Manuscript refereed by Dr Thomas Hartwig, Fraunhofer Institute IFAM, Germany

Powder Injection Moulding of Titanium from TiH_2 Powders

E. Carreño-Morelli[1], W. Krstev[1], B. Romeira[1], M. Rodriguez-Arbaizar[1], J.-E. Bidaux[1], S. Zachmann[2]

[1]Design & Materials Unit, University of Applied Sciences Western Switzerland, CH-1950 Sion
[2]Nabertherm GmbH, 28865 Lilienthal, Germany

Abstract

Titanium parts have been processed from feedstocks composed of titanium hydride powders, low density polyethylene, paraffin wax and stearic acid. A two-step debinding process has been used, which consists of solvent debinding in heptane at 50°C followed by thermal debinding at 500°C. Sintering was performed at 1200°C. Both thermal debinding and sintering were performed under protective atmosphere in a MIM furnace equipped with molybdenum heating elements and a debinding retort. Special care in powder handling, feedstock preparation, debinding and sintering atmospheres, allowed to limit the residual oxygen, nitrogen and carbon contents, which were determined by quantitative analysis. The mechanical properties of net-shape sintered parts were measured by tensile tests. A tensile strength of 580 MPa and an elongation of 1.8% were obtained. Experimental watch bracelet segments were injection moulded, showing good shape preservation and reproducibility.

1. Introduction

The excellent properties of titanium and titanium alloys have been extensively reported, as well as the complex processing steps, which are currently necessary for the production of engineering parts with these materials [1]. As a consequence, the interest of producers and end-part users on net-shape technologies is growing. Recently, considerable progress in powder injection moulding of titanium and its alloys has been accomplished [2-5]. This is due to the advances in production of good quality base-powders, binders and sintering facilities. However, cost of raw materials, especially for gas atomized powders, is still a limiting factor for a number of applications. In this work, net-shape manufacturing of titanium parts has been performed by powder injection moulding from titanium hydride powders, which have the attractiveness of being less reactive than fine titanium powders, easier to handle, and cheaper [6-7].

2. Experimental

2.1 Raw materials and feedstock processing:

Two types of angular TiH_2 powders from AG Materials Inc., Taiwan, were used: a fine TIH-25AA grade (Dv50=9.80 µm, Figure 1) and a coarse TIH-020A grade (Dv50=19.55 µm). Details on particle size parameters are given in Table 1.

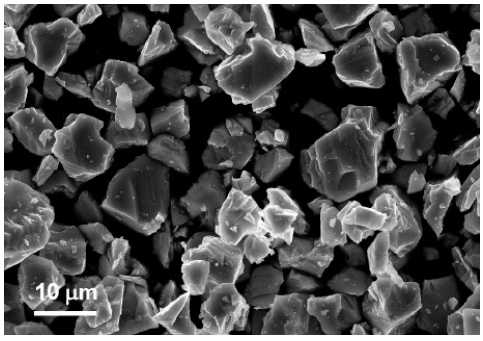

Figure 1. Scanning electron microscopy of starting powder TiH_2 (AG Materials, TIH-25AA)

TiH_2	Dv10 [µm]	Dv50 [µm]	Dv90 [µm]
TIH-25AA	6.11	9.80	13.48
TIH-020A	11.89	19.55	31.42

Table 1. Particle size parameters of fine and coarse TiH_2 powders, after producer data sheet

The binder consisted of 55wt% paraffin wax (Fluka Chemie GmbH, Buchs, Switzerland), 35wt% low density polyethylene (LDPE Riblene MP30, Dupont, Switzerland) and 10 wt% stearic acid (Fluka Chemie GmbH). The binder volume fraction was 40 vol%. Feedstocks for powder injection moulding were prepared in a Coperion LUK 1.0 sigma blade mixer (Werner & Pfleiderer, Stuttgart, Germany). Mixing was performed at 140°C for 4h. Then, polymer-powder granules were obtained by cooling down and crushing the mixture by slow shearing.

2.2 Injection moulding:

Tensile test specimens (Figure 2) and experimental watch bracelet segments were injection moulded in an Arburg 221K 350-100 machine (Arburg GmbH + Co KG, Lossburg, Germany).

