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Metal injection moulding of titanium and titanium-aluminides

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Abstract Metal injection moulding (MIM) attracts growing interest as an economic net-shape manufacturing technique for the processing of titanium and titanium alloys. Even for titanium-aluminides, intended for high-temperature applications, MIM is seen as a reasonable technique to overcome processing problems with conventional methods. In this paper, basic requirements in terms of raw materials, facilities and processing in order to produce high performance components are presented. Main focus is laid on the well-known Ti-6Al-4V alloy. It is shown that the tensile properties of specimens after MIM processing can exceed the requirements given by ASTM standards even without performing an additional HIP process. For an oxygen content ranging from 0.15 to 0.33 wt% plastic elongation yields excellent 14%. Fatigue measurements performed by means of 4-point-bending tests show that grain size is more important than residual porosity in order to achieve a high endurance limit. This is shown by addition of boron powder which refines the microstructure dramatically. The modified alloy Ti-6Al-4V-0.5B yields an endurance limit of 640 MPa compared to 450 MPa of MIM parts made from standard alloy powder. Sintered components from Ti-45Al-5Nb-0.2B-0.2C (at%) powder made by inert gas atomising (EIGA technique) and processed by MIM exhibit a residual porosity of only 0.2% and tensile properties comparable to cast material.

Introduction

Metal injection moulding (MIM) is an established technology for the fabrication of components with complex geometry. The injection moulding process offers extraordinary possibilities to design fine structural details, thin walls and holes with nearly any desired shape. For larger quantities the economical advantage can be dramatic compared to casting or machining.

To date, more than 20 years experience is available in terms of MIM processing of stainless steel or CoCr-alloy powders and manufacturers all over the world offer this technique commercially. By contrast, titanium and titanium alloy powders are still a speciality in the field of MIM processing [1,2]. Though, especially in this case using MIM has several advantages. Machining and casting of titanium materials are difficult and time and cost consuming. In addition, the raw material is expensive, thus, resource efficient powder metallurgical methods can be beneficial.

Despite these advantages MIM of titanium is definitively not standard yet. The sensitivity of titanium against oxygen and carbon requires special facilities and processing and the composition of the binder system is crucial. The availability of suitable powders and feedstock is not satisfactory to date. However, MIM of titanium and its alloys has been developed very successfully during the last decade [3-8] and excellent properties can be achieved, if processing is performed adequately and powder of right quality is chosen, as it will be shown in the following. In addition, since spring 2011 ASTM standard F2885-11 for MIM processed Ti-6Al-4V intended for surgical implants is established, revealing the industrial interest in this technique.

In this paper basic requirements for the successful application of MIM on titanium based materials are presented, before going into detail on processing and mechanical properties of specific alloys like the well known Ti-6Al-4V alloy and the intermetallic titanium-aluminide Ti-45Al-5Nb-0.2B-0.2C (at%).

Basic requirements for MIM processing of titanium based materials.

MIM processing. The main challenge is the sensitivity of titanium against oxygen. Titanium is used as an oxygen getter material in vacuum technology because of the great affinity between these two elements and the high solubility of oxygen in titanium. Because of its strong effect on mechanical properties the pick-up of oxygen has to be limited during the whole MIM processing chain. Baril [9] showed very clearly in which stages of the MIM process oxygen is primarily incorporated. These are the processing steps at temperatures above 400 °C, namely thermal debinding and especially sintering. In addition, also carbon pick-up is a severe issue due to the polymeric binder usually used. Again, the most critical processing steps are thermal debinding and the beginning of the sintering regime.

This means that preferentially powder and binder with an oxygen and carbon content as low as possible should be used. e.g. in the case of the Ti-6Al-4V alloy the grade 23 (according to ASTM B348) variant can be used which contains 0.13 wt% oxygen as maximum compared to grade 5 containing up to 0.2 wt%. Accordingly, binder components with low oxygen content should be used. In addition, as much as possible of the binder should be removed prior to thermal processing, e.g. by solvent debinding at low temperatures. During thermal debinding the transport of the residuals of the cracked polymer chains is essential and can be performed e.g. by a slight flow of argon gas.

