Processing of a low modulus Ti-Nb biomaterial by Metal Injection Moulding (MIM)

J.-E. Bidaux, C. Closuit, M. Rodriguez-Arbaizar, D. Zufferey, E. Carreño-Morelli

Design & Materials Unit, University of Applied Sciences Western Switzerland
Rte du Rawyl 47, CH-1950 Sion, Switzerland

Ti alloys containing β stabilising elements such as Nb, Zr and Ta are particularly promising as implant materials because of their excellent combination of low modulus, high strength, corrosion resistance and biocompatibility. A low elastic modulus is important for implants to avoid stress shielding and associated bone resorption. The difficulty of producing complex shapes of these alloys by conventional methods makes Metal Injection Moulding attractive. In this work, Ti-17Nb alloy parts with densities of 94% of theoretical density have been produced by metal injection moulding of a feedstock based on blended elemental powders. Scanning electron microscopy reveals a typical α-β Widmanstätten microstructure with a precipitated α phase layer along the grain boundaries. The parts exhibit an ultimate tensile strength of 768 MPa and a plastic elongation of over 5%. The modulus of elasticity, about 84 GPa, is more than 20% lower than that of CP Ti and Ti-6Al-4V.

Ti-6Al-4V is still the most commonly used titanium alloy for biomedical applications [1,2]. However, studies have pointed out that the toxicity of aluminium and vanadium ions can lead to long-term health problems [3,4]. Moreover, the elastic modulus of Ti-6Al-4V (~110 GPa), although generally considered as low, remains high compared to that of human bone (10-40 GPa). A large elastic modulus mismatch gives rise to the phenomenon of stress shielding that can cause bone resorption and loosening of the implant [5,6]. Therefore considerable research is currently on-going to develop titanium alloys better suited to biomedical applications.

Ti-Nb based alloys have attracted interest as a possible replacement for Ti-6Al-4V [7,8]. Nb is recognised as non-toxic and non-allergenic. In addition, niobium is a β phase stabiliser. The β phase has a lower modulus of elasticity compared to the α phase. Therefore a decrease of the elastic modulus of titanium is expected with increasing niobium content [9]. Values of the elastic modulus as low as 74 GPa combined with tensile strengths as high as 760 MPa have been reported for α-β Ti-Nb alloys processed by conventional methods [10,11]. A particularly low elastic modulus of 55 GPa was measured for a Ti-40Nb alloy with a fully β structure, however at the cost of a lower tensile strength [11].

Metal Injection Moulding (MIM) is a cost-effective near-net shape process for titanium alloy components [12]. In a recent paper, a preliminary study by the present authors has shown the feasibility of processing Ti-Nb alloys by MIM [13]. MIM Ti-17Nb parts with a tensile strength of 749 MPa and an elastic modulus of about 83 GPa were successfully produced. However, the plastic elongation was limited to 2.5%. In the present paper, new results showing the fabrication of MIM Ti17Nb parts with improved strength and plastic elongation are reported. The microstructure of these parts is characterised by scanning electron microscopy and X-ray diffractometry.

