BIOCOMPATIBLE TiNbTaSn-BASED ALLOYS OBTAINED BY RECYCLING

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Abstract

This paper was prepared as a part of research and development activities carried out within the framework of the project of the Technology Agency of the Czech Republic reg. no. FW06010136. The aim is to design technological procedures to produce biocompatible alloys, to verify these procedures for the content of undesirable gases and inclusions. Piece semi-finished products in the state of Ti in the G1 grade from a tubular sputter target, Nb in the form of sheared from a sputter target, Ta in the form of evaporative springs, Sn is in the form of reworked blanks. The processing procedure was designed on modern metallurgical technology using plasma melting in a cold crucible. This reprocessed medical grade TiNbTaSn alloy was subsequently reworked into a semi-finished product by suitable ultrasonic atomization on a titanium core platform. The powder thus produced in the 10 to 100 μm fraction was submitted to further downstream experiments. The possibilities of 3D print of the prepared powder were tested.

Keywords: Plasma metallurgy, titanium scrap, titanium alloys, recycling, atomization

1. INTRODUCTION

Titanium holds a prime position in aerospace, biomedical, automotive, and chemical processing industries due to unique features: low density, higher tensile strength, higher operating temperature, excellent corrosion resistance, forgeability and castability [1]. The major resource for recycling titanium is in-house Ti scraps generated during smelting and fabrication processes instead of post-consumer Ti products. Although the nominal recycling ratio of post-consumer Ti products is low, the actual recycling rate including cascade recycling in the smelting and fabrication industry is high. The major impurities in Ti scrap are oxygen and iron. High-grade Ti scrap with low O and Fe concentrations is used for remelting Ti and its alloys. At present, the melting methods of titanium mainly include vacuum arc melting (VAR), electron beam cold hearth melting (EBCHM), vacuum induction melting (VIM) and plasma arc meting (PAM). Technologies for the anti-contamination or efficient O and Fe removal must be developed for the efficient utilization of Ti [2, 3]. The separation and control of undesired elements are key to recycling scrap or end-of-life (EoL) metal products, as the quality of regenerated metals is often impaired by contamination from the alloying elements in the scrap [4]. Recycling titanium scraps to produce ingots can reduce energy consumption and CO_2 emissions by approximately 95 % [5].

Titanium scraps such as swarf (or cutting chips, turnings) generated in the fabrication of titanium alloy parts, are collected and cleaned to remove impurities such as oil and tool fragments. The cleaned scraps are then recycled by remelting. The concentration of oxygen, the major impurity in titanium scrap, inevitably increases after remelting, and, hence, high-grade titanium ingots cannot be produced from titanium scrap only. In practical alloy production, the oxygen concentration in titanium alloys is suppressed by remelting the titanium scrap with a low-oxygen virgin titanium sponge [2]. Low density inclusions mainly come from nitrogen and oxygen contamination of titanium. These inclusions are difficult to detect and are the most harmful defects of titanium. With the increase of nitrogen, β, α and δ phases form respectively [6].

Ti-5553 alloy (nominal composition Ti-5Al-5V-5Mo-3Cr wt%) is one of the most recently developed commercial metastable beta titanium alloy which has been used by Boeing in manufacturing of 787 aircraft body structures and landing gears. Hot pressing was used to recycle Ti-5553 machining swarf to turn the waste into useful material. Hot pressing is a viable processing route to recycle Ti swarf to cost-effectively produce a qualified solid material for post-processing and engineering applications. After hot pressing, double-aging treatment (HT-600 ºC/4 h + 700 ºC/0.5 h) provides optimized microstructure composing of desirable shape, size and proportion of the α phase precipitates [7].

The most promising ways are the technologies based on severe plastic deformation, such as equal-channel angular pressing, solid-state field-assisted sintering technology-forge, and the Conform process [8]. Titanium-recycled powder for additive manufacturing is mainly produced using gas atomization techniques. The continuous extrusion process (Conform^{TM}) was employed to consolidate waste titanium alloy feedstocks in the forms of gas atomized powder and machining swarf into wire [9]. Samples of wire were further cold-drawn down to 40% reduction, using conventional wiredrawing equipment. Recent advances in additive manufacturing, wherein the desired components are directly 3D printed from pre-alloyed powders/wires have given a definite advantage for cost-prohibitive titanium alloys [10].

