DENSIFICATION STUDY OF TiH_2 POWDER COMPACTS

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ABSTRACT

Recent research has indicated the good possibility to use TiH_2 powder in press and sintering operations to obtain titanium components with high final density. In this work, compaction behavior of TiH_2 powder treated with a lubricant is studied. The effect of compaction pressure on green density is investigated. Subsequent sintering trials show on the effect of green density and heat treatment parameters on final density and dimensional change.

INTRODUCTION

Höganäs AB has started to look into the titanium market, and one goal is to produce a Ti or Ti alloy powder possible to use in a conventional press and sintering process. Powder techniques for component manufacturing where Ti alloys are used include MIM, CIP and additive manufacturing, but the use of Ti for press and sinter is at present very limited. Overviews of the titanium PM technology and applications are found in [1-7]. The combination of titanium alloys and near net shape processing is very attractive since it allows good material utilization, and difficult and expensive machining operations can be avoided.

As base powder in press and sintering operations for production of Ti components, either a metal powder or a hydride powder such can be used. The choice of base powder will highly influence the green strength and compaction behavior. For a metal powder, like CP-Ti, the powder particles will deform during compaction, the oxide scale will break up and expose metal surfaces susceptible to cold welding, resulting in strong bonds between powder particles. TiH_2 on the other hand is a hard and brittle phase, and compaction of TiH_2 powders can give quite high green densities. The reason is that the problem with

friction and cold welding, which can be pronounced for Ti, is reduced. The hydride particles rearrange and break during compaction, and a high green density can be obtained. Wang et al. describe sintering of TiH_2 powders, and have performed trials resulting in relative sintered density greater than 99% [8]. Robertsson et al. compared press and sintering of Ti and TiH_2 powder, and reached higher green density with TiH_2 [9].

A problem with TiH_2 is that since no bonds are formed between powder particles during compaction, very low green strength will be obtained. For this system it is therefore necessary to use some sort of additive to enhance green strength, and make green components possible to handle. For effective compaction, a lubricant has to be added, and the best solution to the green strength problem is to use a lubricant which can also provide green strength to the component. Introduction of an organic lubricant to a Ti powder mix has to be done with caution; Ti has very high affinity for both C and O, and all residues of the lubricant present at high enough temperature will be dissolved in the titanium matrix and affect mechanical performance of the sintered part. A demand on a lubrication system for Ti is therefore that it effectively can be removed at sufficiently low temperature, without leaving any residues in the powder compact.

To be able to use a powder in commercial production of pressed and sintered components, the powder mix must have sufficient flow properties. A common problem with many of the so called low-cost production routes for Ti powder is that the powder obtained usually has a small particle size and irregular shape, resulting in very poor flow properties. One way to increase flowability is to mechanically alter the particle shape. This can be done by milling. The powder will, however, retain the small particle size, and there is also the risk of introducing more oxygen in the milling process. Another method is plasma spheroidization. The powder particles are then introduced into a plasma torch, where they are melted into spherical shape. This, however, significantly increases production cost. Also, spherical particle shape is usually not an advantage when it comes to compaction and green strength of the compacts. It is a method more suitable for powder to be used in additive manufacturing applications where high tap density is important. An alternative to altering the shape of the particles is to modify surface properties. This has been done successfully by treating the particles with a binder, which also acts as lubricant and green strength enhancer [10].

In traditional steel PM, it is usually desired to have as low change between tool and as sintered dimensions as possible. The components are compacted to sufficiently high density, and during sintering bonds are formed between particles, but shrinkage or swelling is kept at a minimum. Density levels around 90% of theoretical are common. This density level is not enough for good performance of Ti alloys, and therefore one has to compact to close to full density, or accept shrinkage during sintering. As mentioned, CP-Ti is difficult to compact, while high density levels have been reached with TiH_2. However, with TiH_2 shrinkage will nevertheless take place due to the change in molar volume associated with the removal of hydrogen to obtain metal Ti. Consequently, shrinkage has to be accepted when working with Ti alloys in press and sintering operations.

EXPERIMENTAL

Earlier trials have shown on difficulties to handle CP-Ti in the compaction process, and therefore the powders used in this study were of the type TiH_2. Also a 60Al-40V alloy powder was used. The most common Ti alloy is Ti-6Al-4V, and with PM techniques this alloy can be obtained by different methods; pre-alloyed powder can be used, elemental Ti, Al and V can be mixed in the right proportions, or, as in this study, an AlV master alloy could be added to Ti powder.