The most important issue is the sintering regime. Titanium alloys are commonly sintered at temperatures significantly above 1200 °C for at least 2h. At this temperature the oxygen and carbon levels of the atmosphere near the parts has to be as low as possible. Applying a high purity vacuum below 10^{-4} mbar is beneficial. Using argon gas is also possible, but will result in slightly lower sintering density because argon is trapped in the sintering pores and hinders the shrinkage. Finally, the contact of the unprotected powder with air should be avoided.

Oxygen. As mentioned above oxygen pick-up is the main issue during processing titanium powder, but it is controllable. If adequately processed the amount of additional oxygen can be below 0.05 wt%. Thus, it is possible to fulfil the limit of 0.2 wt% for the Ti-6Al-4V grade 5 specification. On the other hand the following study reveals that in terms of mechanical properties it is beneficial to allow higher amounts of oxygen. As figure 1 shows, an oxygen content up to about 0.32 wt% just increases the strength without deterioration of ductility.

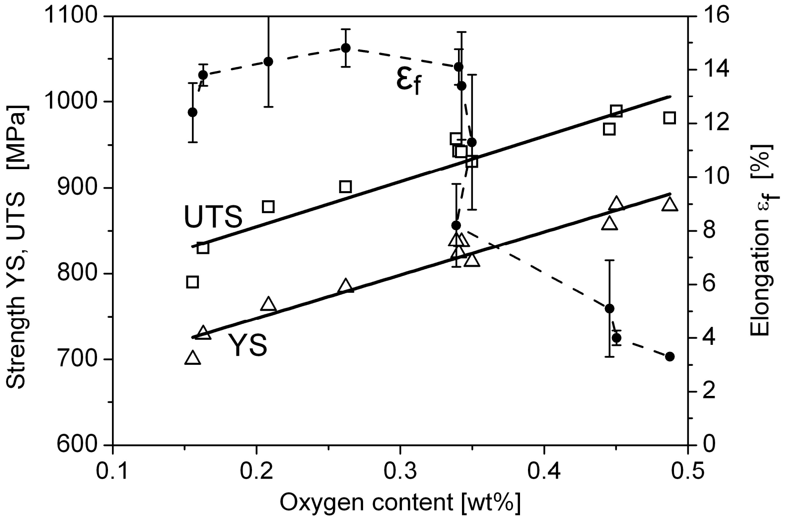


Figure 1. Dependence of yield strength YS, ultimate tensile strength UTS and plastic elongation ε_f on the oxygen content of MIM processed Ti-6Al-4V.

The residual porosity of all samples was 3.5% and the grain size about 120 µm. It is important to note that the microstructure of MIM processed material differs from forged or rolled material. Therefore, also the response to interstitials content can be different. Thus, specifications and limits established as standards for forged material should not simply be transferred to MIM material.

Microstructure. Titanium alloys are commonly sintered within the single-beta phase region. Therefore the grain growth is not hindered by the presence of a second phase and a rather large grain size compared to wrought material is a characteristic of MIM material. In addition, during cooling a typical lamellar structure of alpha and beta phase will occur in $\alpha+\beta$ alloys like Ti-6Al-4V. In contrast, thermo-mechanically treated wrought material features a fine globular microstructure. Furthermore, a certain amount of porosity remains after sintering. Thus, mechanical properties will generally differ from those of wrought material. However, compared to cast material the MIM microstructure is significantly finer and very homogenous. If the grain size of MIM material has to be significantly reduced, it is necessary to use grain refiners as it will be shown below.

