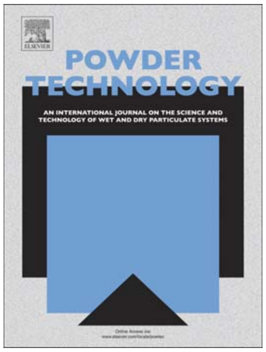

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PII: S0032-5910(17)30512-0
DOI: doi:10.1016/j.powtec.2017.06.053
Reference: PTEC 12629

To appear in: *Powder Technology*

Received date: 19 April 2017
Revised date: 20 June 2017
Accepted date: 21 June 2017

Please cite this article as: Ali Dehghan-Manshadi, Michael Bermingham, Matthew Dargusch, David StJohn, Ma Qian, Metal Injection Moulding of Titanium and Titanium Alloys: Challenges and Recent Development, *Powder Technology* (2017), doi:10.1016/j.powtec.2017.06.053

Metal Injection Moulding of Titanium and Titanium Alloys: Challenges and Recent Development

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Abstract

Metal Injection Moulding, MIM, is a well-developed net or near-net shape manufacturing technique for stainless steel, copper and ceramic materials. This process has received increasing attention over the last decade as a promising technique for the manufacture of intricate titanium parts for a range of applications in biomedical, aerospace, automotive and other industries. Historically, the necessity to use expensive fine sized spherical (<45 μm), low-oxygen titanium powder has hindered the industrial application of titanium MIM from an economic perspective. However, recent efforts have shown promise in adapting low-cost non-spherical hydride-dehydride (HDH) titanium powder in the MIM process. HDH powder is considerably less expensive than fine spherical powder and thus there is significant potential in expanding the number of titanium MIM applications. This paper reviews recent developments in MIM of titanium and its alloys as well as the outstanding challenges with a special focus on MIM of HDH titanium powder.

Keywords: metal injection moulding; titanium; sintering; porosity; density; microstructure.

1. Introduction

Metal Injection Moulding (MIM) is an established net-shape manufacturing process that combines powder metallurgy with plastic injection moulding [1-3]. It combines the most useful characteristics of powder metallurgy (e.g. low cost, simplicity, flexibility of composition selection and inexpensive raw materials) and plastic injection moulding (e.g. ability to manufacture complex parts and rapid production) to manufacture small-to-medium sized intricate components and is particularly suited to mass production [4]. The process offers significant design freedom in shape complexity but most MIM parts are restricted to smaller than about 100 mm in size for high dimensional accuracy and consistency [3, 5].

The application of MIM to produce titanium components (MIM-Ti) has been considered for a number of years [1, 6-11] but progress has been slow. There is essentially no established business today due to the need of using expensive fine (≤45μm), low-oxygen spherical Ti powder. Owing to the relatively low density of molten titanium and the high melting point of titanium or liquidus temperature of titanium alloys, the portion of -45μm spherical titanium powder produced by gas atomisation is low [12]. However, there are other spherical powder production techniques such as the plasma wire based atomisation process which offer more control on purity and powder size [13]. However, in general, the cost of fine (≤45μm), low-oxygen and spherical titanium powder remains excessively high for industrial applications. This is the primary reason for the lack of MIM-Ti business today compared to the established MIM-stainless steel business. The high affinity of titanium for oxygen and carbon requires special considerations during MIM processing (including the requirement for a specialised binder system), which can increase the cost of production but this additional cost is insignificant compared to the cost of the powder.

Consequently, from an economic perspective, MIM-Ti parts are not yet competitive enough when compared to similar parts made by machining or casting (e.g. as-cast dental implants). However, as the cost of powders is the greatest barrier to economically manufacturing MIM-Ti components, using inexpensive titanium powders is expected to improve the competitiveness of a MIM-Ti industry. In that regard, the use of low cost hydride-dehydride (HDH) Ti powder has the potential to completely change the situation and has therefore received much attention [2, 14-20].

Despite the issues surrounding the high cost of manufacture, effort has been made to produce MIM-Ti parts for industrial applications. In addition, the first Standards Specification for application of MIM-Ti in manufacturing of surgical implants from Ti-6Al-4V and un-alloyed Ti, has recently been published by ASTM [21, 22]. This paper provides an overview of the current status of MIM-Ti technology and discusses potential future opportunities.

2. The MIM process

In a typical MIM process, metallic powders are mixed with polymeric materials (binders) to form a feedstock which can be injection moulded using conventional plastic injection moulding machines. This fluid feedstock enables the MIM process to be used for manufacturing geometrically complicated components. After the selection of the appropriate powder and binder systems, the materials are mixed and kneaded under a protective atmosphere and at a temperature slightly higher than the melting point of the binder (usually in the range of 140-170 °C). This forms the feedstock for subsequent injection moulding. The ratio of metal powder to polymer, which is known as “solid loading”, is an important factor for MIM processing and must be selected so that the mixture has good flowability whilst minimising the fraction of polymer. The mixing procedure is critically important for successful MIM processing and must ensure that after mixing every individual metal powder is covered by a thin layer of binder to provide enough flowability for processing by injection moulding. In this regard, high shear mixers are preferred. In the case of MIM-Ti the entire mixing process should be performed under a protective atmosphere of argon gas to prevent any oxygen pickup by the Ti powder. In the next step, the feedstock is granulated into small pieces <3.0 mm for an easy and smooth injection moulding process. The injection moulding process is usually performed in conventional plastic injection moulding machines. However, some special consideration may be required for the selection of injection dies. For instance, due to the large size of metal powders and the feedstock’s low flowability compared with polymeric materials, a larger injection gating and runner system is recommended for MIM [6]. After injection moulding, the binder needs to be removed from the injection moulded components (known as green parts) through two separate steps. During the first step, the main binder component, which is usually a wax based polymer such as paraffin wax, is removed by a solution debinding process. It is critical that the main binder component is completely removed during this stage which ensures a porous part for the easy removal of the second component during the next step (thermal debinding). An important issue during thermal debinding of Ti feedstock is using a protective environment to prevent any atmospheric oxygen and nitrogen contamination in the Ti components. A continuous flow of high purity argon gas is recommended to protect the Ti component and also to flush the decomposed binder from the furnace. During the last step the MIM component, which now is a porous part purely containing metal powder slightly bonded together during the thermal debinding process (brown part), is sintered at high temperature and under high vacuum to form a solid component. The quality and mechanical properties of the final products are very dependent on the sintering stage and as such a high vacuum (usually better that 10^{-5} mbar) is required to minimise oxygen contamination during sintering.

3. Critical parameters for MIM-Ti

a) Powders for MIM-Ti

Among all available Ti powders, spherical Ti powder made by gas atomisation (from liquid), plasma atomisation (from wire), or plasma spheroidisation (from non-spherical powder) with an average particle size of 30µm or smaller is ideal for the MIM process due to its good flowability and the resulting uniform shrinkage during sintering. Fine spherical powder also improves the surface finish of the final sintered products, but as the particle size becomes smaller the impurity content tends to increase (especially oxygen). Coarser powders and/or a mixture of coarse and fine powders may be used to increase the solid loading or density of green parts [2, 23]. Using coarse powders reduces the debinding time, but makes the injection moulding process more challenging. With all of these factors in mind, the optimum particle size for MIM of Ti is considered to be around 45μm [6].

However, the primary disadvantage associated with such fine spherical Ti powder is its high cost. Alternatively, non-spherical Ti powder with higher oxygen contents is readily available at a fraction of the cost (3-6 times cheaper) of low-oxygen spherical Ti powder. In this regards, effort has been made to develop viable MIM processes using HDH Ti powders [2, 6, 15-19, 23]. One attempt is to use the powdered titanium hydride (TiH_2) [15-19, 24], of which the de-hydrogenation will occur during thermal debinding and sintering of the MIM parts. The released hydrogen can also help prevent extra oxygen pickup by the final sintered part [6]. For instance, Carren˜o-Morelli et al. [18] demonstrated the potential of TiH_2 powders in MIM-Ti by manufacturing components with excellent elongation of 15% and tensile strength of 666 MPa. In another study, Park et al. [25] used a powder modification process to reduce the sharpness of HDH powders and make them more spherical. This process improved the tap and apparent density of HDH powders, resulting in an improvement in the solid loading and mould-ability of HDH powders [25]. Using a mixture of HDH and spherical powders is another alternative to reduce the final cost of MIM parts and also improve the suitability of HDH powders for MIM processing [2, 23]. German [2] mixed a fraction of small HDH powder with large gas atomised powders and reported a solid loading of up to 72% (typical solid loading for MIM-Ti is in the range 62-68% for spherical powders).

Figure 1 compares the SEM images of three different Ti powders available for MIM process. Gas atomised powder (GA) as the most common powder has spherical shape with good flowability, consistent shrinkage and smooth surface finish after sintering. Spherical powders manufactured through Advanced Plasma Atomization (APA) process offer more control on size, shape and purity of powders and exhibit exceptional flowability and packing properties [13]. Hydride-dehydride powders have irregular shapes, low packing density, poor flowability, high impurity content and less favourite for any powder metallurgy process. However, their low cost made them an attractive choice for MIM.