Our previous article [11] described experiences with a preparation of titanium alloys by using plasma metallurgy including chemical analyzes of the input and remelted material, an analysis of structural characteristics using light and electron microscopy and a measurement of selected mechanical properties. The obtained results imply that recycling of titanium scrap using remelting is possible and feasible. The goal of our activities is to develop and verify technological processes leading to the fully industrial production of Ti alloys in the form of a powder semi-finished product using waste. The proposed technological processes will be used for the manufacture of ingots corresponding to semi-finished products for industrial atomization using inert gas - i.e. the contactless technology of atomization of reactive metals and the manufacture of products with a high degree of added value. The aim of this work is preparation of biocompatible TiNbTaSn-based alloys obtained by recycling in the form of powders by ultrasonic atomization.

2. METHODOLOGY

The Advanced Metal Powders (AMP) is the only Central European processor and manufacturer of titanium alloys and custom powders for additive technologies. AMP forms a successful research team together with CTU (Prague).AMP has two types of metallurgical plasma furnaces designed as a manufacturing line for the production of powders for additive technologies: H-PAM (plasma furnace with a horizontal crystallizer) for the production of pre-alloys and processing of raw materials into bars and V-PAM (plasma furnace with a vertical crystallizer) for the production of ingots for atomization.

These technological equipment are designed to produce powders suitable for research purposes. Next equipment: laboratory atomizer working on the principle of ultrasound, digital microscope with image analysis, networking station under inert gas, XRF chemical composition analyzer calibrated for non-ferrous metals. Aim of the research and development is to develop the efficient technological processes that preserve the high quality of the feedstock while being highly competitive.

Problem definition: Quality dimensions, raw materials, quantities, homogeneity, chemical composition, production volume. At the same time, there was a demand for scrap suitable for reprocessing - the need to develop a new technology - a crystallizer and a plasmatron. As technologies were used: developed separation process – optical separation, plasma technology with electrically bonded arc plasma, ultrasonic laboratory scale atomization, horizontal recycling crystallizer (developed by AMP), water jet cutting technology, vibratory sieving with combined ultrasonic oscillations. As basic materials were used: pure Ti, Nb, Ta, Zr, ..., alloys Ti64 (TiAl6V4), Ti6246 (TiAl6Sn2Zr4Mo6), TiNbTaSn, etc. Using anodization in the bath and optical separation. Scrap may be contaminated with other metals (stainless steel, CoCr alloys...).

3. EXPERIMENT

Research on physical properties of the scrap, based on which can be separated. As scrap metals were used: Ti target cut-up to strips, Nb wire and sheets, Ta springs, Sn rods – see **Figure 1**.