Experimental

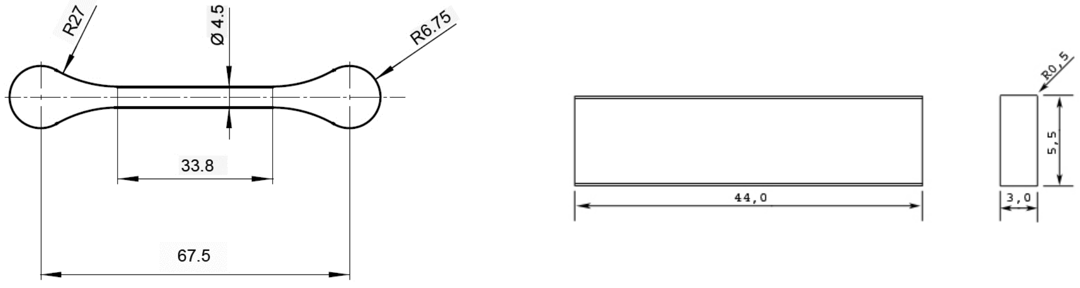
Sample production. For all results shown in this paper the following MIM processing setup was employed.

Gas-atomized alloy powders with a diameter < 45 µm were used in all cases, produced by the EIGA technique (**E**lectrode **I**nduction Melting **G**as **A**tomization). The Ti-6Al-4V grade 23 powder was provided by TLS Technik GmbH, Bitterfeld, Germany. Ti-45Al-5Nb-0.2B-0.2C (at%) was made in-house from an ingot which was provided by GfE Gesellschaft für Elektrometallurgie mbH, Nürnberg, Germany. After powder production the powder was sieved. For the experiments with Ti-6Al-4V-0.5B alloy boron powder (grade I, 95 % purity) was supplied by H.C. Starck, Germany, and mixed with Ti-6Al-4V grade 23 powder before feedstock production

As binder a mix of paraffin wax, polyethylene-vinylacetate copolymer and stearic acid was used. Feedstock preparation took place inside a glovebox system under controlled argon atmosphere by means of a z-blade kneader. The powder load was 65 vol%.

Injection moulding was performed on an Arburg 320S injection moulding machine. The samples produced for tensile test measurements were shaped according to ISO 2740 as dog-bone specimens (Figure 2a). As samples for 4-point-bending testing the geometry shown in figure 2b was used. All fatigue samples were shot peened after sintering using zirconia particles with a diameter of 200 µm to ensure comparable surface quality.

Sintering was performed at temperatures between 1350 °C and 1500 °C for 2h under high vacuum in a cold-wall furnace with Mo-shielding and tungsten heater. For investigation of the influence of porosity some samples were hot-isostatic-pressed with 100 MPa at 915 °C after MIM-processing. In the following they are denoted by the suffix “+HIP”.



a) b)

Figure 2. Geometry and dimensions after sintering in mm of tensile (a) and fatigue (b) test specimens.

Characterisation. Tensile tests were performed on a servohydraulic structural test machine equipped with a 100 kN load cell at a strain rate of 1.2×10^{-5} s^{-1} at room temperature in air. In the case of Ti-45Al-5Nb-0.2B-0.2C [at%] additional tests were performed under air at 700 °C. The high-cycle 4-point-bending fatigue tests were performed on a resonance machine fabricated by

RUMUL. The experiments were carried out in air at room temperature under load control with a cyclic frequency of ~95 Hz (sine wave) at a load ratio $R=\sigma_{min}/\sigma_{max}$ of 0.2. The fatigue endurance limit was defined as 10^7 cycles.

Light microscopy and scanning electron microscopy (ZEISS – DSM962) were used to investigate the microstructure. The level of interstitial elements (O, N, C) were determined using a LECO melt extraction system (TC-436AR and CS-444). The residual porosity was calculated from the density of the sintered samples, measured using the Archimedes method. A density of 4.41 g/cm^3 for the dense Ti-6Al-4V material was determined by measuring a MIM+HIP sample. The porosity of the Ti-45Al-5Nb-0.2B-0.2C [at%] samples were determined by optical pore analysis using Olympus Analysis Pro software. Grain size was determined according to ASTM E112-96 (linear intercept technique). Electron backscatter diffraction (EBSD) was performed on a ZEISS (ULTRATM 55) scanning electron microscope. Spatially resolved EBSD maps were acquired at 15 keV using a step size of 0.2 μm.