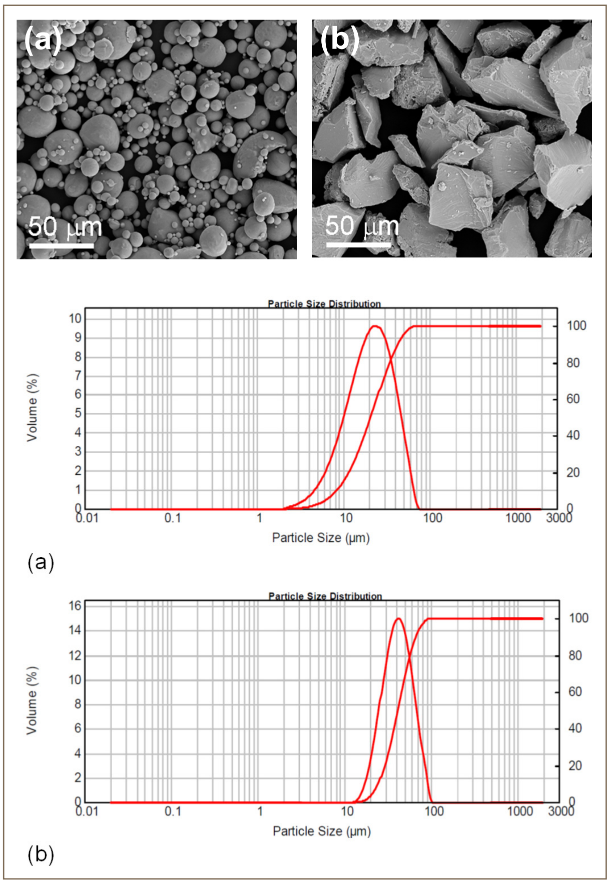

Fig. 1 Scanning electron microscopy and particle size distribution of titanium (a) and niobium (b) base powders

Experimental

Gas atomised Ti (Dv10 = 8 µm, Dv50 = 21 µm, Dv90 = 43 µm, TLS Technik GmbH & Co) and angular Nb (Dv10 = 25 µm, Dv50 = 41 µm, Dv90 = 67 µm, H.C. Starck GmbH) powders (Fig. 1) were used. The particle size distribution was determined by laser diffractometry using a Malvern Mastersizer 2000 apparatus. The powders were mixed with a polymer binder in a Coperion Werner & Pfleiderer double sigma mixer to form a feedstock. The binder consisted of 55 wt% paraffin wax, 35 wt% low density polyethylene and 10 wt% stearic acid. The binder volume fraction was 40 vol%. Tensile test specimens (ISO 2740) were injection moulded using an Arburg 221K machine. Binder removal was accomplished by solvent debinding in heptane at 50°C for 20 hrs. The parts were then thermally debinded at 500°C for 2 hrs and then sintered at 1300°C for 4 hrs under argon in a single thermal cycle in a Nabertherm VHT08-16MO MIM furnace. Fig. 2 shows the thermal debinding and sintering cycle. Tensile strength, elongation and elastic modulus were measured by tensile testing using a Zwick 1475 machine equipped with extensometers with a gauge length of 22 mm. Test parameters were set according to standard DIN EN ISO 6892-1 method B. The density of sintered parts was measured using the Archimedes method. The samples microstructure was studied using a LEO 1525 scanning electron microscope equipped with energy dispersive X-ray analysis (EDX). X ray diffraction patterns were recorded using an X'pert Pro PANalytical X-ray diffractometer (B.V., Almelo, The Netherlands) and a CuKα source (λ= 1.54060 Å). The interstitial contents in both base powders and sintered parts were measured by conventional melt extraction using a LECO TCH 600 apparatus for nitrogen and oxygen and a LECO CS 230 for carbon.

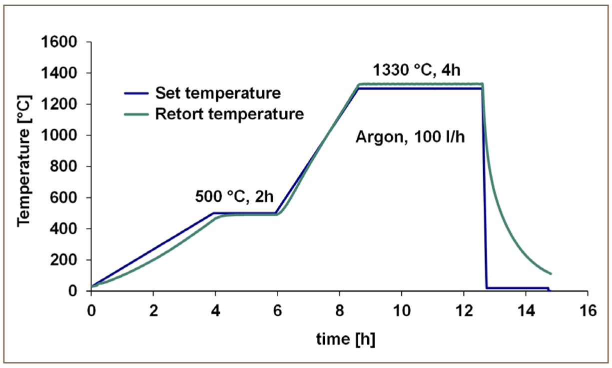

Fig. 2 Thermal debinding and sintering cycle

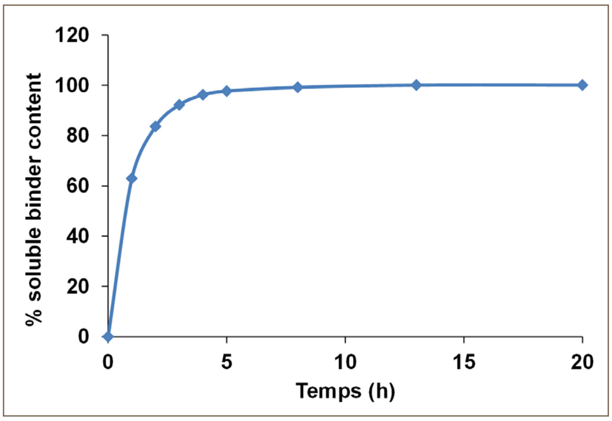

Fig. 3 Soluble binder components extraction as a function of time at 50°C

Results and discussion

As shown in Fig. 3, after 20 hours solvent debinding at 50°C, the soluble components of the binder, i.e paraffin wax and stearic acid, are fully extracted.