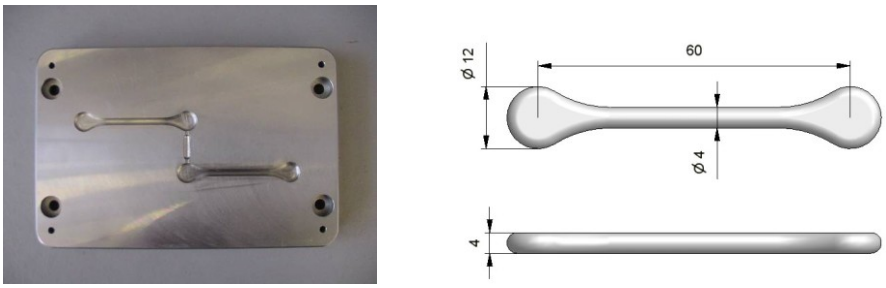

Figure 2. Mould half for tensile test specimen and dimensions of the mould cavity in mm

The mould for watch bracelet segments (Figure 3, [8]) consists of single cavity inserts in a mould frame. A slide block with two pins is mounted on the mobile mould half. An angular pin slider in the fixed mould half forces motion of the slide block when the mould closes. It allows to obtain transverse holes along the parting line for further assembly of the segments to each other. Mould temperature was of about 40°C.

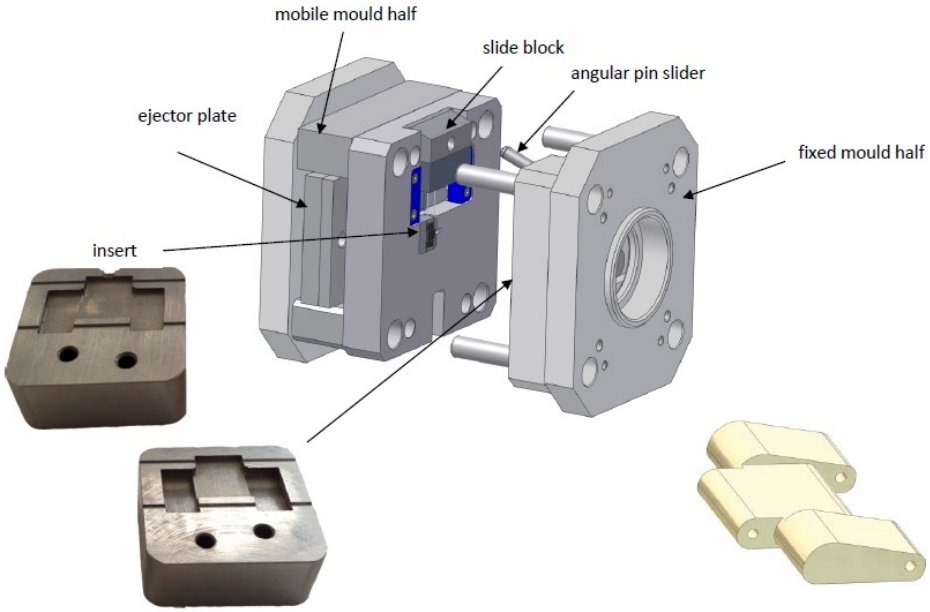

Figure 3. Tooling for moulding watch bracelet segments: mould frame, inserts and slide

2.3 Debinding and sintering:

After shaping, the parts were subjected to successive treatments of solvent debinding, thermal debinding, dehydrogenation and sintering.

Solvent debinding was performed in heptane at 50°C for 10h, which allowed to remove more than 98% of paraffin wax and stearic acid.

Thermal debinding, dehydrogenation and sintering steps were accomplished in a single thermal cycle in a Nabertherm VHT8-16MO MIM furnace, which is equipped with molybdenum heating elements and a debinding retort (Figure 4). The furnace design allows safe evacuation of products resulting from binder burnout without contaminating the heating elements. During debinding, a gas flow is currently activated into the furnace chamber, and gas aspiration is directly made from the retort. During sintering, the gas flow is activated into the retort, and aspiration is made from the furnace chamber. A binder trap, which is periodically cleaned, avoids contamination of the vacuum pump. Thermal cycles can be done under vacuum or controlled atmosphere of Ar, N_2 or H_2. Figure 4 show details of the furnace chamber and retort.

