MF³. The main conclusions can be summarized as follows:

- The binder system and the debinding process affected relative density, oxygen and carbon contamination, and, consequently, the mechanical properties of the manufactured components.
- Thermal pre-debinding proved to be a viable option only for the PVB-free feedstock (composition A), resulting in relative densities of 94 to 95 %. However, when applied to PVB-containing systems, this approach led to significantly increased oxygen (0.3 wt%) and carbon (0.94 wt%) contents compared with the limits specified in ASTM F2885-17. Despite this, the elevated carbon content promoted sintering, yielding the highest densities (up to 98.4 %) for composition B.
- The utilization of IPA in the debinding process reduced oxygen and carbon contamination in PVB-containing feedstocks. After 96 h in IPA, the carbon content decreased to 0.21 wt%. However, this method was limited to parts with thicknesses below approximately 2 mm, restricting its applicability to thin or small components. Relative densities obtained by IPA debinding were slightly lower (97–97.5 %) compared to TPD.
- Layer orientation exhibited no statistically significant influence on mechanical properties when an optimized binder system was used. Instead, density, print-induced porosity, and impurity content were identified as the dominant factors. Composition B yielded the most favorable mechanical performance, achieving ultimate tensile strengths of up to 900 MPa and elongations of up to 13.5 % after 48–72 h of IPA debinding. In contrast, composition A suffered from pronounced print-related defects, resulting in inferior mechanical performance and increased failure rates, particularly for specimens machined from large cubes. However, composition A can be a viable option for large components if the print-induced defects are prevented and hot isostatic pressing is applied to increase the density.

For targeted medical implant applications, the combination of the PVB-based feedstock (Composition B) and an IPA solvent debinding step of 72 h is recommended. This strategy consistently yields components that fully comply with the relative density (>96 %), oxygen content (≤0.20 wt%), and mechanical properties specified by ASTM F2885-17. However, achieving complete standard compliance is currently limited by elevated carbon levels (0.21–0.32 wt%) and a geometry constraint restricting part thickness to under 2 mm to prevent debinding-induced defect formation. Therefore, future work will focus on the design of alternative infill architectures, such as gyroid or cubic structures with reduced infill density, to prevent crack formation during solvent debinding, enhance binder removal, and further reduce carbon contamination. Additionally, mixed solvent systems based on water and IPA will be explored to accelerate debinding while minimizing defect formation. However, in the long term, it would be advisable to search for a substitute for PVB that has similar properties but leaves no impurities in the samples.

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CRediT authorship contribution statement

Ralf Eickhoff: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Steffen Antusch:** Investigation, Methodology, Writing – review & editing. **Iwiza Tesari:** Investigation, Methodology, Writing – review & editing. **Martin Mikulics:** Investigation, Methodology, Writing – review & editing. **Hilde Helen Hardtdegen:** Investigation, Methodology, Writing – review & editing. **Dorit Nötzel:** Investigation, Writing – review & editing. **Aycan Kutlu:** Investigation, Methodology, Writing – review & editing. **Thomas Hanemann:** Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ralf Eickhoff reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Steffen Antusch reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Iwiza Tesari reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Martin Mikulics reports financial support, administrative support, and equipment, drugs, or supplies were provided by Research Centre Jülich. Hilde Helen Hardtdegen reports financial support, administrative support, and equipment, drugs, or supplies were provided by Research Centre Jülich. Dorit Nötzel reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Aycan Kutlu reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Thomas Hanemann reports financial support, administrative support, article publishing charges, and equipment, drugs, or supplies were provided by Karlsruhe Institute of Technology. Thomas Hanemann reports administrative support and equipment, drugs, or supplies were provided by University of Freiburg. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.msea.2026.150905>.

Data availability

Data will be made available on request.

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