Fig. 4 shows both green and sintered parts. Good shape preservation is observed. The average shrinkage between the green and sintered parts is (14.5 ± 0.3)% for the length and (13.3 ± 1.5)% for the diameter. The density of the sintered part is (4.62 ± 0.02) g/cm³ i.e. approximately 94% of the theoretical density, 4.91 g/cm³. To estimate the theoretical density, a rule of mixtures based on the densities of pure titanium, 4.51 g/cm³ [14], and pure niobium, 8.57 g/cm³ [15], was used.

The interstitial contents in both base powders and sintered MIM parts are shown in Table 1. The values for titanium powder (MIM powder) are within the limits of Ti grade 1. The impurity content of the niobium powder is lower than that of the titanium powder, which is consistent with its coarser particle size. In spite of the impurity uptake during the whole MIM process, the impurity content of the MIM Ti-17Nb part remains close to that specified by the main ASTM standards for α-β titanium alloys [16].

A scanning electron microscope image of a polished cross-section of a MIM part is shown in Fig. 5. The microstructure is typically of the Widmanstätten type. The equilibrium phase diagram (Fig. 6) indicates that the stable phase after sintering is the β phase. Upon subsequent cooling to room temperature, precipitation of the α phase occurs; giving rise to the observed two phase α-β lamellar structure. The dark grey lamellae in Fig. 5 correspond to the α phase and the light grey matrix to the β phase [17]. The α phase precipitates preferentially along the former β phase grain boundaries (α layer). The grain size is between 100 and 300 µm. A few pores are visible. Some isolated inclusions (bright grey areas) are observed along the grain boundaries. A scanning electron microscopy image of an

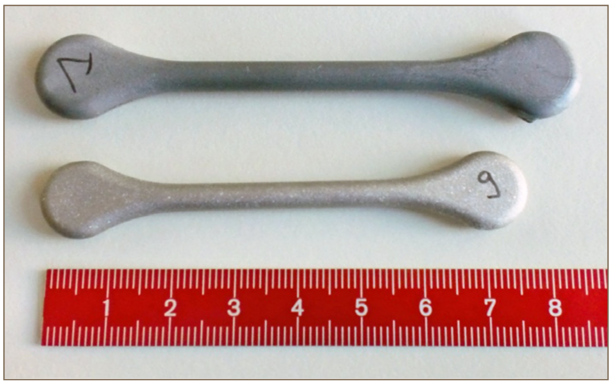

Fig. 4 Injection moulded and sintered MIM Ti-17Nb test specimens

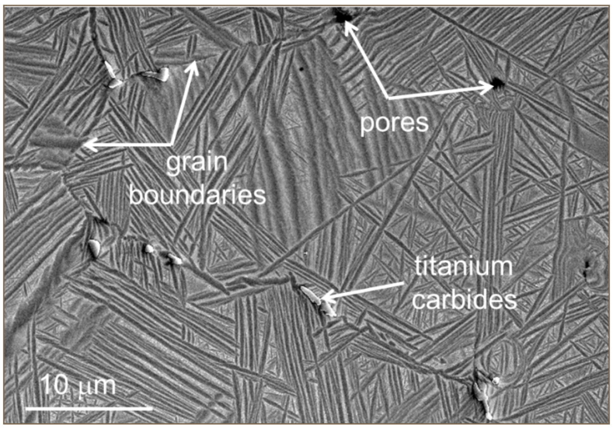

Fig. 5 SEM observation of a polished cross-section of a MIM Ti-17Nb test specimen (secondary electrons)

Material	O (wt%)	N (wt%)	C (wt%)
Ti powder	0.16	0.010	0.009
Nb powder	0.072	0.004	0.002
MIM Ti-17Nb part	0.19	0.05	0.05

Table 1 Interstitial contents in base powders and sintered parts

Location	C (wt%)	Ti (wt%)	Nb (wt%)
A1	5.9	83.6	17.6
A2	10.0	78.9	19.0
A3	10.1	84.8	15.5
B1	32.8	86.3	10.3
B2	43.5	87.6	10.5
B3	35.4	85.5	11.9