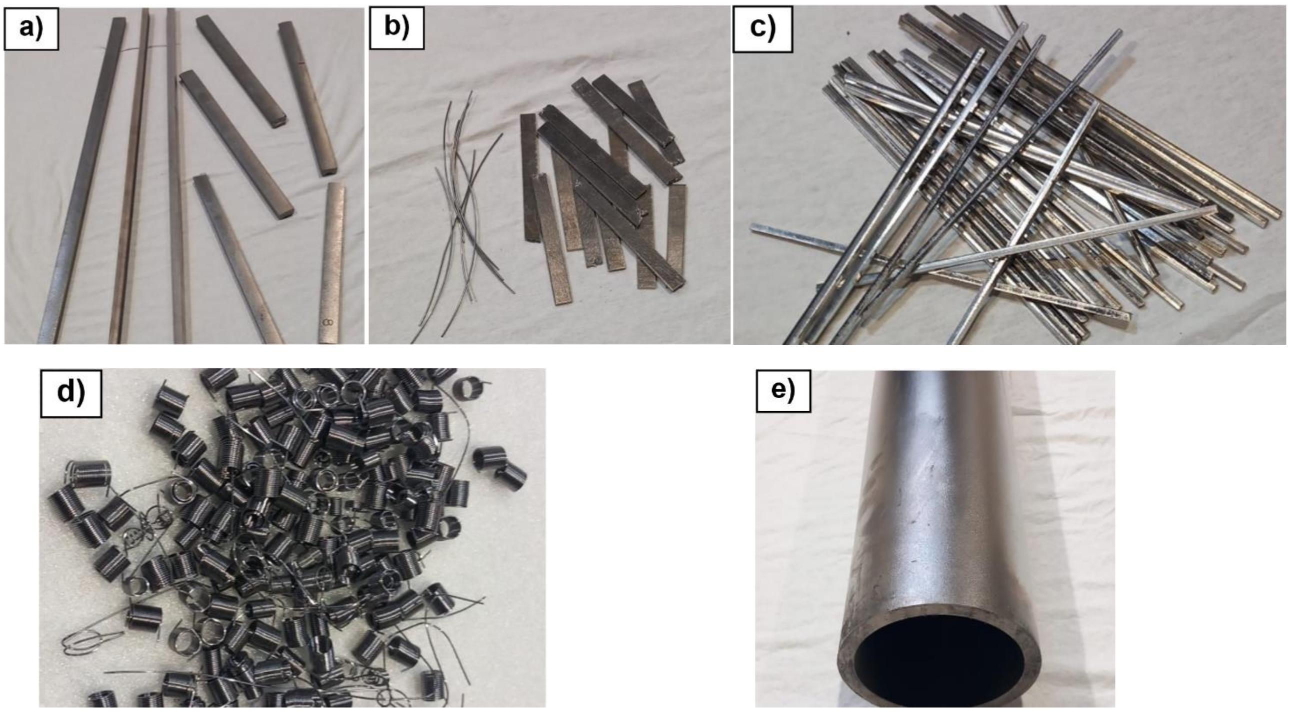


Figure 1 Shape of input scrap materials for plasma melting: a) TiG1, b) Nb, c) Sn, d) Ta, e) TiG1 PVD target

The input material for the preparation of the TiNbTaSn alloy was first chemically purified, chemical analyzes and weighings were carried out according to the stoichiometric composition of the alloy. Raw material was testedy with XRF technology. The metal samples were prepared by cutting them to a size and shape suitable for melting in a plasma furnace. This was followed by the placement of the lead in the copper crystallizer in such a way as to obtain as homogeneous an ingot as possible in the entire volume - see **Figure 2**.

Figure 2 The method of distributing the input material to the H-PAM copper crystallizer.

The TiNbTaSn alloy was remelted several times in H-PAM according to the procedure described in [11] to achieve the required homogeneity. The result of the melting was four rods with an oval cross-section and a length of 180 cm. The next step was to obtain an ingot of circular cross-section with a diameter of 70 mm and a length of 100 cm by melting in V-PAM under pure argon.

Table 1 shows the chemical composition of the TiNbTaSn alloy after the plasma melting process. The composition of the alloy corresponds to the assumptions.

Table 1 Chemical composition of TiNbTaSn alloy after plasma melting – XRF analysis (wt%)

Element	**Ti**	**Nb**	**Ta**	**Sn**
Required	64 - 65	23 - 24	3.5 - 4	7 – 8.5
Measured from bars	64.5	23.8	4	7.7

The obtained ingot was subsequently cut using a water jet and reforged into bars using forming - hot + cold forging. **Figures 3** and **4** document the microstructures (Olympus DSX1000 and Carl Zeiss Jena Neophot 32).

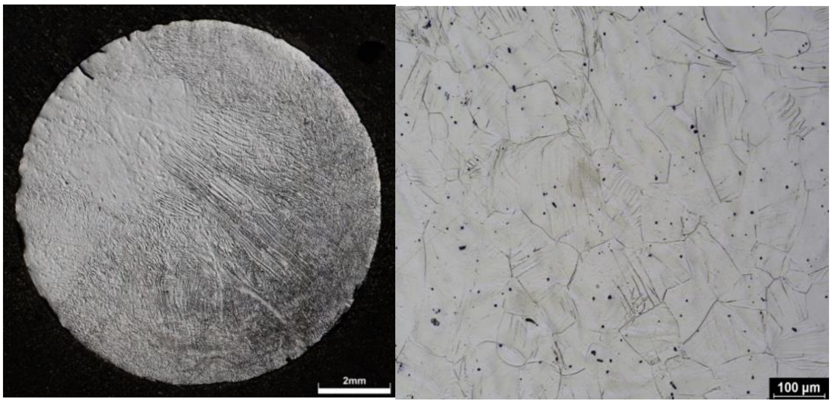


Figure 3 Macrostructure (left) and microstructure (right) of the hot-forged TiNbTaSn specimen ø 10 mm