Figure 1. *SEM micrograph of three different Titanium powders a) gas atomised (GA) b) plasma atomised (APA) and c)Hydride-dehydride (HDH)*

b) Binders for MIM-Ti

The selection of a suitable binder that leaves minimum oxygen and carbon residue after debinding is a critical step in MIM-Ti. The most important characteristics of a binder include [26]:

- Good adhesion to Ti particles;
- Low melting temperature for injection moulding;
- Dimensional stability during debinding;
- Complete decomposition at low temperature (<260 °C) without any residue after thermal debinding;
- Not chemically reactive with Ti;
- Provide sufficient green strength and is environmentally friendly;

As no single binder material can satisfy all of these criteria, thus a mixture of different components are commonly used as the binder system. Over the years binder systems have been tailored for MIM of Ti components and are mostly based on well-known binder systems developed for MIM of other materials such as stainless steel [14, 26-33]. In 2012 Wen et al. [26] reviewed most binder systems developed for MIM-Ti, but since then, new binder systems [28, 30, 34, 35] have been reported. However, a complete and exclusively tailored binder system for MIM-Ti is yet to be developed. In addition, specific applications may require special attention to binder selection. For instance, the manufacture of Ti components for biomedical application may require the application of a water-based binder system instead of the more common wax-based binders [30, 32, 36]. This is due to the toxicological concerns with organic solvents which need to be used for debinding of wax-based binders.

4. Mechanical properties of MIM-Ti and Ti alloys

MIM-Ti parts are small and intricate. Most of these parts only require moderate properties, although superior mechanical properties are always desired. Density, interstitial content (oxygen, carbon and nitrogen), microstructure and alloying content can all affect mechanical properties and they continue to be the focus of research in order to improve the mechanical properties of MIM-Ti.

a) Density

Owing to the use of fine powder (<45μm), a high sintered density (98%) in MIM-Ti parts is readily achieved when sintered at temperatures ≥1300°C. Small additions of alloying elements such as iron [37-40], nickel [41, 42] or boron [42, 43] can improve the final density of sintered Ti components. In addition, post-processing may be needed to improve the density for specific applications. For instance, where fatigue resistance is important, a shot peening process has been shown to reduce the surface porosity which improved the fatigue strength by 100MPa [44, 45]. Hot isostatic pressing (HIP) is a common process used to improve the density and mechanical properties of MIM and other powder metallurgy components. This process can substantially improve the ductility of PM parts by closing the remaining porosity.

b) Contamination by interstitial elements

Oxygen decreases tensile ductility, cold workability, fatigue strength and stress corrosion resistance of Ti and its alloys. Figure 2 shows an example of the negative influence of oxygen on elongation and the positive effect on strength of Ti components [7, 46, 47]. Although other interstitial elements such as nitrogen, carbon and hydrogen could have a detrimental influence on the properties of sintered parts, experience has shown that during MIM the pickup of these elements is negligible in comparison with oxygen [6].

Figure 2. *Effect of oxygen content on mechanical properties of Ti (adopted from [7])*

The predominant sources of oxygen contamination are the initial powder and the sintering atmosphere but oxygen contamination can also come from the binder, the debinding furnace as well as the sintering supports (setters) [48]. Therefore, it is important to avoid introducing extra oxygen contamination during MIM processing, as well as employing methods to reduce the oxygen content of the final products. For example, it is necessary to operate in a high-purity argon environment (more costly) through each MIM process step (mixing, debinding and sintering), and use binder systems containing less carbon and oxygen, appropriate sinter supports (such as Yttria or Zirconia plates) and oxygen scavengers [2, 6, 18, 49-51].

Table 1 summarises recent efforts to control oxygen and carbon content during MIM-Ti and its alloys. This table also provides some information on selected powder and binder systems and indicates how these selections affected the density and mechanical properties of final products. It is clear that using new binder systems, TiH_2 powder rather than HDH Ti powder, a reducing atmospheres for debinding and sintering stages as well as developing new Ti alloys and mixtures can effectively improve the final properties of MIM-Ti components. The results indicate that limiting the oxygen content to less than 0.3wt% for a commercially pure

Ti component or to 0.2% for a Ti-6Al-4V component is possible through accurate selection of powder and binder while also controlling the injection, debinding and sintering processes.

***Table 1**: A summary of some published data on MIM of Ti and selected Ti-alloys during last 20 years [18, 24, 45, 52-69]*

Prevention of carbon contamination is much easier to achieve than it is for oxygen by using a flow of high purity argon cover gas during the debinding process. It is necessary to limit the carbon content to less than 0.08wt% in order to avoid titanium carbide formation within the structure [70]. If present, titanium carbides may reduce the elongation and fatigue properties, reduce corrosion resistance and enhance the Young's modules of Ti alloys [70], and accordingly, their formation should be generally avoided in MIM-Ti components. However, in some novel studies, the positive behaviour of extra carbon has been exploited in MIM-Ti. Tingskong et al. [71] was able to improve the density of sintered components from 95% in pure Ti-6Al-4V to 97.5% with the addition of 1.0% graphite to the Ti-6Al-4V feedstock. This carbon addition also improved all of the mechanical properties of MIM components including the yield strength, UTS, elongation and hardness. Such improvement in the mechanical properties of MIM-Ti components was attributed to the precipitation of fine TiC particles in the microstructure and an extensive refinement of α and β-Ti microstructures [71].

c) Microstructure

A uniform, fine microstructure, including grain size, lamellar size, phase distribution and morphology is necessary to improve the mechanical properties of the final products. As a high temperature is necessary for sintering of Ti and Ti alloys (usually in the range of >1250 °C), microstructure coarsening is expected, although due to using fine powders the grain coarsening in MIM is not as problematic as in other manufacturing processes such as casting. However, controlling the morphology and size of α and β lathes and grains is necessary for achieving the desired final mechanical properties and many attempts have been made to control these features. For instance for α+β structures (such as Ti-6Al-4V) achieving a fine lamellar α+β microstructure is desirable due to its better mechanical properties as seen in Figure 3.

Figure 3. *Dependence of yield strength on inverse square root of a lath thickness for lamellar (a + b) Ti–6Al–4V (adopted from [72-80])*

There have been many attempts to refine the final microstructure and/or to achieve the microstructural morphologies suitable for improved mechanical properties (such as fine lamellar structures). The most successful process may be a small addition of grain refining agents such as boron, LaB_6 and TiC to the feedstock [43, 45, 81-83]. Post sintering heat treatments may also improve the ductility and strength of MIM components through their modification of microstructure. Figure 4 shows examples of general microstructures obtained in MIM of different Ti alloys. The presence of a coarse microstructure is clear especially for pure Ti (Figure 4a) and Ti-6Al-4V (Figure 4b). Also, Figure 4c illustrates a large improvement in the microstructure and density of Ti-6Al-4V components by addition of 0.5% boron to the feedstock.

Figure 4. *Microstructure of MIM-Ti samples a) pure Ti with a density of 96.5% [84], b) Ti-6Al-4V with a density of 96.4% [44], c)) Ti-6Al-4V0.5B with a density of 97.7% [45] and d) Ti-16Nb with a density of 95% [60].*

d) Alloying

Improvements to the mechanical properties of Ti components by small (or large) additions of other elements have always been considered in all manufacturing processes including MIM. Despite using common alloys which have already been developed for other conventional processes (e.g. CP-Ti [15, 17, 55], Ti-6Al-4V [43, 85, 86], Ti-Nb [59-61, 65, 69], Ti-Mo [67, 87], Ti-Mn [17, 68], Ti-Ni shape memory [88, 89] and Ti-Al [62] alloys), the addition of small amounts of alloying elements such as B and rare earth elements (Ce, La, Y_2O_3, etc) as well as other elements such as Fe, Ni and Zr which add a liquid phase to the sintering process, have been found to have a considerable influence on the final properties of MIM components [43, 90].

5. Dimensional accuracy of MIM-Ti components

Dimensional reproducibility, uneven shrinkage and distortion are significant challenges for Ti-MIM. These challenges, which are common for MIM of all materials, are more extreme for large-sized parts, which generally limit the part size for MIM to 50mm, wall thickness of <5.0mm and weight of <50g. The most important reasons for such dimensional constraint and distortion in MIM components can be divided into three categories [5, 91, 92]:

a) *<u>Component factors</u>*: component size, geometry and wall thickness can significantly influence the distortion and dimensional stability of sintered parts. This is because large components carry a greater chance of containing residual binder (despite passing through a debinding stage) and are more prone to shrinkage after sintering [5, 93, 94]. Also, since long debinding times are required to remove the binders from large and thick sections, oxidation of powders may occur during such long debinding durations which can introduce oxides and other defects in MIM parts. This problem is more risky for Ti (compared with other metal powders such as stainless steel and copper) due to the high affinity of Ti to oxygen and carbon. Furthermore, large and geometrically complicated parts can cause non-uniform green density distribution, resulting in distortion during debinding and sintering.

   Material composition may also influence component distortion during the MIM process. For instance, when phase transformations occur during sintering, the dimensional stability of the component may deteriorate significantly [91] on account of the sudden volume change in material during transformation, particularly when the compact was not fully sintered and the inter-particle bonding is still weak.

b) *<u>Feedstock factors</u>*: powder characteristics such as size, shape and distribution, binder systems, mixing processes and powder loading can significantly influence distortion and dimensional accuracy of MIM products [2, 5, 92, 95]. For instance, irregularly shaped particles (such as HDH Ti powders) tend to show more (and uneven) shrinkage compared with spherical powders. Also, coarse powders have been found to show more distortion compared with fine powders [96].

   One important source of distortion in MIM components occurs during solution debinding on account of swelling of the binder system. As the amount of swelling depends mainly on the thickness of the specimen, content and type of the binder and solvent temperature [97-99], components with non-uniform thicknesses may suffer more from swelling resulting on cracks, slumps and distortions.

c) *Processing factors*: injection moulding parameters as well as debinding and sintering parameters can severely influence dimensional accuracy as well as distortion of MIM samples. For instance, fast heating rates during debinding and sintering can cause sample distortion [91]. Also, surface roughness of the sintering support plate can cause sample distortion [91]. Therefore, extreme care is required to optimise all steps of the MIM-Ti process in order to control shrinkage and prevent distortion in the final products.