MIM of Ti-6Al-4V and Ti-6Al-4V-0.5B

In the following MIM processed Ti-6Al-4V will be referred to as Ti64 and Ti-6Al-4V-0.5B as Ti64-B, respectively. The following tables compare the microstructural (Table 1) and the mechanical (Table 2) properties of MIM processed samples sintered at two different temperatures and of samples which experienced an additional HIP process. Furthermore, table 2 shows the minimum values required by the common ASTM standards for wrought material (B348) and for MIM material (F2885-11).

Table 1. Microstructural and elemental data of the MIM processed samples.

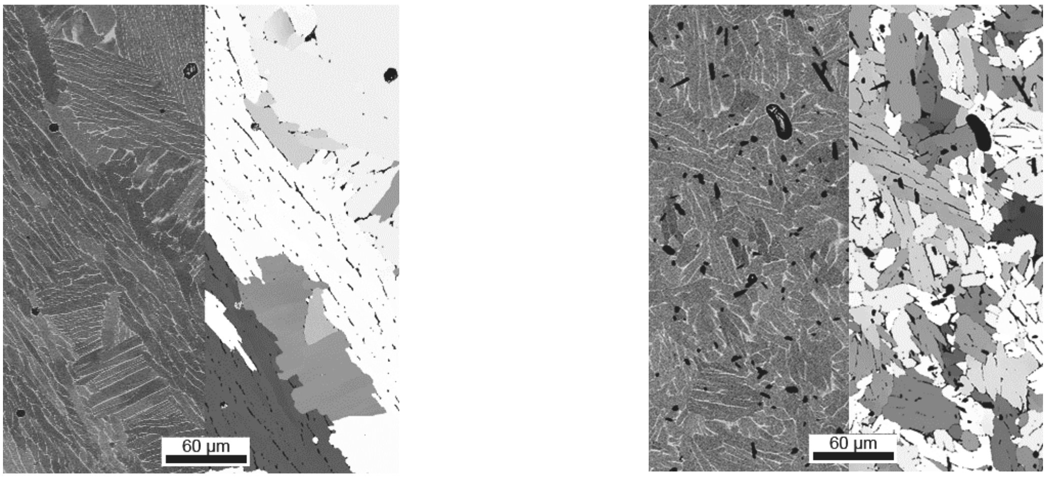
Material	Sintering temperature	Porosity [%]	Grain size [μm]	O [wt%]	N [wt%]	C [wt%]
Ti64	1350 °C	3.6	148	0.23	0.017	0.041
Ti64	1400 °C	3.3	247	0.19	0.015	0.058
Ti64+HIP	1350 °C	0.0	174	0.23	0.018	0.048
Ti64-B	1400 °C	2.3	18	0.20	0.016	0.039
ASTM F2885-11	*n.a.*	*n.a.*	*n.a.*	*0.20*	*0.050*	*0.080*

Obviously, sintering temperature strongly influences the resulting grain size, whereas there is no clear effect on the interstitial content. Indeed, experience shows that the pick-up of oxygen is more depending on the number of sinter parts in the furnace than on temperature. However, in all cases the oxygen content is within the range where good ductility is expected according to figure 1. This is proved by the tensile test results in table 2. Furthermore the results show that residual porosity is very important for strength and ductility. It is even more decisive than the interstitial content. Although Ti64 sintered at 1400 °C features lower oxygen content and larger grains, the tensile properties are better than those of the samples sintered at 1350 °C. An even larger increase of strength and elongation ε_f is achieved by applying an additional HIP process after MIM processing. In this case the porosity is effectively zero and the requirements of grade 23 and even grade 5 standards for wrought material are fulfilled clearly. Without HIP grade 23 specification can be achieved e.g. by purposely increasing the oxygen content based on the chart in figure 1. In addition, it is important to note that especially the yield strength depends on the strain rate applied during tensile testing. This has to be taken into account when comparing different studies.

Table 2. Mechanical data of the MIM processed samples.