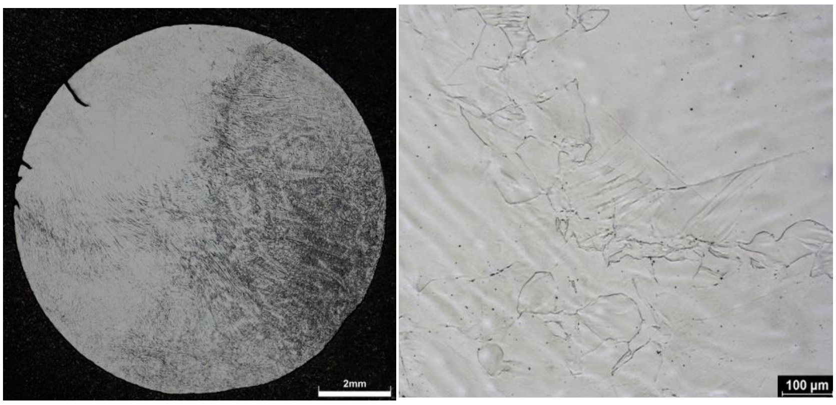


Figure 4 Macrostructure (left) and microstructure (right) of the cold-forged TiNbTaSn specimen ø 10 mm

The microstructure hot-forged specimen of TiNbTaSn (**Figure 3**) shows the partial recrystallization process took place during the hot forging. On the overview (**Figure 3** left) the signs remaining after the forging process are still visible, yet in certain areas (**Figure 3** right) the microstructure has the recrystallized character. In the case of cold-forged specimen (**Figure 4**) both overview and detail view of the microstructure are indicating on the forging process that took place – see deformed grains in the **Figure 4** right). The microstructure of both states of the alloy consists of polyedric grains that are characteristic for β titanium alloys – the deformation of grains is caused by forging process since there was no homogenizing heat treatment afterwards.

For both hot-forging and cold-forging the forging folds do appear on the surface of the specimens and thus may cause undesired contamination of the alloy during the subsequent processing.

Table 2 Results from the mechanical testing of hot-forged and cold-forged TiNbTaSn specimens

Specimen	$R_{p0.2}$ (MPa)	R_m (MPa)	*A* (%)	Hardness HV_1
Hot-forged	622 ±6	759 ± 14	9 ± 1	246 ± 6
Cold-forged	659 ±21	725 ± 4	17 ± 3	236 ± 1

Results of the tensile test (conducted on Instron 5582) are shown in the **Table 2** while the plotted force-displacement graphs of the tensile tests are being shown in the **Figure 5**. There are slight discrepancies between hot-forged and cold-forged specimens. Hot forged ones are having a little higher ultimate tensile strength while the yield stretch is lower when compared to cold-forged specimens. The elongation of the material has almost the double value in the cold-forged specimens when compared to hot-forged ones. The hardness remains almost the same.

The behavior of the specimens during the testing has been almost identical as shown in the force-displacement graphs shown in the **Figure 5**. The only differences in behavior are noticeable in the case of hot-forged specimens (drawn in red). They are caused by partial recrystallization occurring during the hot-forging process which is noticeable on the microstructure of the hot-forged specimens (**Figure 4**). Results of mechanical testing cannot be directly compared since the alloy isn't standardized. The properties of this alloy manufactured by casting are available in the article [12] which however does not state exact values. Values of yield strength and tensile strength presented in this article are slightly lower than those presented in [12].