The above challenges associated with distortion and shrinkage of MIM-Ti components become more critical for complex parts. Large components with simple geometries that have flat surfaces to rest on for support during debinding and sintering can be manufactured by the MIM process. However, MIM manufacturing of more complex parts (but with less requirement on dimensional accuracy) is still possible using multi surface supports and more accurate selection of resting surfaces as well as a suitable binder system, heating rate and sintering temperature. For instance, Miura et al. successfully fabricated a large complex Ti-6Al-4V component by careful selection of powder type and size, binder system, heating rate during debinding as well as the position of supports during debinding and sintering [5, 92].

6. Recent developments in MIM-Ti

With a gradual increase in MIM-Ti research, novel techniques and new materials are being developed for this process. To assess the progress of MIM-Ti research and development, a Google patent search was performed to summarize the patents which were filed exclusively for MIM-Ti over the last two decades (Table 2). In this table, the patents mostly deal with new binders, new feedstock materials and new manufacturing methods for specific components (especially for biomedical applications). Figure 5 summarizes the number of MIM-Ti related patents filed in each year taken from Table 2. Overall, the number of patents filed each year is limited to just a few, indicative of insufficient business opportunities and research development in MIM-Ti.

Figure 5. The number of MIM-Ti related patents filled from 1990 (data collected from Google Patent search)

Table 2. *A summary of patents filed during recent decades exclusively or more significantly for MIM-Ti*

Highlighted below are a few novel developments selected from the patents listed in Table 2.

- Patent JP2005281736 disclosed a new solution for low cost manufacturing of MIM-Ti alloy components with high mechanical properties and low oxygen content. They mixed different fractions of TiH_2, HDH titanium and 60Al-40V pre-alloyed powders to manufacture Ti-6Al-4V components with low oxygen and excellent mechanical properties. Optimum mechanical properties of YS = 910 MPa, UTS = 950 MPa and El = 14% were obtained by mixing 25 wt% TiH_2 and 75 wt% HDH powders. The resulting relative density is 97% and oxygen level is 0.31%. Contrary to other reports [16], they observed that increasing the TiH_2 fraction in the powder mixture increases the oxygen content, which resulted in a decrease in elongation.
- A new binder system was reported in patent US7883662B2 for the control of the oxygen and carbon content in MIM-Ti components. Using an aromatic binder system including naphthalene, polystyrene and stearic acid, the oxygen and carbon level in the final Ti-6Al-4V sintered parts remained at very low levels of 0.197wt% and 0.05wt% respectively, which is in the accepted range by ASTM F2885 standard for MIM-Ti surgical tools.
- Patent CN105382261 described a novel technique to improve the dimensional accuracy of MIM-Ti components. The inventors mixed titanium powders with different average particle sizes to produce MIM feedstock and found the optimum mixture for best dimensional accuracy. For instance, using three powders with average sizes of 46.8μm, 34.5μm and 24.4μm and ratios of 68:24:8 percent, they obtained a high dimensional precision of ±1%, uniform structure, low oxygen level of <0.25wt% and high mechanical properties.

- Patent CN103266319 developed a new technique based on the insert molding and MIM-Ti processes to cover the surface of cast Ti implants by a thin and porous layer to improve the biocompatibity and reduce the Young modulus of the implants. For instance, using TiH_2 powders with average particle size of 40μm and oxygen content of 0.3wt%, the inventors created a porous coated surface with oxygen content of 0.32wt%, porosity of 60% and bonding strength of 420MPa. The density and bonding strength of the coated parts can be manipulated by changing the Ti powder shape, particle size, binder system and sintering conditions.

To better evaluate the most recent developments on MIM for Ti and its alloys, a selection of industrially important Ti alloys are discussed in following sections.

a) Commercially Pure (CP) Ti

Commercially pure titanium (CP-Ti) has received the most research and development work on MIM practice. Despite the common industrial application of CP-Ti, another reason for the popularity of CP-Ti in MIM practice is related to the greater acceptable tolerance for oxygen content, which can be up to 0.4% for grade 4 (in comparison the acceptable oxygen limit for Ti-6Al-4V is only 0.2%). Frequent research and industrial scale work on MIM of CP-Ti indicate that this process is able to manufacture components with chemical composition as well as mechanical properties in the accepted range by ASTM standards. For example, using plasma atomised spherical powders with an oxygen level of 0.14%, Sidambe et al [55] manufactured Ti components through the MIM process with final oxygen content, elongation and tensile strength of 0.2wt%, 20% and 470MPa, respectively. All of these values fulfil the requirements of ASTM standard for CP titanium grade 2, which is an excellent achievement for the MIM process. However as mentioned previously, the high cost of spherical powders with low oxygen level is a major barrier for MIM of CP-Ti. In this regards many attempts have been made to use HDH powders as a cheaper alternative to the spherical powders. The current authors [84] used HDH Ti powders to manufacture Ti components with mechanical properties close to CP-Ti grade 3, which is an important development for MIM-Ti industry to manufacture cost effective Ti parts. The obtained mechanical properties can satisfy the requirement for many industrial applications such as automotive, marine and medical. A summary of the most recently reported data on the properties of CP-Ti components manufactured through MIM process is presented in Table 1. Data in this table suggest that MIM has a great potential to be used as a commercial manufacturing technique for many industrial components made from Ti and its alloys. However, different MIM processing conditions and especially initial powders can produce samples with different properties. For instance, Figure 6 compares the microstructure of samples manufactured from gas atomised and HDH powders. As clear, under similar sintering conditions, gas atomised powders produced microstructures with less porosity with round pores. However, samples manufactured through HDH process have more porosities and also pores are elongated with sharp edges. Such morphology of pores could deteriorate the mechanical properties of final product.

Figure 6. *Microstructure of MIM proceed CP-Ti samples from a) gas atomised powders [55] and b) HDH powders [84]*

Another important development in MIM of Ti to manufacture components with good mechanical properties is the use of titanium hydride (TiH_2) powder as an alternative to the costly fine spherical powders. As mentioned previously, release of hydrogen atoms during thermal debinding and sintering on MIM parts prevent oxygen pickup by Ti keeping the oxygen level as low as the initial powders [15, 17, 18].

b) Ti-6Al-4V alloy

Ti-6Al-4V (Ti64) which is the most common commercial alloy of Ti has also received great consideration by business and researchers for the manufacture of industrial as well as biomaterial parts. While Ti64 is extensively used in the aerospace industry, the high quality standards required for application of any component in aerospace, means the MIM process faces significant hurdles before it can be accepted by this industry. Nonetheless, research has demonstrated that it is possible for the MIM process to manufacture Ti64 components with superior mechanical properties close to the ASTM standard range [5, 43, 51, 100, 101] especially by small addition of other elements such as B [43, 45], C [71], Gd [58] and TiC [81]. However, most research work on MIM of Ti64 alloy has been specifically designed for biomedical applications [43, 83, 102] rather than other applications such as aerospace. Table 1, summarizes powder and binder characteristics as well as properties obtained from some selected research on MIM of Ti64 alloys. It is clear that tensile strength of up to 800MPa and elongation of 15% are achievable through this process, which is very promising properties for a PM technique. Examples of the microstructures obtained from MIM of Ti64 samples shown in Figure 7 [43]. This figure indicate that a typical lamellar structure with a small fraction of remain porosity exist in the microstructures, expecting adequate mechanical properties [43].

Figure 7. *Optical microstructure of MIM proceed Ti-6Al-4V samples after sintering at a) 1250 °C and b) 1400 °C [43]*

c) Ti-10V-2Fe-3Al

Ti-10V-2Fe-3Al (Ti-10-2-3) alloy which is a near beta alloy with superior combination of strength and toughness as well as high fatigue life, has been developed for application in many aircraft structural parts [103, 104]. Although, this alloy has been designed for the manufacture of aerospace components through casting, forging and then machining processes, it has attracted much research interest for powder metallurgical activities [105-108]. The MIM process of this alloy has also received consideration in recent years [66, 109]. For example, Sagara et al [66] manufactured Ti-10-2-3 superelastic components by MIM processing of elemental powder followed by solution treatment and aging. Under optimised MIM conditions, they reached a high density of 97%, tensile strength of 1050MPa and elongation of 5.0% (Table 2). These properties are in the range of 80-85% of wrought materials, which are very promising for the MIM process, and there is room for even more improvement by post processing techniques such as hot isostatic pressing.

d) Titanium Aluminides (TiAl)

Titanium aluminide (TiAl) alloys with high strength-to-density ratio and excellent resistance to creep and oxidation at high temperature are structural materials for various applications [110]. The manufacture of TiAl components through different PM processes including MIM [62-64, 111, 112], has been considered for many years due to the alloy's limited ductility and inadequate hot workability to be manufactured through conventional casting, hot working and machining processes [113]. One of the first attempts to manufacture γ-TiAl using the MIM process was performed by R. Gerling and F.-P. Schimansky [111], using spherical and fine pre-alloyed powders. However, the mechanical properties of the manufactured parts was low (even after post HIP) compared with cast alloys mostly due to the high impurity level (O, C and N). Figure 8 represents the microstructures of MIM proceeds TiAl samples and after HIP process [112]. This figure indicate while as-MIM samples have a large fraction of porosities (4.5 vol%) but an almost pore free microstructure obtained after HIP process. However, the ductility of the samples did not improved after HIP due to the high oxygen level [112].