Two different TiH_2 powders were used, one produced by Höganäs AB through solid state reduction, and one more "classic" milled TiH_2 powder. **Figure 1** shows scanning electron micrographs of the two TiH_2 powders. As can be seen, the morphology is quite different between the powders, with a more rounded irregular shape of the Höganäs powder, and a more angular appearance of the milled TiH_2. Both powders have relatively small particle sizes, but some larger particles are present in the milled powder. Physical properties are presented in Table 1. Here is also the 60Al-40V powder, which was used as master alloy, included. This master alloy was jet milled in protective atmosphere down to a particle size distribution with an X_{50} of 6µm. The master alloy powder was then admixed to the TiH_2 to achieve the alloy Ti-6Al-4V after sintering. The fine mean particle size of the master alloy should make distribution of alloying elements in the powder mix relatively homogeneous.

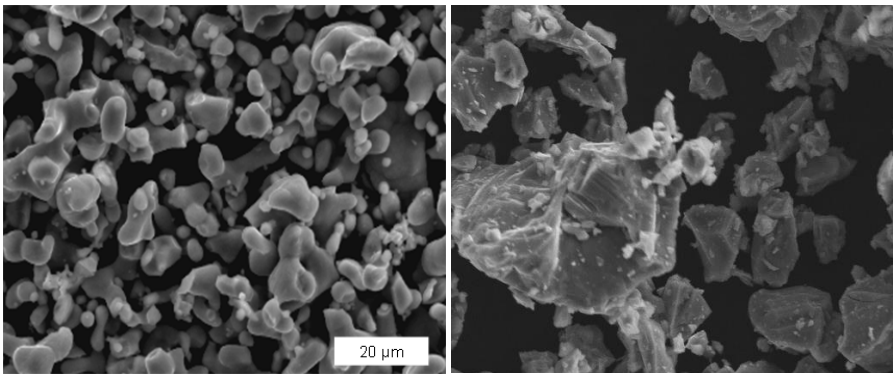


Figure 1. SEM micrographs of the TiH_2 powders used in the study; Höganäs solid state reduced TiH_2 (left), and milled TiH_2 (right).

Table 1. Physical properties of the powder.

	Höganäs TiH_2	Milled TiH_2	60Al-40V
X50	6-10 µm	16.7 µm	6 µm
Apparent density	1.29 g/cm^3	1.05 g/cm^3	-
Tap density	1.7 g/cm^3	-	-

To obtain flowability, a pre-treatment of the powder with a polymeric lubricant was utilized. In the treatment process, a lubricant addition of 2% by weight was used. This treatment increased flow of the fine powders, and made it possible to effectively handle in a press and sintering operation. Table 3 shows flow values for the powders measured with a Gustavsson flowmeter. The measurement was not performed according to standard. Due to the low density of the powder, only 25 g of powder was used instead of the required 50 g. The time was then doubled for comparison reasons.

The binder treatment also provided sufficient green strength to the compacts. No measurements of strength levels were performed, but the compacts could easily be handled without breaking or dusting. For compaction, no further addition of lubricant to the system was necessary.

Table 2. Flow properties for lubricant treated powder.

	AD (g/cm^3)	Flow (s/50 g)
Höganäs TiH_2	0.76	105
Milled TiH_2	0.99	88

Compaction of cylindrical specimens with a diameter of 25 mm was performed using a single action tool, at compaction levels between 200-800 MPa (29-116x10^3psi). 20 g of material was used for each specimen. Green density was obtained by measurement of dimensions and weight.

Delubrication and sintering trials were performed in different laboratory furnaces in Ar and vacuum, where Ar was used during delubrication to effectively transport lubricant residues from the components. Sintering was performed at 1300°C (2372°F) for 2h.

After sintering density was obtained by using weight in air and weight in water method.

RESULTS AND DISCUSSION

Both of the powders used in this study are difficult to compact to high green density. Compaction curves are found in Figure 2. The irregular shape of the Höganäs powder is a disadvantage when it comes to compaction, and for all compaction pressures, the milled powder reaches approximately 8-10 % units higher in green density. The curves show that for both powders there is a response for increased pressure all the way up to 800 MPa (116x10^3psi). There is a tendency to flattening, but based on the shape of the curve it is reasonable to assume that higher densities could be possible to reach with higher pressure. High pressure compaction can, however, be problematic. More heat will be generated during the process, and with the fine powders in this study there will be an increased risk for particles falling between punch and die, causing the tool to seize. Fine particle sizes are more easily handled at low compaction pressures, where smaller punch and die clearance can be used.

To visualize the densification necessary to achieve full density, relative density curves are presented in Figure 3. The solid lines show density relative to what is actually possible to achieve in green state, where

the volume of the binder also has been included. For the milled powder it can be seen that there is still approximately 6 % of porosity at the highest compaction force. For the Höganäs powder the porosity level for the same pressure is approximately 13%.