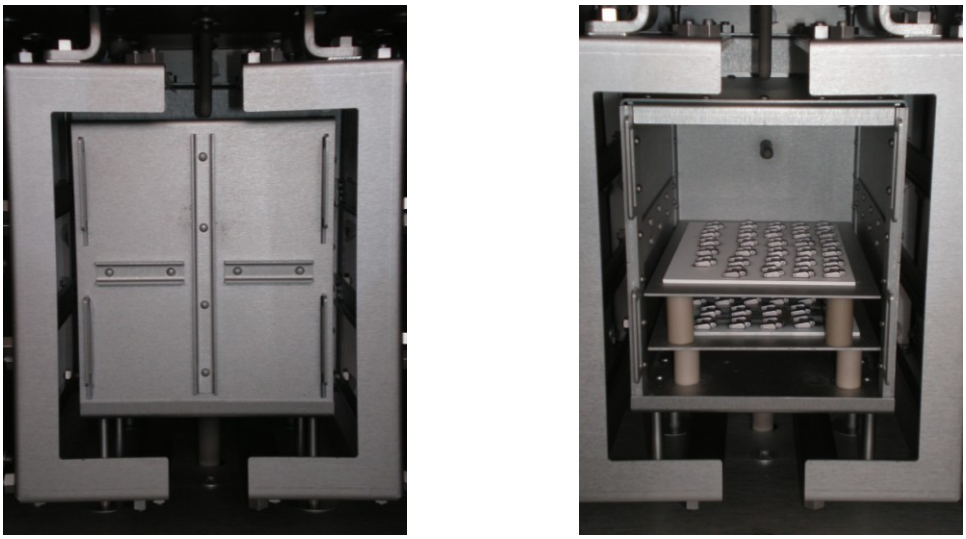

Figure 4. Details of the debinding and sintering furnace: (a) heating elements and debinding retort closed, (b) sintered watch bracelet segments on zirconia coated alumina support, placed on molybdenum plates inside the retort.

Thermal decomposition of the LDPE backbone polymer was accomplished during a debinding step of 1 h at 500°C under argon (Figure 5). A gas flow of 100 l/h is used for a continuous renewal of the debinding atmosphere.

Thermogravimetric analysis of TiH_2 powders performed in a Setaram TAG 24 device allowed to establish that 500°C is also an appropriate temperature for dehydrogenation. Hydrogen removal proceeds during the subsequent heating to reach the sintering temperature. At about 700°C, dehydrogenation is completed. Sintering was performed at 1200°C for 1h under flowing argon.

2.4 Materials characterization:

Density measurements were performed by using the Archimedes method. Mechanical properties were characterized by standard tensile tests. Metallographic preparation of sintered samples was performed by diamond polishing followed by oxide polishing with colloidal silica. Scanning electron microscopy was performed in a LEO 1525 microscope. Quantitative analysis was performed by fusion and infrared detection with LECO systems to establish the content of interstitial elements O, N, C in base powders and sintered parts.

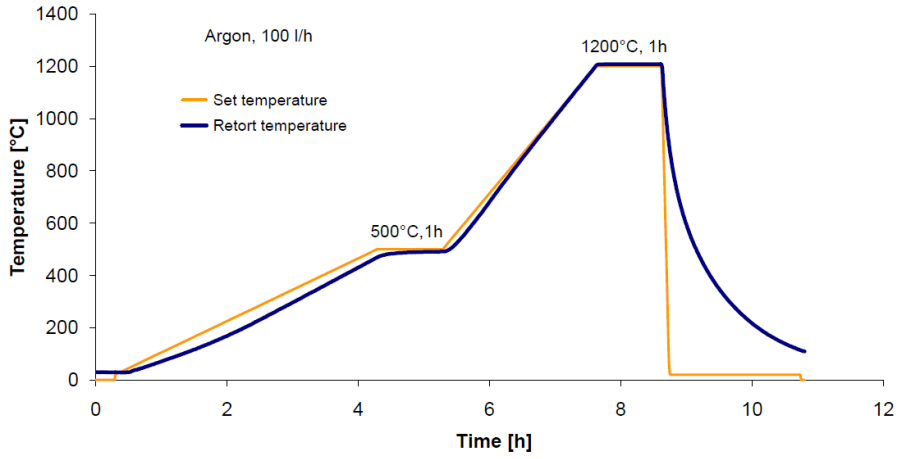

Figure 5. Thermal cycle for processing Ti parts from solvent debinded TiH_2 based feedstocks

3. Results and discussion

Figure 6 shows green parts (as injected) and net-shape parts (after debinding and sintering). Good green strength is due to low density polyethylene, which is the backbone polymer of the multicomponent binder. The goal of the solvent debinding step is to remove paraffin wax and stearic acid, leaving an open porosity to allow proper thermal debinding of the backbone polymer. In this way, bubble gas formation during polymer burnout is avoided, reducing internal stresses and the risk of part damage or geometry distortion.