Material	Sintering temperature	Yield strength [MPa]	UTS [MPa]	ε_f [%]	Endurance limit [MPa]
Ti64	1350 °C	720	824	14	450
Ti64	1400 °C	744	852	15	n.a.
Ti64+HIP	1350 °C	841	937	17	500
Ti64-B	1400 °C	787	902	12	640
ASTM B348 grade 23	*n.a.*	*> 760*	*> 825*	*> 10*	*n.a.*
ASTM B348 grade 5	*n.a.*	*> 828*	*> 895*	*> 10*	*n.a.*
ASTM F2885-11, sintered	*n.a.*	*> 680*	*> 780*	*> 10*	*n.a.*
ASTM F2885-11, +HIP	*n.a.*	*> 830*	*> 900*	*> 10*	*n.a.*

As mentioned above increasing the sintering temperature in order to receive lower porosity effects strong grain growth. While this appears to be less important in terms of tensile properties, fatigue properties of Ti64 are determined mainly by the grain size as shown in [10]. The comparison of Ti64 samples with and without HIP treatment shows that the endurance limit rises by just 10% when the porosity is eliminated, while the yield strength is increased by nearly 17%.



a) MIM Ti64, sintered at 1400 °C / 2h b) MIM Ti64-B, sintered at 1400 °C / 2h

Figure 3. EBSD images of alpha-phase showing the effect of boron addition on grain size

In order to investigate the effect of a fine microstructure on fatigue Ti64-B samples were prepared by MIM. During heating to sinter temperature the elemental boron powder reacts with titanium to TiB. During sintering in the beta region the growth of the beta grains is impeded by grain boundary pinning by these titanium boride particles. In addition, during cooling the alpha-phase nucleates at the particles. This leads to more and smaller alpha grains. As shown in table 1, the grain size is reduced to 18 µm although the material was sintered at 1400 °C. This strong difference is also visible in figure 3, showing EBSD images of the alpha phase for samples with and without boron addition, both sintered at 1400 °C. It is also worth to notice that the residual porosity is reduced to nearly 2.3%. This is assumed to be connected to the pinning of the grain boundaries: the pores remain in the region of the grain boundaries where diffusion is much faster than in the volume. The lower porosity causes an increase in yield strength of about 9% compared to Ti64 sintered at 1350 °C, while the ductility is reduced slightly, which is probably due to the titanium boride particles. On the other hand, the effect on fatigue resistance is dramatic: the endurance limit is increased by 42% to 640 MPa. This value is well within the range of wrought material, although considerable residual porosity still exists.

These results show clearly, that the mechanical properties of the MIM processed Ti-6Al-4V alloy depend on details of the processing and can be varied to such an extent, that even common standards for wrought material can be fulfilled. However, if specific properties like fatigue resistance have to be optimised, slight alloy variations should be considered. This is easily done by powder metallurgy methods.

MIM of Ti-45Al-5Nb-0.2B-0.2C (at%)

Titanium aluminides are composed of the two hard and brittle intermetallic phases α_2 and γ. MIM processing of this alloy class provides additional challenges compared to Ti-6Al-4V. Firstly, as typical in high temperature materials the diffusivity is low. This means high temperatures close to the solidus are needed in order to gain sufficient sintering. On the other hand a high sintering temperature implies increased risk for loss of volatile elements like Al and for oxygen uptake. Secondly, the resulting microstructure of titanium aluminides depends strongly on details of temperatures, holding times as well as heating and cooling rates during sintering and cooling. Therefore, accurate process control basically for each sintering part is necessary. Figure 4 represents the binary phase diagram of Ti-Al according to [11]. Alloying elements like Nb affect the position of equilibrium lines, or for higher contents even stabilize additional phases not present in the binary system.

In this paper the results for Ti-45Al-5Nb-0.2B-0.2C (at%) processed by MIM are presented. The alloy is also known as TNB-V5. Boron is added to the base system Ti-Al-Nb due to its capability of grain refinement by forming titanium borides. Carbon addition leads to fine titanium carbides strengthening the matrix. For sintering a temperature of 1500 °C close to the solidus proved to be adequate for achieving high density: the residual porosity amounts to values between 0.2 and 0.5%. The reason for the low porosity is not clear yet. It cannot be totally excluded that a small amount of liquid phase is already created during sintering which improves the densification. On the other hand no distortion or melted surface is visible on the sintered samples.