Figure 8. *Optical microstructure of γ-TiAl produced by (a) MIM process and (b) MIM followed by HIP process [112]*

Further studies improved the properties of MIM fabricated TiAl components by improving the process parameters, binder systems and composition of materials [62, 64, 113]. Table 2 summarizes some results obtained from MIM of TiAl components. These results indicate that despite improvement in the properties of TiAl samples manufactured by MIM, the biggest challenge is still high oxygen pickup during the debinding and sintering processes. In fact, in all three cases presented in Table 2, the oxygen level more than doubled during the sintering process. This demonstrates that further improvement is required to limit such oxygen pickup.

e) Other Ti alloys

The possibility of MIM manufacturing of a few other Ti alloys have been studied by different research groups. The alloys include but are not limited to: Ti-15V-3Cr-3Sn-3Al [114], Ti-24Nb-4Sn-8Zr, TiNi [115], Ti-Nb-Zr [69], Ti-Mo[67], Ti-Mn [68] and Ti-Nb [60, 116-118]. The mechanical properties obtained from some selected alloys are summarized in Table 2.

f) MIM of Porous Ti and Ti alloys

MIM combined with space holder techniques has the potential to manufacture porous components for biomedical applications. A US patent filled in 2003 by Nelles et al. [119], is among the first attempts to provide a MIM-based manufacturing technique for porous metals including Ti. They described the principals for MIM of different metallic materials with open porosity of at least 10% and using KCl or NaCl as space holders.

Although, currently there is no industrial production for porous medical implants using MIM technology, there are many research and development works that have evaluated the possibility of this technique [17, 19, 88, 120-123]. For example, Carreno-Morelli et al [19] manufactured highly porous Ti parts using MIM of titanium hydride powders and the space holder technique with very low elastic modulus in the range of 4-22 GPA, which is close to that of human bone. Chen et al. [120] also fabricated porous Ti parts with up to 60% porosity using HDH Ti powders and NaCl as the space holder. Figure 9 shows examples of porous Ti microstructures with different porosities manufactured by MIM process [120]. These microstructures indicate development of a well interconnected porosities, which are essential for biomedical applications [124].

Figure 9. *SEM micrograph of porous Ti samples manufactured by MIM and space holder technique. a) 42% porosity, b) 52% porosity, c) 62% porosity, d) 72% porosity [120]*

MIM process also employed to manufacture Ti-6Al-4V porous components. For instance, Engin et al [125] produced micro-porous Ti-6Al-4V samples using a MIM technique and poly-methyl-methacrylate (PMMA) as the space holder. Such research indicates that MIM has the potential to manufacture many porous implants and scaffolds from Ti and its alloys. Especially considering the fact that most of the medical implants possess a complex geometrical shape, MIM could be an appropriate technique for manufacturing such complex components. However, the direct use of standard injection moulding machines for porous components could be problematic, due to the high volume of large space holder particles in the feedstock and the possibility of separation of the binder and space holder particles in the nozzle and die gates. Therefore, some modifications to the injection machine and injection dies may be necessary for the successful MIM of porous components using space holder techniques.

7. Application of MIM for the manufacture of Ti components

After decades of research and development, MIM of Ti is gaining attention for applications where the use of titanium can be fully justified: biomedical implants, military and firearms, electronic, automotive, aerospace and chemical devices. In biomaterial and implant fields, MIM can be used to manufacture both high density and porous components. With the development of non-toxic binder systems (such as water soluble binders) this potential has increased. So far, the manufacture of several biomedical components from Ti and Ti alloys has been reported [45, 55, 60, 68, 82, 126-129] and more advanced production in this range is expected in the near future. For instance, Ebel et al. [45] developed a new Ti-6Al-4V alloy containing small additions of boron (0.5wt% B) with mechanical properties that satisfy the ASTM standard for Ti-4Al-4V ELI wrought material. As clear from Table 2, a wide range of patents which have been filed in recent years, are related to manufacturing methods for different biomedical implants and tools through MIM-Ti processes.

As medical implants usually need porous structures, many attempts have been made to manufacture porous Ti components [120, 123, 130]. However, an important challenge for the manufacture of highly porous Ti implants through MIM is to retain the geometrical shape during sintering. Various efforts have been made to overcome this issue. For example, Daudt et al. [121, 131] applied a plasma treatment on MIM samples after solution debinding and prior to thermal debinding. This treatment cleans the surface of binder by a microwave plasma device without affecting its bulk properties, resulting in easier decomposition during the next thermal debinding step. They found that plasma treatment on partially debinded MIM samples resulted in better shape retainment, higher dimensional accuracy as well as more open surface porosity on highly porous MIM samples. Another challenge for manufacturing biomedical implants through MIM has emerged from the fact that many biomedical implants require different levels of porosity or porosity gradients. To manufacture components with different levels of porosity, Barbosa et al [126] successfully used a two-component MIM technique, which was able to inject two different materials in one specially designed die.

Military and particularly the firearms industry are major consumers of metal injection moulded products because MIM is a flexible process that can produce high quality, precise net shape parts while eliminating the need for expensive secondary processes. To date, many small firearms components are manufactured by MIM of steel and the development of economically feasible MIM-Ti components (specially using cheaper HDH Ti powders) has the potential to replace some of these products.

Figure 10 represents examples of Ti components manufactured using MIM process for industrial as well as medical applications.

***Figure 10**. Examples of a) industrial and b) medical implant parts manufactured using MIM-Ti process by Element 22 GmbH, Kiel, Germany*

8. Concluding remarks

Metal injection moulding of titanium and its alloys is an attractive process for the manufacture of small but complicated components for many industries such as aerospace, automotive, biomaterial and sporting goods. In this regard, noticeable developments have been made on different aspects of this process from powders to binder development and improved process parameters. However, there are still important challenges facing this technology if it is to be used on an industrial scale. The biggest challenge is related to the high cost of low-oxygen fine spherical Ti powder, which makes MIM an unaffordable process for many industrial applications. On the other hand, the availability of low cost HDH and Ti-hydride (TiH_2) powders represents attractive opportunities for the MIM-Ti industry to significantly reduce the manufacturing cost of many complicated titanium components. Although low-oxygen, fine spherical Ti powder is the most appropriate powder for MIM-Ti, emerging research has shown that HDH powder has the capability to be used as a significantly lower cost alternative source of Ti powder for MIM processing. Dimensional stability and reproducibility of MIM-Ti are other significant challenges which need to be addressed. These challenges are even more critical when using non-spherical HDH titanium powders and complicated geometries with different thicknesses. Finally, despite substantial progress on the development of new binders for MIM-Ti, the development of an appropriate binder system that decomposes at low temperature and does not introduce impurities into the titanium metal is yet to be formulated.

Acknowledgments

This work is supported by the Baosteel Australia Research and Development Centre (BAJC). Also, the project is co-funded by the Queensland State Government through the Research Partnership Program.

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Captions:

Tables:

Table 1: A summary of some published data on MIM of Ti and selected Ti-alloys during last 20 years [18, 24, 45, 52-70]

Table 2. A summary of patents filed during recent decades exclusively or more significantly for MIM-Ti

Figures:

Figure 1. SEM micrograph of three different Titanium powders a) gas atomised (GA) b) plasma atomised (APA) and c)Hydride-dehydride (HDH)

Figure 2. Effect of oxygen content on mechanical properties of Ti (adopted from [7])

Figure 3. Dependence of yield strength on inverse square root of a lath thickness for lamellar (a + b) Ti–6Al–4V (adopted from [73-81])

Figure 4. Microstructure of MIM-Ti samples a) pure Ti with a density of 96.5% [85], b) Ti-6Al-4V with a density of 96.4% [44], c)) Ti-6Al-4V0.5B with a density of 97.7% [45] and d) Ti-16Nb with a density of 95% [60].

Figure 5. The number of MIM-Ti related patents filled from 1990 (data collected from Google Patent search)

Figure 6. Microstructure of MIM proceed CP-Ti samples from a) gas atomised powders [55] and b) HDH powders [85]

Figure 7. Optical microstructure of MIM proceed Ti-6Al-4V samples after sintering at a) 1250 °C and b) 1400 °C [43]

Figure 8. Optical microstructure of □-TiAl produced by (a) MIM process and (b) MIM followed by HIP process [113]

Figure 9. SEM micrograph of porous Ti samples manufactured by MIM and space holder technique. a) 42% porosity, b) 52% porosity, c) 62% porosity, d) 72% porosity [121]

***Figure 10**. Examples of a) industrial and b) medical implant parts manufactured using MIM-Ti process by Element 22 GmbH, Kiel, Germany*