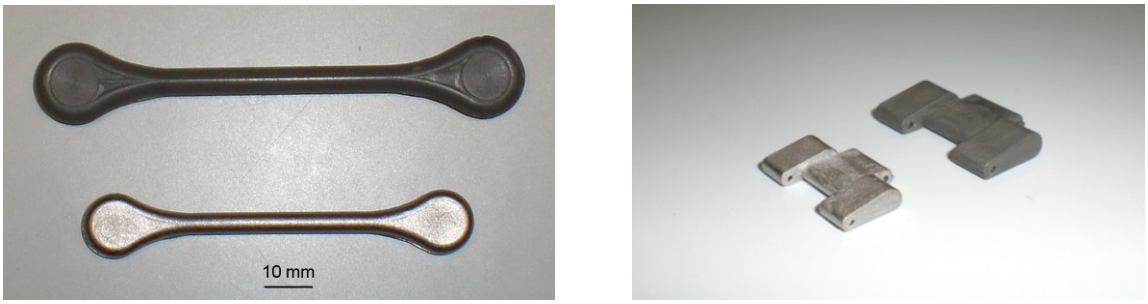

Figure 6. Green and sintered PIM-Ti parts

The linear shrinkage of sintered titanium parts is of about 19%. This high value is because in addition to the current contraction during debinding, there is also a contraction during the dehydrogenation of the TiH_2 base powder.
PIM titanium parts from fine TIH-25AA powders have a density higher than 98% of the theoretical density and tensile strength of 650 MPa, but low ductility (Table 2). This is related with a too high oxygen content of about 0.6 wt%, which was measured by fusion and infrared detection. The use of controlled Ar atmosphere during powder handling, mixing and green part storage allowed to reduce the oxygen content to 0.45 wt.%. However, no significant improvement in ductility was observed.
Better results are obtained with PIM titanium parts from coarse TIH-020A powders. Sintered density is lower, but ultimate tensile strength of 580 MPa meets the requirements for Ti grade 4. In addition, elongation to fracture is improved to reach 1.8 % plastic strain (Figure 7). This is related with a lower interstitial content in coarse powders, especially oxygen, as shown in Table 2. However, the elongation to fracture is much less that the one of titanium grade 4. Further improvement in ductility would be possible by optimizing the debinding, dehydrogenation and sintering cycle (e.g. by increasing sintering temperature and time), and by using TiH_2 powders of higher purity.

	Dv50 [µm]	O [wt.%]	N [wt.%]	C [wt.%]	sintered density [%]	UTS [MPa]	elongation [%]
TIH-25AA powder	9.80	0.25	0.24	0.16	-	-	-
PIM-Ti (a)	**-**	**0.60**	**0.013**	**0.10**	**98.2**	**650**	**0.7**
TIH-020A powder	19.55	0.07	0.14	0.013	-	-	-
PIM-Ti (b)	**-**	**0.38**	**0.046**	**0.045**	**95.8**	**580**	**1.8**
Ti grade 4	-	0.4	0.03	0.08		550	15

Table 2. Interstitial content and mechanical properties of base powders, titanium standard grade 4, and PIM-Ti processed from fine (a) and coarse (b) TiH_2 powders

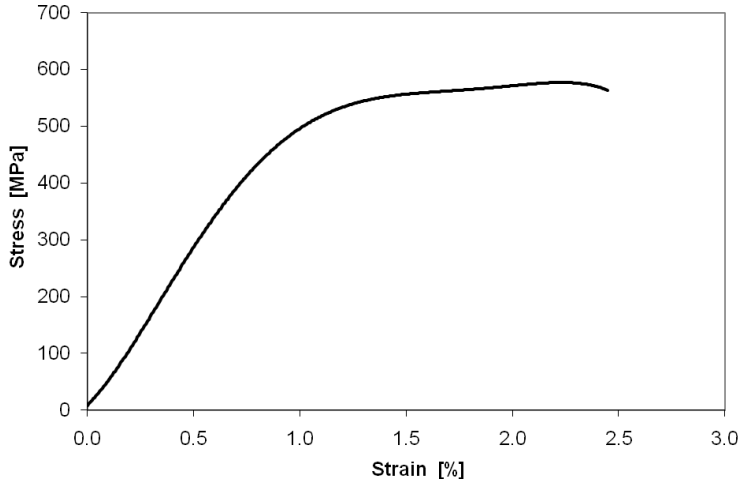

Figure 7. Tensile stress-strain curve of sintered PIM-Ti (b)

The microstructure of sintered parts is shown in Figure 8. An equiaxed grain structure is found, with reduced grain size near the surfaces. Residual round porosity is also observed.