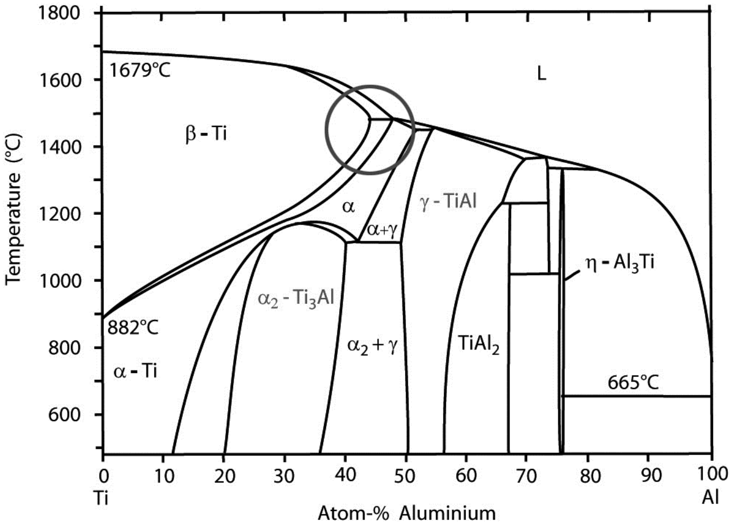


Figure 4. Binary phase diagram of Ti-Al according to [11]. The circle marks the region were sintering takes place.

The resulting microstructure after sintering for 2h and furnace cooling reveals the typical lamellar structure consisting of layers of α_2 and γ phase (Figure 5). The mean colony grain size is about 80 µm and the oxygen content was analysed to be around 1200 µg/g. Both values are well comparable to those of typical cast material. The white needle shaped features in figure 5 are titanium borides. Only few and well rounded pores can be observed.

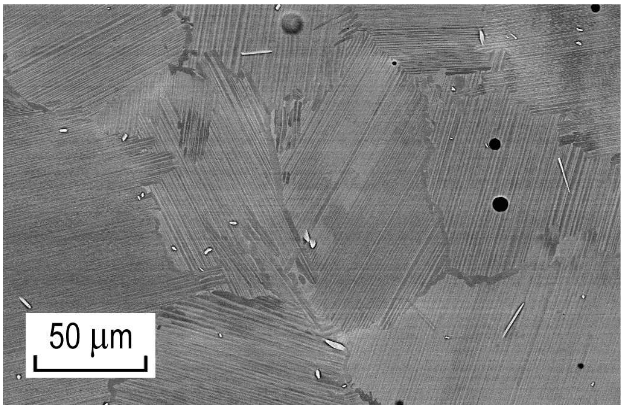


Figure 5. Typical SEM micrograph of Ti-45Al-5Nb-0.2B-0.2C (at%) processed by MIM.

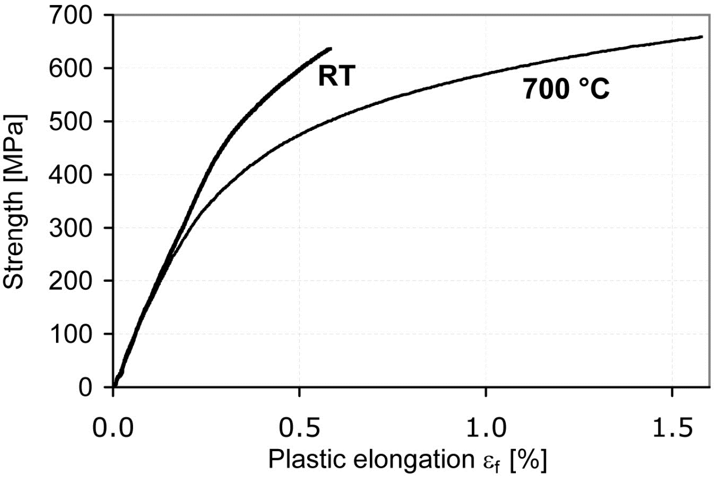


Figure 6. Tensile test results performed at room temperature (RT) and at 700 °C: Ti-45Al-5Nb-0.2B-0.2C (at%) alloy processed by MIM, sintered under vacuum.