Figure 1

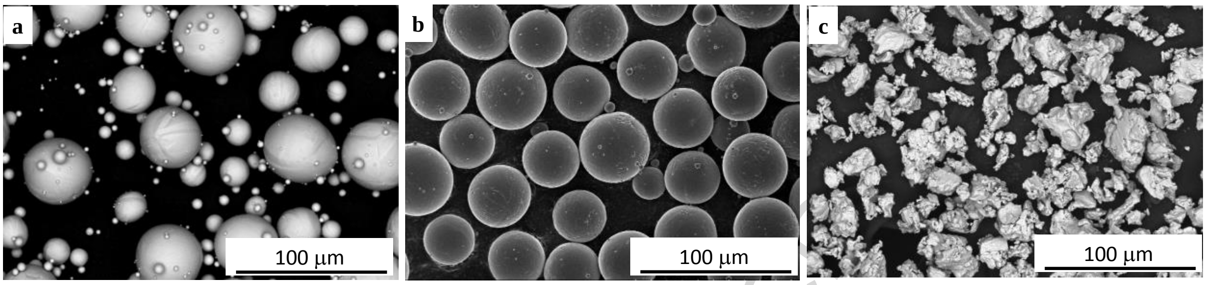
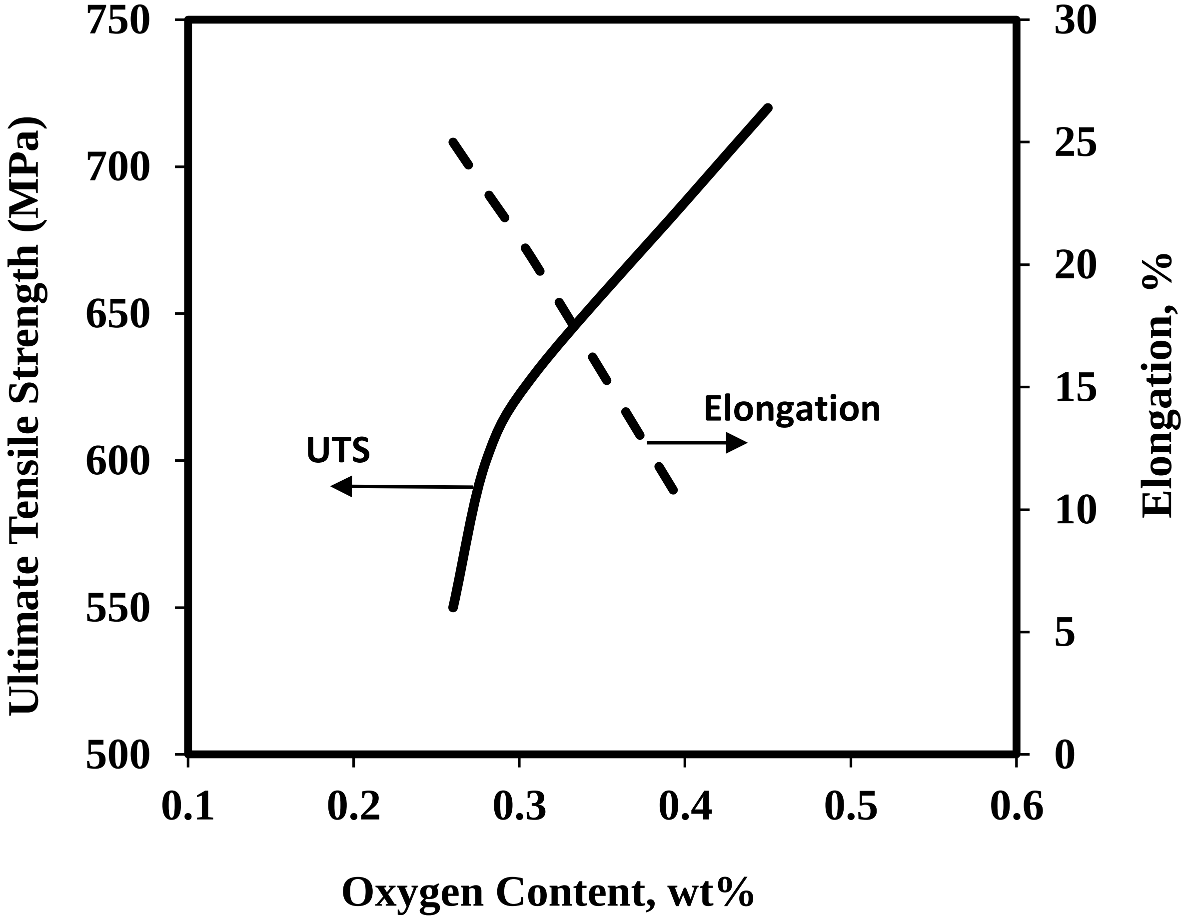


Figure 2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550
500
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15
10
5
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Elongation, %
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Elongation
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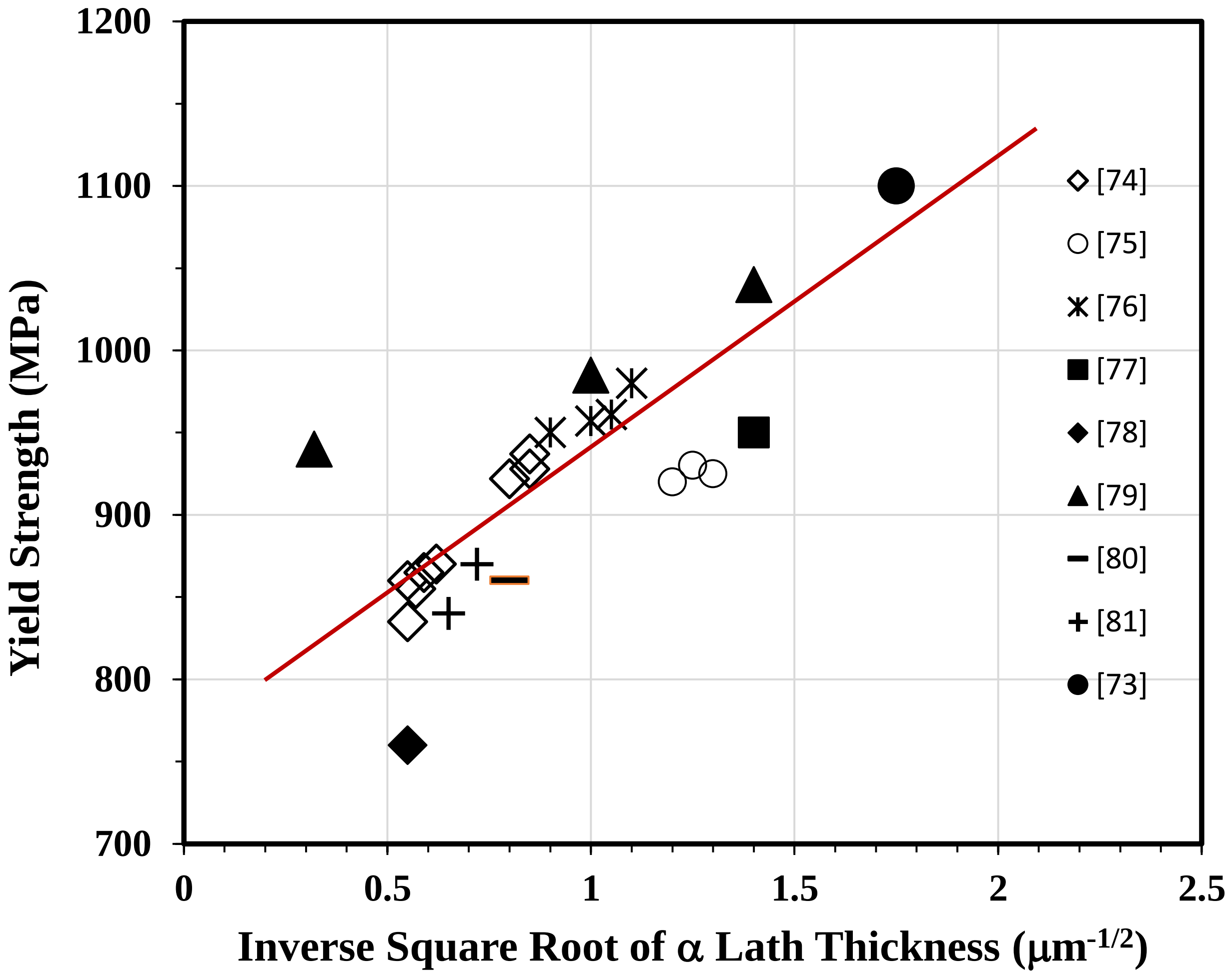
0.3
0.4
0.5
0.6
Oxygen Content, wt%

Figure 3: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1100
1000
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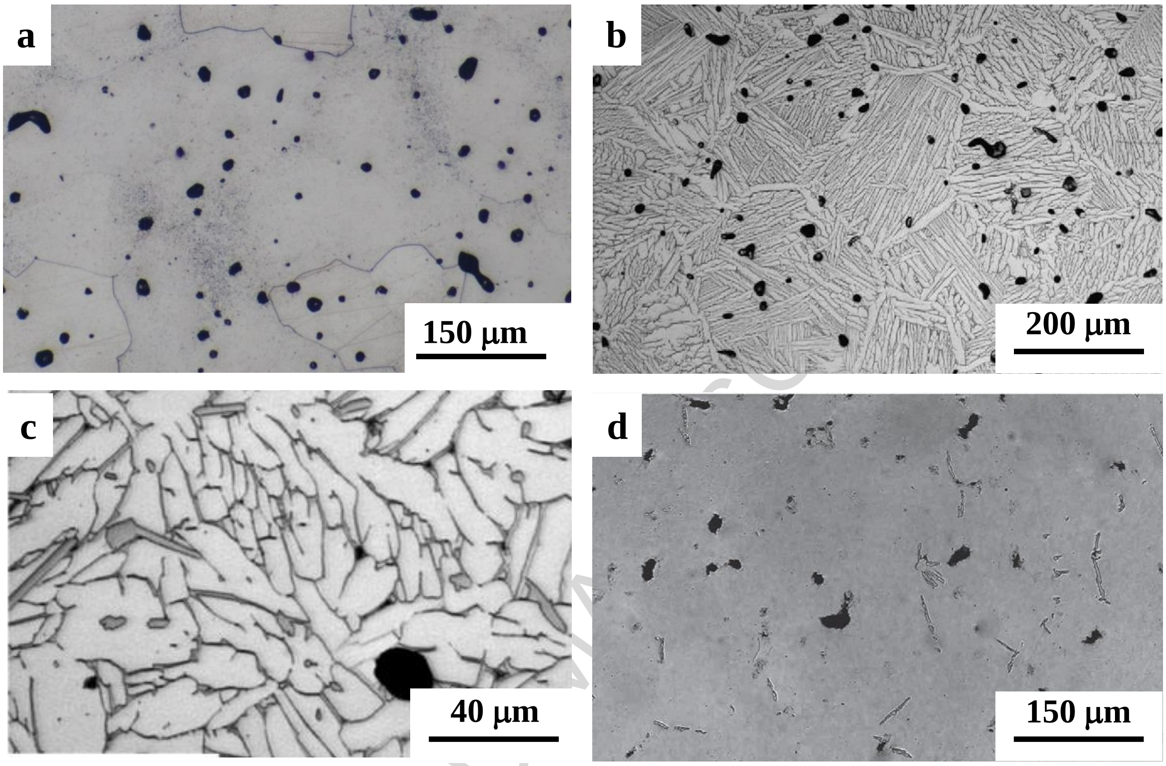
2
2.5
Inverse Square Root of α Lath Thickness (μm-1/2)
◇ [74]
○ [75]
✳ [76]
■ [77]
◆ [78]
▲ [79]
− [80]
+ [81]
● [73]