If the binder is considered as porosity and is removed from the calculation, and green density is related to pure TiH_2, the relative density values drop with ~4-4.5 % units at 800 MPa ($116x10^3$psi), and with somewhat less at lower pressures. The gap represents the volume of the binder. During compaction the binder redistributes and fills out the porosity in the green component. With high compaction pressure, and porosity levels moving towards zero, lowering amount of binder becomes important for densification. At low compaction levels reduction of amount of binder content will have little effect on final green density. If possible, the amount of binder should nevertheless be reduced, in order to limit the amount of impurities necessary to remove during debinding.

The third curve shows density related to pure Ti, i.e. here also hydrogen has been removed from the calculation. What the curve represents is density related to full density obtained after sintering. It is clear from the curve that even if high green density is reached for the TiH_2+binder system, there is still substantial densification needed during sintering in order to achieve full density of the final components. For the milled powder, the density related to Ti at the highest compaction level is 71%, and for Höganäs powder only 66%. This corresponds to a linear shrinkage of approximately 11 and 13% needed for full density after sintering for milled and Höganäs TiH_2, respectively. In the lower compaction pressure end, the corresponding shrinkage is 17 and 19%, respectively.

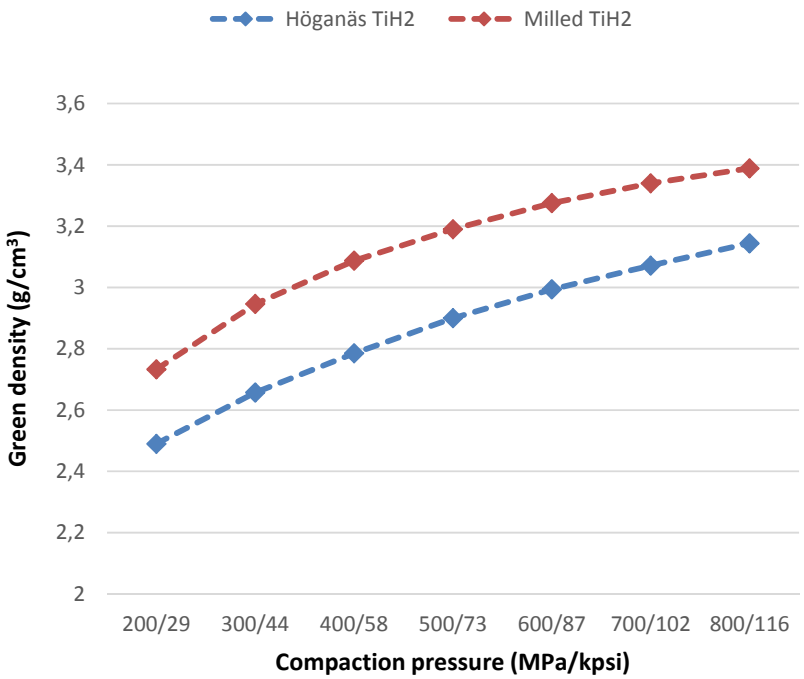


Figure 2. Compaction curves for Höganäs TiH_2 and milled TiH_2.

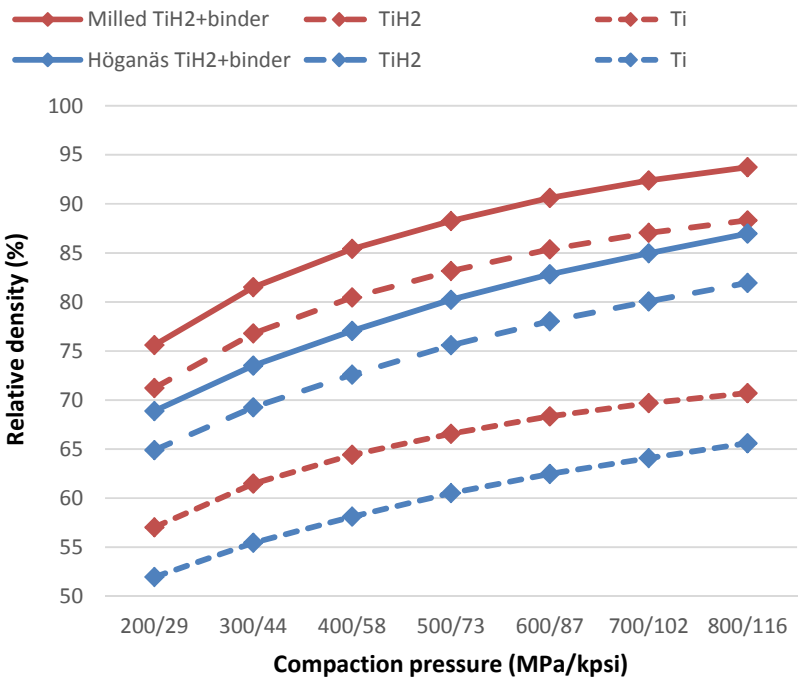


Figure 3. Relative density for the powders, relate to the TiH_2+binder system, to pure TiH_2, and to pure Ti.