Figure 6 displays the results of tensile tests on Ti-45Al-5Nb-0.2B-0.2C (at%) samples sintered for 2h at 1500 °C under vacuum. The tensile strength is not reduced at high temperature, while plastic elongation increases from 0.2 to 1.0 %. However, the yield point is significantly lower at 700 °C.

In Table 3 the results are compared with those of cast material. Although the microstructure and oxygen content of cast and MIM samples are almost identical, the cast material shows better strength. It is possible that the difference is caused by different specimen conditions. The cast samples were HIPped, machined to standard geometry and polished, while the MIM processed specimens were of dog bone geometry and just sintered and polished with fine abrasive paper. Further investigations have to be performed on this matter. However, these first results are very promising and further improvement is likely.

Table 3: Comparison of tensile test data of cast and MIM processed Ti-45Al-5Nb-0.2B-0.2C (at%)

Temperature	Sample	UTS [MPa]	ε_f [%]
RT	MIM	630	0.2
	Cast	745	0.1
700 °C	MIM	650	1.0
	Cast	720	1.4

Summary

In spite of the special challenges related to the sensitivity of titanium to oxygen excellent mechanical properties can be achieved by Metal Injection Moulding and even standards for wrought material can be satisfied. Decisive is the adequate choice of powder, binder, powder handling route and sintering process. An optimised microstructure of the sintered parts is essential for good properties and can be varied by processing and alloy composition in a certain range. If high tensile strength is required, an additional HIP process should be taken into account. However, if excellent fatigue properties are demanded slightly modified alloys like Ti-6Al-4V-0.5B should be considered. Simple powder blending offers enormous possibilities for improvement.

On the other hand even pure Ti-6Al-4V alloy powder can lead to properties nearly equivalent to those of wrought material and sufficient for most applications. Furthermore, it was shown that actually MIM processing of high temperature titanium aluminides is possible and the mechanical properties are comparable to those of cast material.

References

[1] T. Ebel, “Titanium and titanium alloys for medical applications: opportunities and challenges”, PIM International, Vol 2 No 2, June 2008, 21-30

[2] R. German, “Titanium powder injection moulding: A review of the current status of materials, processing, properties and applications”, PIM International, 3 No 4, December 2009, 21-37

[3] B. Oger, T. Ebel, W. Limberg, “The Manufacture of Highly-Ductile and Geometrically Complex MIM-Parts Based on TiAl6V4”, Proc. Euro PM2006, 2, Gent, 23-25 Oct. 2006

[4] Y. Itoh, T. Harikou, K. Sato, H. Miura, “Improvement of Ductility for Injection Moulding Ti-6Al-4V Alloy”, Proc. PM World Conf. 2004, Vol. 4, EPMA, Shrewsbury (2004), 445-450

[5] R. Zhang, J. Kruszewski, J. Lo, “A study of the effects of sintering parameters on the microstructure and properties of PIM Ti6Al4V alloy”, PIM International, 2 No 2, 2008, 74-78

[6] E. Nyberg, M. Miller, K. Simmons, K. S. Weil, “Microstructure and mechanical properties of titanium components fabricated by a new powder injection molding technique”, Mat Sci Eng C 25 (2005), 336-342

[7] Shibo G, Xuanhui Q, Xinbo H, Ting Z, Bohua D (2006), “Powder injection molding of Ti-6Al-4V alloy”, J Mat Proc Tech, 173, 310-314

[8] 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”, Mat. Sc. Eng. A 527 (2010) 3929–3935

[9] E. Baril, “Titanium and titanium alloy Powder Injection Moulding: Matching application requirements”, PIM International, Vol 4 No 4, December 2010, 22-32

[10] O.M. Ferri, T. Ebel, R. Bormann „The influence of a small boron addition on the microstructure and mechanical properties of Ti-6Al-4V fabricated by metal injection moulding”, Adv Eng Mat. 13 (5) (2011) 436-447

[11] C. McCullough, J. J. Valencia, C. G. Levi, R. Mehrabian, “Phase equilibria and solidification in Ti-Al alloys “, Acta Met, 37 (1989) 1321.