Figure 4:



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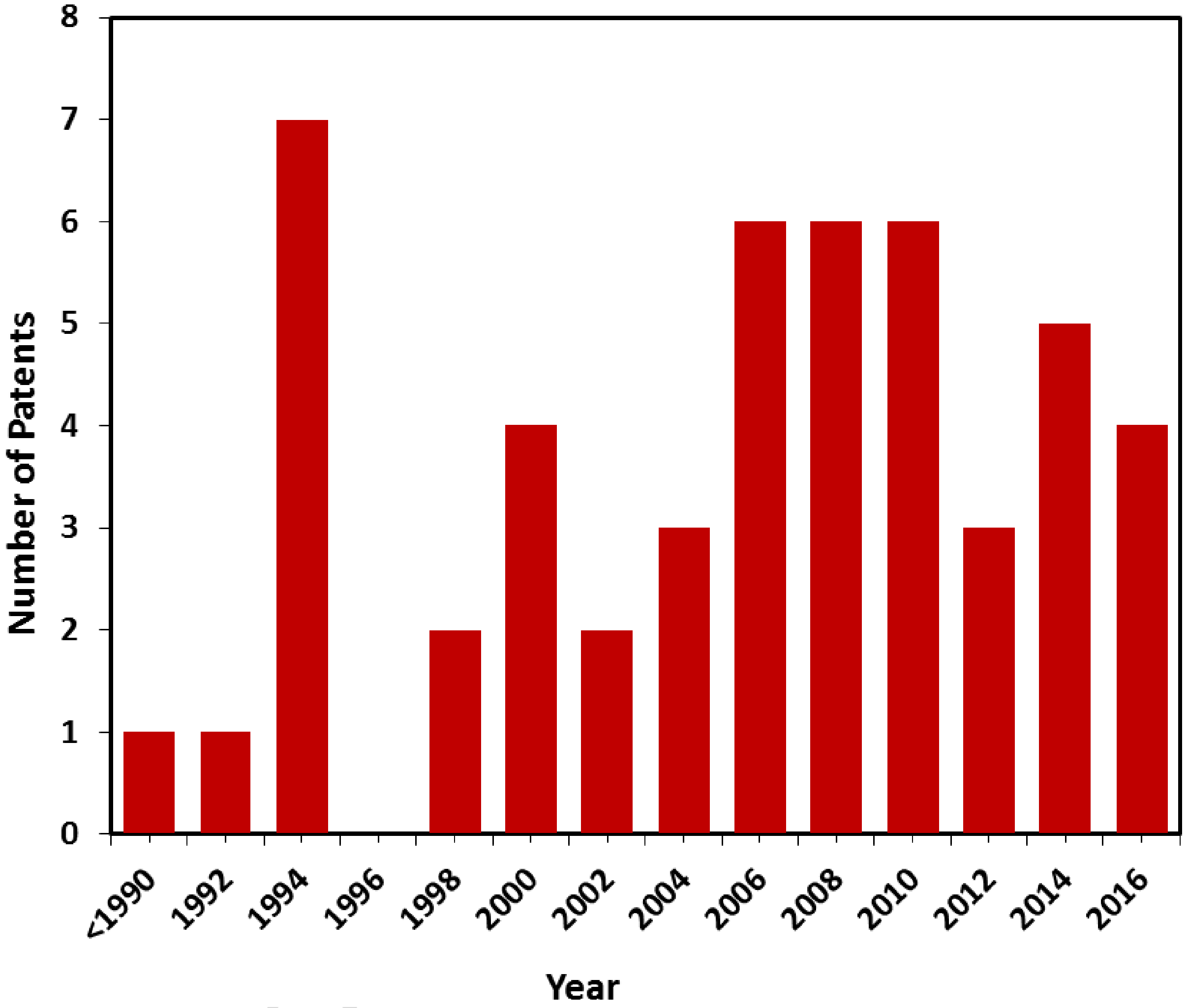
Number of Patents
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Figure 6:

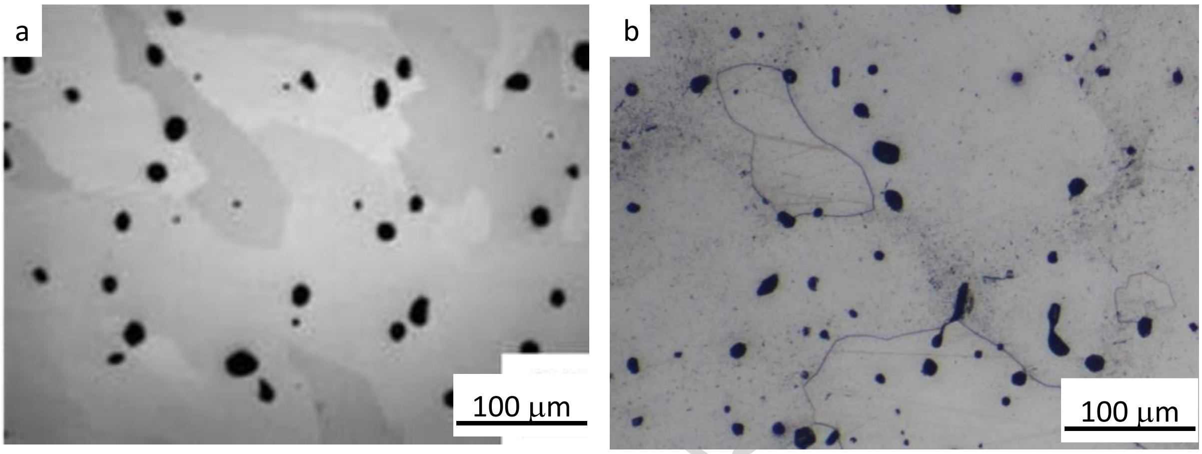


Figure 7:

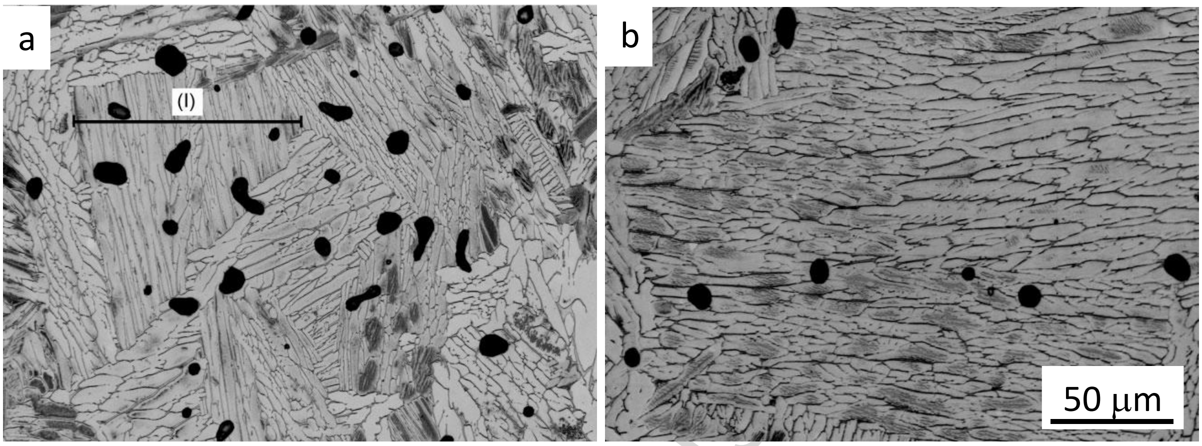


Figure 8:

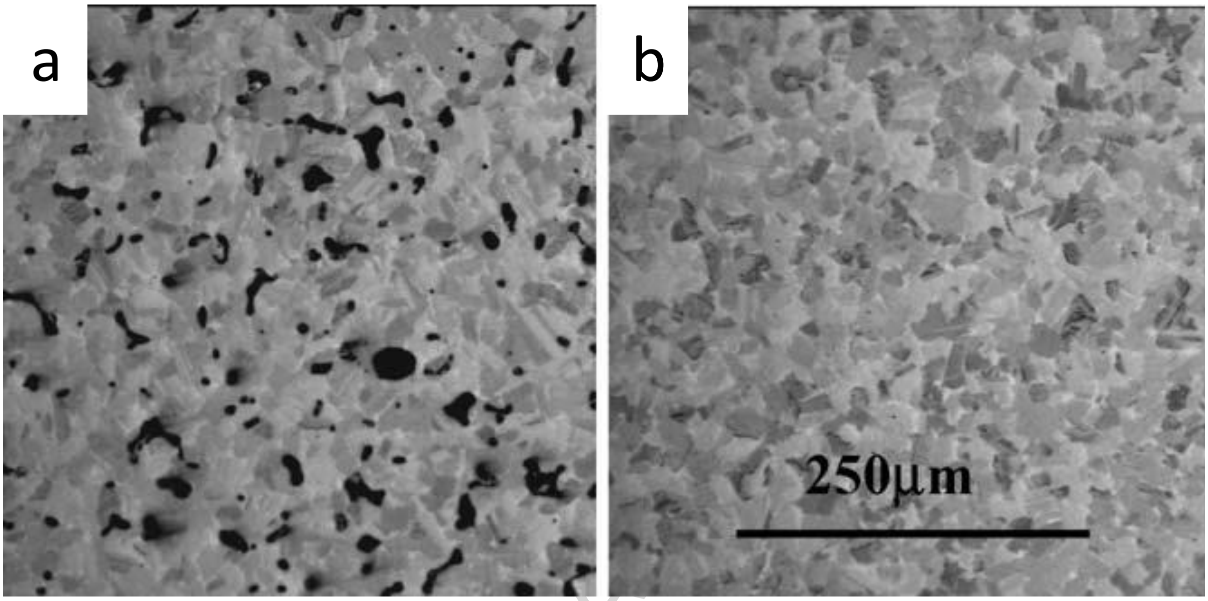


Figure 9:

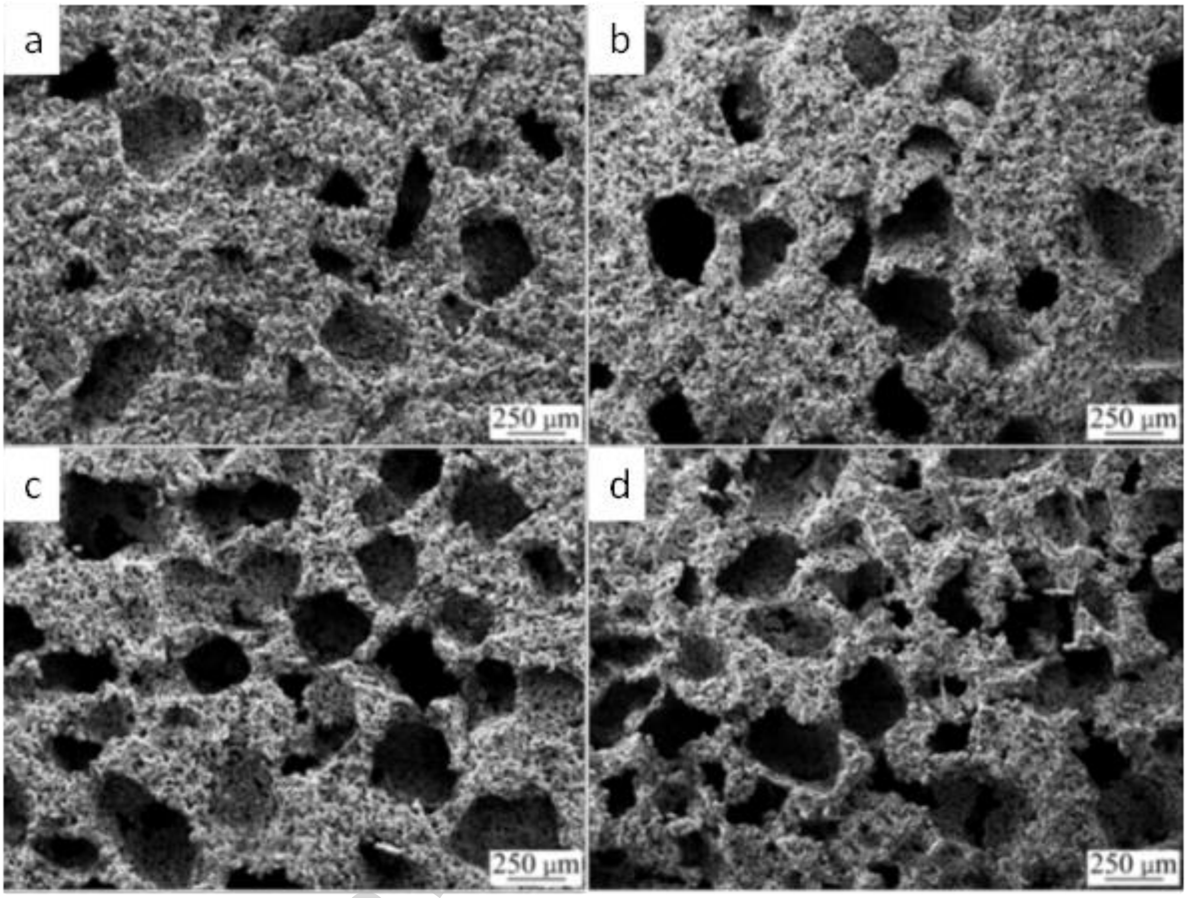


Figure 10

Table 1

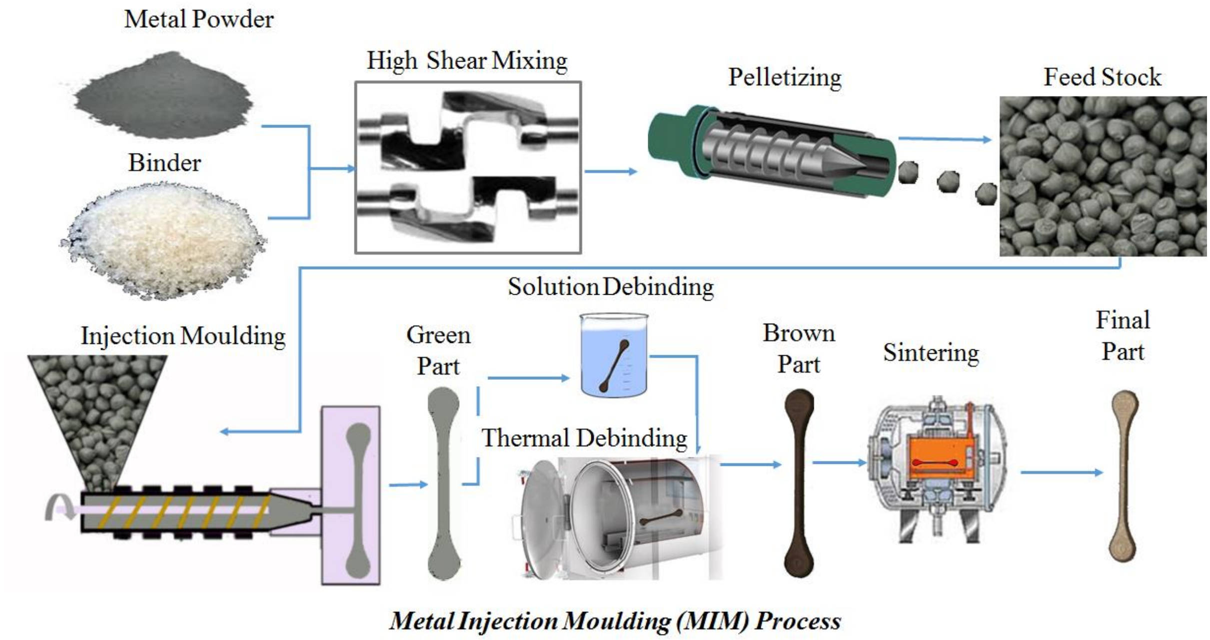
	Material	Powder Size (mm)	Binder	O in powder (wt%)	N in powder (wt%)	C in powder (wt%)	O after debind (wt%)	N after debind (wt%)	C after debind (wt%)	O in Sinter (wt%)	N in Sinter (wt%)	C in Sinter (wt%)	Density	YS (Mpa)	UTS (Mpa)	El (%)	Ref.
Pure Ti	TiH_2	35	PW-LDPE-SA	0.07	0.14	0.013				0.3	0.03	0.065	97.1	519	666	15	[18]
	GA Ti	25	PW-PE-SA	0.15	0.02	0.015				0.38			98		806	2	[52]
	85%GA,15%HDH	50	PW-PEG-LDPE-PP-SA	0.3	0.004	0.06							97	419		4	[53]
	GA Ti	45	PW-PP-SA-CW	0.17	0.02	0.02							95.5	378	455	10.3	[54]
	GA Ti	45	PEG-PMMA-SA	0.143	0.05	0.012				0.2					475	20	[55]
Ti-6Al-4V	Ti64	45	PW-PE-SA	0.13	0.02	0.05	0.26		0.09	0.19	0.02	0.05	96.5	700	800	15	[56]
	Ti64(90% GA-10% HDH)	45	PW-PEG-LDPE-PP-SA	GA 0.18 HGH 0.3	0.02 0.02	0.06 0.05				0.35		0.08	97.5	748	835	9.5	[57]
	Ti64 (using TiH_2)	45	PW based	0.1	0.024	0.003	0.015	0.018	0.12	0.17	0.001	0.011	99.5		855	3.8	[24]
	Ti64-0.5B	45	---	0.11						0.2	0.02	0.04	97.7	787	902	11.8	[45]
	Ti64	45	PW-EVA-SA							0.23	0.017	0.04	96.4	720	824	13.4	[58]
	Ti64-1Gd	45	PW-EVA-SA							0.24	0.022	0.05	94.5	655	749	9.9	[58]
Ti-Nb	Ti-10Nb	45	PW-EVA-SA	Ti 0.07,	0.04	0.005				0.203	0.07	0.06	96.5	552	638	10.5	[59]
	Ti-16Nb	45	PW-EVA-SA	Nb 0.22	0.09	0.015				0.255	0.05	0.06	94.3	589	687	3.58	[60]
	Ti-22Nb	45	PW-EVA-SA	Ti 0.16	0.01	0.009				0.022	0.05	0.06	94	694	754	1.43	
	Ti-17Nb (GA Ti)	30	PW-LDPE-SA	Nb 0.07	0.004	0.002				0.16	0.044	0.06	95.5	620	741	5.1	[61]
Ti-Al	Ti-45Al-5Nb	45	PW-EVA-SA	0.05	0.006					0.11	0.02		99		625	0.15	[62]
	Ti-47Al-4Nb	45	PW-PE-SA	0.08	0.014	0.004				0.18	0.017	0.04	96	409	433	0.6	[63]
	Ti-45Al-3Nb-1Mo	45	Pw-PVA-SA	0.085						0.16		0.12	(99 after hip)	571		0.12	[64]
Other Ti Alloys	Ti-24Nb-4Zr-8Sn	45	PW-EVA-SA	0.033	0.03	0.08				0.33	0.03	0.08	97.6	627	655	4.2	[65]
	Ti-10V-2Fe-3Al	24		0.29	--	0.02				0.3		0.07	97		1020	4.8	[66]
	Ti-12Mo	38	PEG-PP-EVA-HDPE	0.35	0.005	0.009				1.13		0.32	95.5		900		[67]
	Ti-12Mn (GA Ti)	45	PW-PMMA-PP-SA	0.16		0.06				0.252	0.01	0.06	94	930	980	2.5	[68]
	Ti-22Nb-2Zr	45	PW-PVA-SA										96.8	680	790	3.5	[69]
	Ti-22Nb-4Zr	45	PW-PVA-SA										96.5	690	800	4.7	[69]
	Ti-22Nb-10Zr	45	PW-PVA-SA										96.5	730	845	4.6	[69]