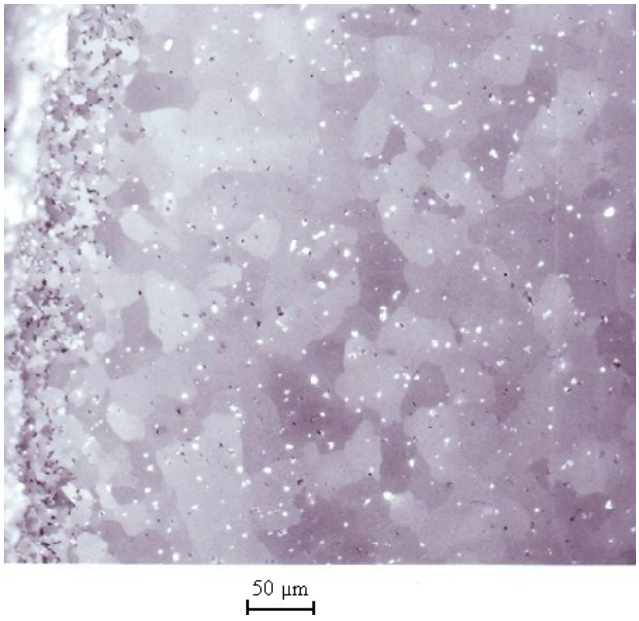

Figure 8. Optical metallography showing the microstructure of sintered PIM-Ti (a)

At present state of research, injection moulded of TiH_2 feedstocks appears as an interesting alternative for manufacturing of lightweight strong parts, when ductility is not the critical requirement.
Sintered watch bracelet segments (Figure 9) show good shape preservation and reproducibility. The variation in weight of green parts is less than 0.4%. The linear shrinkage is about 20%, and the hole diameter ø is reduced from 0.98 mm to 0.78 mm after sintering. A control of weight and dimensions was performed on 63 sintered parts. The variation in weight is again less than 0.4%. The scatter in dimensions *a*, *b* is about 0.4 %, and the scatter in the dimension *c* is about 0.5%.

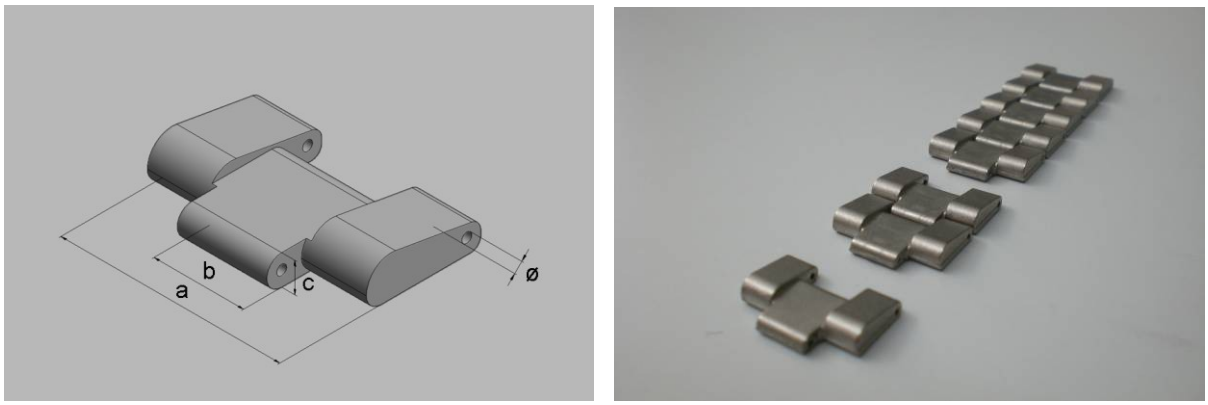

Figure 9. Titanium watch bracelet segments processed from TiH_2 based feedstock

4. Concluding remarks

Titanium hydride powders are an interesting alternative for processing PIM-Ti parts. Despite its angular shape (which is currently associated with low packing and high interparticle friction) and a necessary dehydrogenation step, sintered densities higher than 95% can be obtained. Net-shape as-sintered parts show good mechanical properties, good shape preservation and reproducibility. Further improvements in ductility will be related with the optimisation of debinding, dehydrogenation and sintering cycles, and with the availability of powders of improved purity.

Acknowledgments

The technical support of A. Steiner and D. Zufferey (HES-SO Valais). J. Dänzer (BFH-Biel), and R. Figi (EMPA-Dübendorf) is gratefully acknowledged.

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