Table 2 EDX composition analysis

Property	MIM Ti-17Nb	Hot rolled Ti-17Nb*	CP Ti grade 2**	Ti-6Al-4V ELI***
E (GPa)	84 ± 4	90	105	114
YS (MPa)	640 ± 25	680± 5	>275	>795
UTS (MPa)	768 ± 22	700± 5	>345	>860
El. (%)	5.4 ± 1.3	11	>20	>10

* Extrapolated from literature data for hot rolled, annealed and slow cooled α-β Ti-Nb alloys [11]

** ASTM F67 (unalloyed titanium for surgical implants)

*** ASTM F136 (wrought material extra low interstitial for surgical implants)

Table 3 Mechanical properties of MIM Ti-17Nb compared to those of reference materials

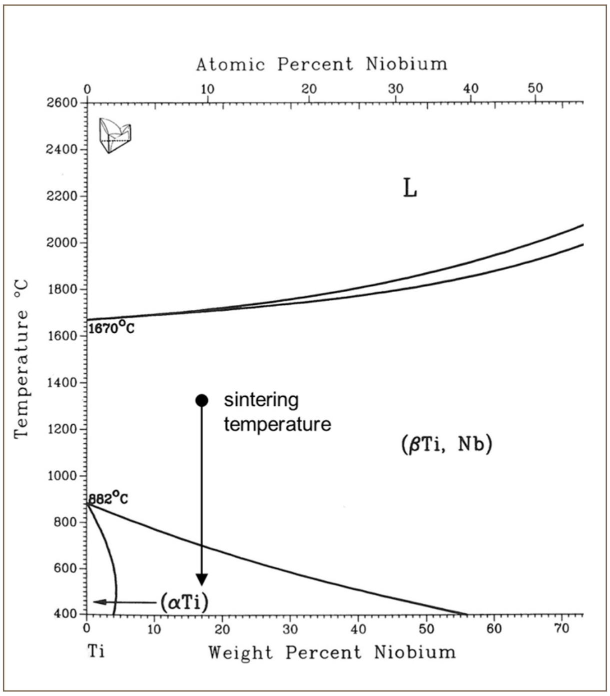

Fig. 6 Low Nb section of the Ti-Nb phase diagram [18]

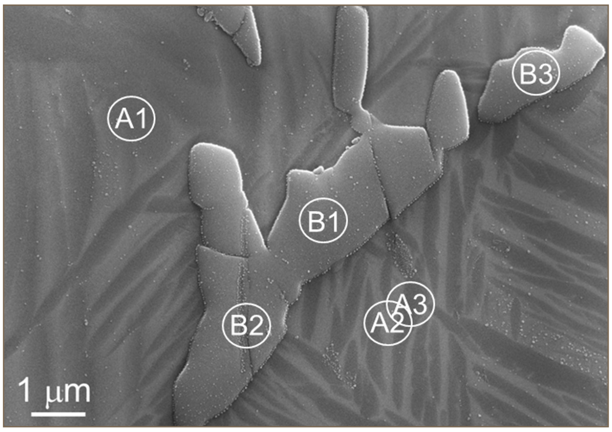

Fig. 7 SEM observation of a titanium carbide inclusion in a MIM Ti-17Nb test specimen (secondary electrons)

inclusion is shown in Fig. 7. Detailed EDX composition analyses of the inclusion and its surrounding matrix were performed (Table 2). Whereas the Nb content in the matrix (A1, A2, A3 areas) matches the alloy nominal composition, significant Ti and C enrichment, and Nb depletion (B1, B2, B3 areas) are observed within the inclusion. It can be concluded that the inclusions are titanium carbides. These carbides probably result from the reaction of titanium particles with residual binder during processing.

X-ray diffraction measurements confirm the scanning electron microscopy observations. A typical X-ray diffraction pattern of a polished cross-section of a MIM specimen is shown in Fig. 8. All visible peaks can be indexed as α or β phase. Some additional peaks, too small to be visible on Fig. 8, might be associated with the above mentioned carbides.