PW: paraffin wax; LDPE: low density polyethylene; SA: stearic acid; PE: polyethylene; PEG: polyethylene glycol; PMMA: polymethyl methacrylate; PP: polypropylene; EVA: polyethylene vinyl acetate; HDPE: high density polyethylene; CW:Carnauba wax; GA: gas attomosed powder; HDH: hydrie-dehydride powder

Table 2

	Patent Title	Patent Number	Filing Date	Patent Claim
Methods to reduce O and C	Manufacture of Ti sintered material	JPH0254733A	20/08/1988	Manufacture Ti components with low C and O
	Production of it alloy sintered compact by …	JPH06240381A	10/02/1993	Ni, Co, Cu, Ag ... added to Ti mixture to reduce O and C
	Production of titanium sintered body by metal powder …	JPH0790318A JP2793958B2	17/03/1994	Manufacture Ti components with low C and O
	Production of high density titanium sintered …	JP2000017301A	30/06/1998	Manufacture Ti components using mixture of Ti and TiH2
	Method for producing titanium alloy sintered …	JP2005281736A	29/03/2004	Manufacture Ti components using mixture of TiH2 and HDH Ti powder
	Titanium method of precision parts by powder …	KR100929135B1 KR20070050133A	10/11/2005	Manufacture Ti components using TiH2 powder
	Powder injection molding product, titanium …	KR100749395B1	4/01/2006	Manufacture Ti components using TiH2 powder
	Method for manufacturing of high density …	KR20110061779A	2/12/2009	Manufacture of Ti component using Ti hydride powders
	Method of controlling the carbon or oxygen ...	US 9334550 B2	13/10/2010	Develop a method to reduce C and O
	Injection molding method using powder	KR20110041452A	28/03/2011	MIM using TiHx powder
	Method of manufacturing powder injection-molded…	US 20140077426 A1 WO2010010993A1	25/11/2013	MIM using Ti hydride powder
Manufacturing of specific parts	Process for the manufacture by sintering of …	US 5441695 A	22/07/1994	Manufacture Ti decorative parts using MIM
	Process for the manufacture by sintering of a Ti …	US5441695A EP0635325A1	22/07/1994	Manufacture Ti components using TiH2 powder
	Manufacturing method of spectacles frame using …	KR20070106079A KR100778786B1	28/04/2006	Manufacture Ti glass frame using MIM
	Power injection molding method for forming article comprising titanium and titanium coating method	WO 2007066969 A1 KR100725209B1	6/12/2006	Using TiH2 powder for manufacturing a component
	Powder extrusion of shaped sections	US20100178194A1 WO2010081128A1	12/01/2009	Manufacture Ti and other profiles using MIM
	Titanium glasses frame molding method	CN103042219	17/04/2013	Manufacture glasses frame through MIM
	Manufacture method of titanium nail clippers	KR20130110423	10/10/2013	Manufacture of nail clipper through MIM
New Binder	Composition for injection molding of titanium …	JPH0741801A	26/07/1993	New binder for Ti-MIM for less C and O pickup
	Method for manufacturing a sintered body containing titanium and titanium alloys	JP4614028B2 JP2002030305A	13/07/2000	Manufacture Ti components using MIM
	Feedstock composition and method of using same …	US 20050196312 A1	8/03/2004	Develop an aromatic binder system for Ti
	Metal injection molding methods and feedstocks	US 20090129961 A1 US7883662B2	15/11/2007	Develop an aromatic binder system for Ti …
New feedstock	Feedstock and process for metal injection molding	US5064463A	14/01/1991	Using coated Ti (or Al-Mg) with Cu (or Fe-Cu-Ni) to prevent oxygen pickup during MIM
	Method for modifying hydrodehydrogenated Ti …	JPH07268404A	29/03/1994	Modification of HDH Ti powder by milling for MIM
	Sintered Ti-system material product derived from …	US6306196B1 JP2001049304A	4/08/2000	Manufacture Ti-MIM components with mirror finish
	Method for producing components from titanium or …	EP2292806B1 US20110033334A1	4/08/2009	Manufacture Boron added Ti components using MIM
	Powder injection molding process by utilizing low-cost hydrogenated-dehydrogenated titanium powder	CN 104690271 A	12/02/2015	Addition of rare earth boride and/or hydride to HDH powders and ultrasonic-assisted injection molding method
	Precision titanium part manufacturing method	CN 105382261 A	24/11/2015	A method for dimensional control during MIM process
	Ti6Al4V alloy injection forming method	CN 1644278 A	12/01/2005	MIM of Ti64 using mixture of HDH and GA powders

Development of Biomedical implants using Ti-MIM	Orthodontic parts made of titanium	JPH07289566A JP2901175B2	27/04/1994	Manufacture orthodontic parts using MIM
	Titanium precision injection molding method and porous…	KR20040050429A KR100508471B1	10/12/2002	Manufacture porous parts using MIM
	Metal injection moulding for the production of medical …	US20060285991A1	27/04/2005	Using MIM to manufacture implants from Ti
	Manufacturing method for titanium and titanium alloy powder injection molding product	JP2008173424A	18/01/2007	Using MIM to manufacture a thin-walled component with a complicated shape for medical applications
	Metal injection molded titanium alloy housing for implantable medical devices	US 7801613 B2	26/04/2007	Manufacture an implant by a complex method containing MIM, welding and chemical etching
	Metal injection molded titanium alloy housing for implantable medical devices	US20080269829A1 WO2008134198A2 US7801613B2	26/04/2007	MIM of biomedical implant
	Implant production method by Ti and Ti powder alloys	JP2009034473A	2/08/2007	Manufacture Ti implants using MIM
	Methods of forming porous coatings on substrates	US8124187B2 US20110059268A1	8/09/2009	Manufacture medical implants with solid body and porous surface using MIM
	Manufacturing a spatial implant structure …	DE 102010028432 A1	30/04/2010	Manufacture Porous implants using MIM
	Preparation method of porous titanium	CN102242288A	20/06/2011	Manufacture Porous implants using MIM
	manufacturing method and product of porous titanium	KR101380363B1	2/08/2011	Manufacture Porous implants using MIM
	Method for preparing porous titanium coating on …	CN 103266319 B	21/05/2013	Addition of a porous coating layer on solid Ti base
	Preparation method for medical artificial joint material	CN105349831	24/02/2016	Develop a new Ti alloy for implants using MIM
	Manufacturing method for medical bone fixing device	CN105369063	2/03/2016	Developme of a new biomedical Ti based alloy
MIM for Ti-Al	Production process of titanium-aluminum …	KR100302232B1	27/12/1997	Manufacture method for TiAl internetallics using MIM
	Method for fabricating titanium aluminide …	KR20040056651A KR100509938B1	24/12/2002	Manufacture titanium aluminide intermetallic using MIM
	Metal injection molded turbine rotor and jointing …	JP2005060829A JP4698979B2 US7052241B2	27/07/2004	Using MIM to manufacture titanium aluminide turbine rotor combined with a steel shaft for a turbosupercharger
	Injection forming method for preparing high Niobium…	CN 101279367 A	28/05/2008	MIM of high-Nb-TiAl
Process Modification	Method for sintering and molding ti metal powder	JP2000248302A	26/02/1999	A modified debinding process for Ti-MIM
	Debinder method of ti-al based alloy injection …	JP2000328103A	20/05/1999	A de-binding method for TiAl alloy components in MIM process
	Manufacturing method for titanium alloy products	CN 104148644 A	13/08/2014	Manufacture Ti components using MIM at high injection pressure



Graphical abstract