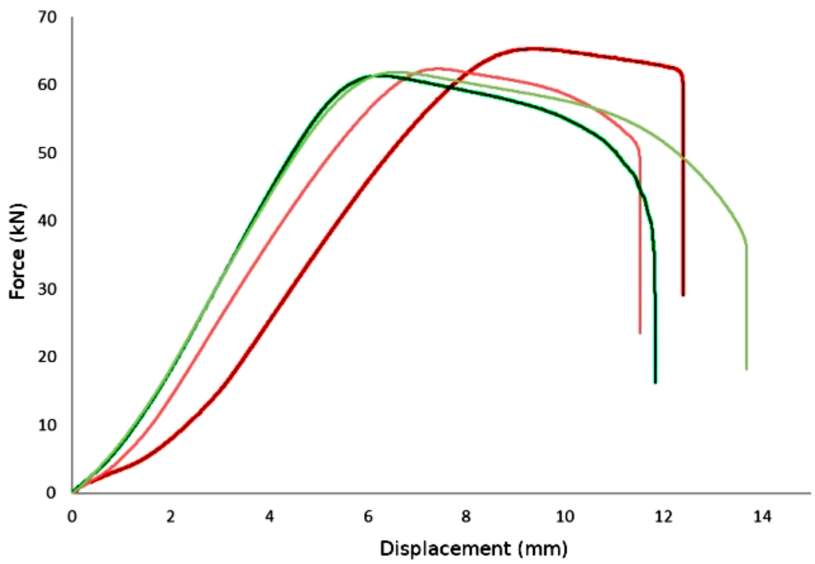


Figure 5 Tensile test of cold-forged (green) and hot-forged (red) TiNbTaSn specimens

Ultrasonic atomization: The atomization process was implemented on a modified atomization platform core for two reasons. The first is the life of the core, which is very quickly worn by this alloy, and the second was the prevention of cross-contamination. The optimization of the evaluation parameters enabled us to produce in a volume of 0.1 l/hour.Morphology of the atomized TiNbTaSn powders is visible in the **Figure 6**.

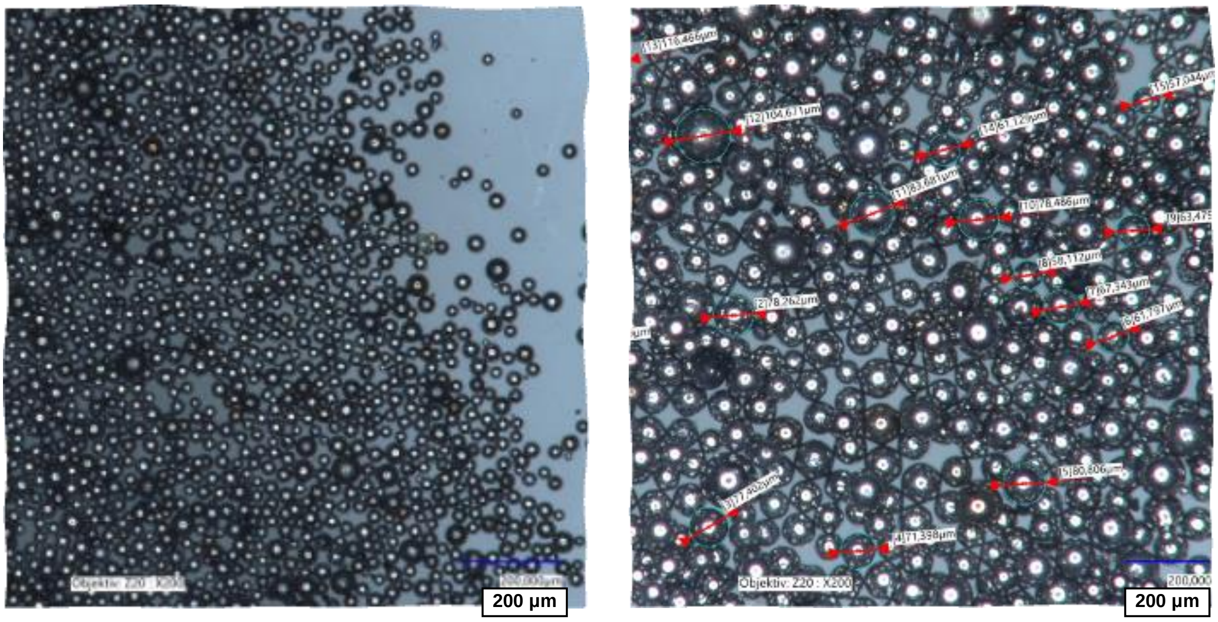
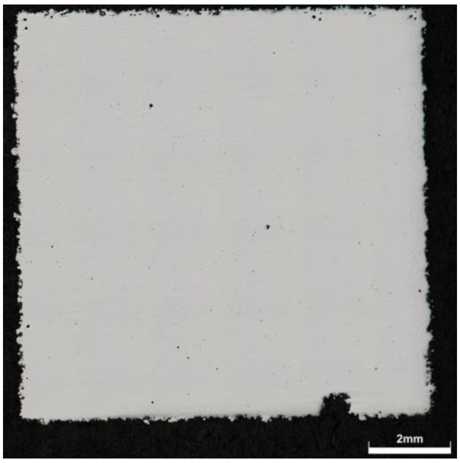