Fig. 9 shows typical stress-strain curves measured by tensile testing. The mechanical properties are summarised in Table 3 and compared to literature values for hot rolled α-β Ti-17Nb and to the ASTM standards of two currently commonly used materials for medical implants, CP Ti grade 2 and Ti-6Al-4V. As can be seen in Table 3, MIM Ti-17Nb exhibits a lower elastic modulus than that of hot rolled Ti-17Nb for a comparable tensile strength. The lower elastic modulus of MIM Ti-17Nb can be explained by its residual porosity (~6%) although the difference in texture between the two materials may also play a role [19]. MIM Ti-17Nb meets by far the strength requirements of Ti grade 2, with the important additional advantage of a more than 20% lower elastic modulus, this without sacrificing biocompatibility. Compared to Ti-6Al-4V, the elastic modulus is reduced by more than 25%. The strength requirements are, however, in this case, not satisfied. Nevertheless, MIM Ti-17Nb remains promising because of the advantage of the better biocompatibility. Moreover, the possibility for further improvement of the mechanical strength by increasing density exists. However, this would result in a simultaneous increase of the elastic modulus, which is not desirable. Other possibilities, to be studied, are the incorporation of additional alloying elements such as zirconium or tantalum, or the use of suitable thermal treatments.

Fig. 10 shows a typical fracture surface after tensile testing. The fracture surface shows the characteristics of a ductile fracture. The fracture is transgranular with a mixture of fine and coarse dimples. Voids are observed at the centre of some of the large dimples.

Conclusions

Ti-17Nb alloys with a relative density of 94% have been produced by Metal Injection Moulding of a feedstock based on blended elemental powders. A typical lamellar α-β Widmanstätten microstructure with intergranular α phase is observed by scanning

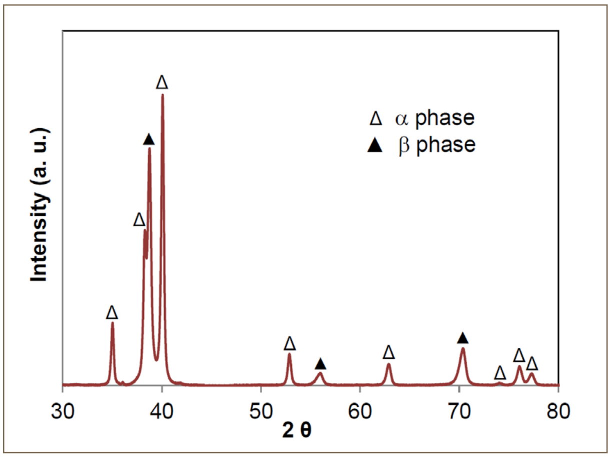

Fig. 8 X-ray diffraction pattern of a MIM Ti-17Nb test specimen

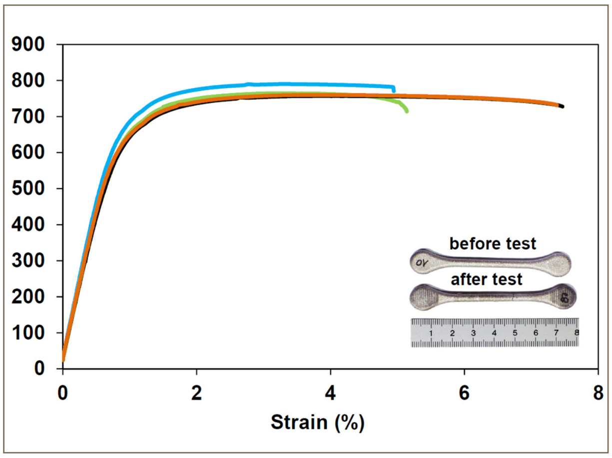

Fig. 9 Typical stress-strain curves from tensile tests of MIM Ti-17Nb specimens

electron microscopy. Some isolated titanium carbides are observed along the former β grain boundaries. The presence of the α and β phases is confirmed by X ray diffraction. The grain size is between 100 and 300 µm. The parts exhibit an ultimate tensile strength of 768 MPa and a plastic elongation of more than 5%. The tensile fracture surface shows the characteristics of a ductile fracture with a mixture of fine and coarse dimples. The elastic modulus, about 84 GPa, is significantly lower than that of both CP Ti and Ti-6Al-4V. Further improvements of the mechanical properties are expected through the incorporation of additional alloying elements and by the use of suitable thermal treatments.