Figure 6 Morphology of the atomized TiNbTaSn powder (mean powder size evaluated by image analysis method was 76 µm)

Gasses content in 3D printed specimens has been evaluated using Bruker Galileo G8 mass spectrometer. The content of oxygen was 0.12 wt% and the content of hydrogen was 0.022 wt%. There is no standard for this alloy stating the maximum allowed content of oxygen or hydrogen. For common alloys, such as Ti-6Al-4V and Ti-6Al-4V ELI, the maximum allowed content of oxygen is 0.15 wt% and 0.13 wt% respectively [12]



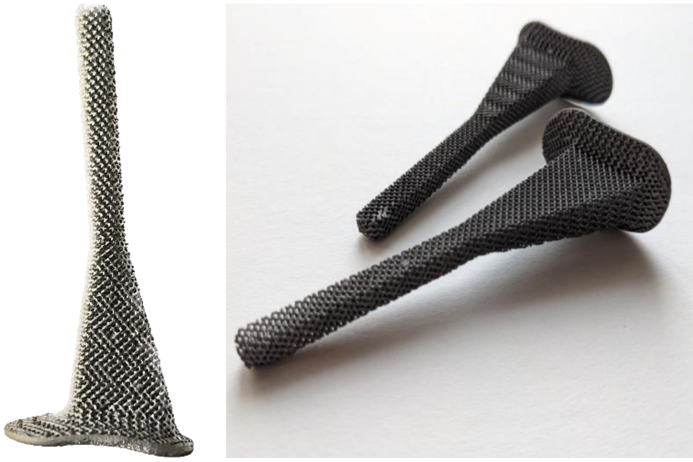


Figure 7 Macrostructure and porosity of the specimen printed from the TiNbTaSn

Figure 8 Implants printed from the recycled TiNbTaSn alloy

Testing specimens were printed using the laser powder bed fusion (LBPF) method (Trumpf TruPrint 1000) from the atomized powder of TiNbTaSn alloy. The porosity of printed specimens has been evaluated (see **Figure 7**). It was concluded that it is possible print from the given powder and obtain low-porosity specimens. Subsequently, the 3D printing process was used to manufacture implant intended for wrist-area application (**Figure 8**). The implant has the structured body to lower its weight and to help the osseointegrating process when implanted.

4. DISCUSSION

The hot-forged and cold-forged specimens do show homogenous microstructure which only affected whether the recrystallization took place or not. The more concerning factor are forging folds that has been found on the surface of specimens. These might be inducing possible contamination due to the oxide layer being folded to the inside of the specimen. The methodology for forging or postprocessing must be set to avoid creation of forging folds. One of the possible solutions is the machining of the surface.

The mechanical properties of the recycled TiNbTaSn alloy do vary depending on whether the specimen was hot-forged or cold-forged. Beside that the mechanical properties seem homogenous and in relative accordance with the literature [13] albeit slightly lower when directly compared with article. This might be caused by the fact that no homogenizing heat treatment was carried out on specimens tested in this article. There was no need for heat treatment since the material was allocated for atomizing process. This is clearly visible in the microstructure of the alloy – in both cases there are visible signs of deformation and only the partial recrystallization took place in the case of hot-forged specimen. This is however not concerning since the material was destined for atomizing process and there was no need for homogenous microstructure.

After the atomizing process the printability of the powder was evaluated. It is possible to print from powder made of recycled alloys using the LBPF method with printing parameters developed in the previous research which was conducted on the powder from non-recycled materials [14]. Furthermore, the printed specimens showed low values of porosity and it was subsequently possible to successfully print model of wrist-area implant from the alloy TiNbTaSn.

5. CONCLUSION

- It is possible to manufacture recycled TiNbTaSn alloy and atomize it to obtain powder usable for 3D printing by LPBF method
- The recycled alloy shows mechanical properties comparable to the alloy obtained by primary metallurgy.
- LPBF printing process from the recycled TiNbTaSn alloy results in low-porosity and homogenous specimens. Furthermore, it is possible to print complex shapes.

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