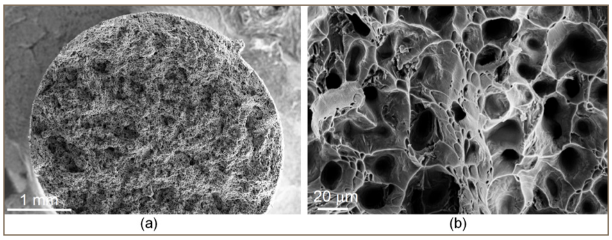

Fig. 10 SEM images of the tensile fracture surface of a MIM Ti-17Nb test specimen; (a) overview (b) detail

Acknowledgments

The financial support of the University of Applied Sciences Western Switzerland under grant MaCHoP 10-09 is gratefully acknowledged.

References

[1] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Titanium based biomaterials, the ultimate choice for orthopaedic implants – A review, *Progress in Materials Science*, 54, 2009, pp.397-425

[2] H. J. Rack, J. I. Qazi, Titanium alloys for biomedical applications, *Materials Science and Engineering C*, 26, 2006, pp.1269-1277

[3] K. Wang, The use of titanium for medical applications in the USA, *Materials Science and Engineering A*, 213, 1996, pp.134-137

[4] M. Niinomi, Recent research and development in titanium alloys for biomedical applications and healthcare goods, *Science and Tech. of Advanced Materials*, 4, 2003, pp.445-454

[5] M. Niinomi, Mechanical biocompatibilities of titanium alloys for biomedical applications, *Journal of the mechanical behavior of biomedical materials*, 1, 2008, pp.30-42.

[6] M. Long, H.J. Rack, Titanium alloys in total joint replacement - a materials science perspective, *Biomaterials*, 19, 1998, pp.1621-1639

[7] E.S.N. Lopes, A. Cremasco, C.R.M. Alfonso, R. Caram, Effect of double aging heat treatment on the microstructure, Vickers hardness and elastic modulus of Ti-Nb alloys, *Materials Characterisation*, 62, 2011, pp.673-680

[8] C.M. Lee, C.P. Ju, J.H. Chern Lin, Structure-property relationship of cast Ti-Nb alloys, *J. of Oral Rehabilitation*, 29, 2002, pp.314-322

[9] G. Lütjering, J. C. Williams, Engineering Materials and Processes, Titanium, Springer Berlin, 2nd edition, p.19

[10] R. Boyer, G. Welsch, E.W. Collings, eds., Materials properties handbook: Titanium alloys, ASM International, Materials Park, USA, 1994, p.97

[11] Y.-H. Hon, J.-Y. Wang, Y.-N. Pan, Composition/phase structure and properties of titanium-niobium alloys, *Materials Transactions*, Vol. 44, N°11, 2003, pp.2384-2390

[12] G.C. Obasi, O.M. Ferri, T. Ebel, R. Bormann, Influence of processing parameters on mechanical properties of Ti-6Al-4V alloy fabricated by MIM, *Materials Science and Engineering A*, 527, 2010, pp.3929-3935

[13] J.-E. Bidaux, C. Closuit, M. Rodriguez-Arbaizar, E. Carreño-Morelli, Metal injection moulding of Ti-Nb for implant application, *European Cells and Materials*, Vol. 22, Suppl. 4, 2011, p.32

[14] M.J. Donachie, Titanium, A technical guide, 2nd edition, ASM International, 2007, p.5

[15] H.E. Boyer, T.L. Gall, eds., Metals Handbook, American Society for Metals (ASM), Desk Edition, Metals Park, Ohio, USA, 1988, p.1.46

[16] M.J. Donachie, Titanium, A technical guide, 2nd edition, ASM International, 2007, p.8

[17] G. Lütjering, J. C. Williams, Engineering Materials and Processes, Titanium, Springer Berlin, 2nd edition, 2007 p. 32

[18] T. Massalski ed., Binary alloy phase diagrams, vol. 2, American Society for Metals (ASM), Metals Park, Ohio, USA, 1986, p.1702

[19] C. Leyens, M. Peters, eds., Titanium and titanium alloys, Fundamentals and applications, Wiley-VCH, Weinheim, Germany, 2003, p.29