When sintered, the fine powders show very high sintering activity, and the shrinkage is substantial. The Höganäs powder shows densities above 99% of theoretical for all compaction pressures, with 99.6 % as highest measurement for 500-800 MPa (73-116x10^3psi) compactions. The milled TiH_2 shows lower density levels, and a stronger dependence on compaction pressure, where 98% of theoretical density is reached after 800 MPa (116x10^3psi) compaction, and 95% after 200 MPa (29x10^3psi). The sintered density is strictly increasing with compaction pressure, and no flattening can be determined. The reason for the higher porosity is the larger powder particle size and smaller specific surface, which leads to lower sintering activity.

The linear dimensional change, green to sintered, can be found in Figure 5. Change in diameter and height was measured. The Höganäs powder shows a smooth variation in DC with compaction pressure, while the milled powder is a bit more unpredictable, especially in the height DC. This becomes very evident when looking at the shrinkage ratios (Figure 6). The larger variations for the milled powder could be a result of wider particle size distribution. A predictable behavior regarding dimensional change is an important factor when it comes to production of component and tolerances needs to be kept tight.

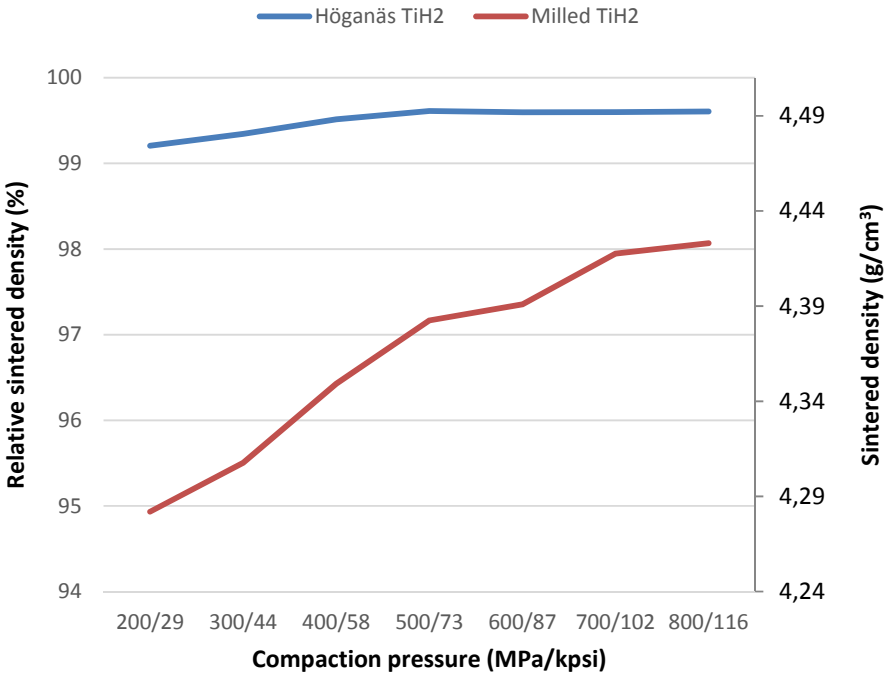


Figure 4. Relative and absolute density after sintering.

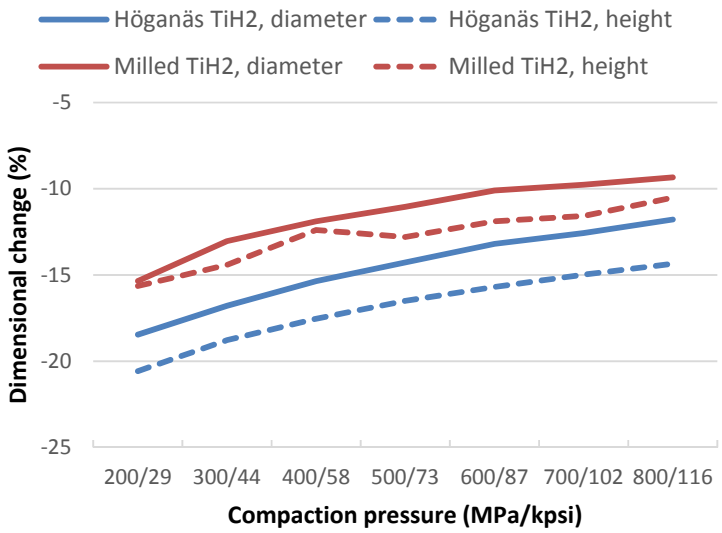


Figure 5. Dimensional change, green to sintered for Höganäs TiH_2 and the milled TiH_2.

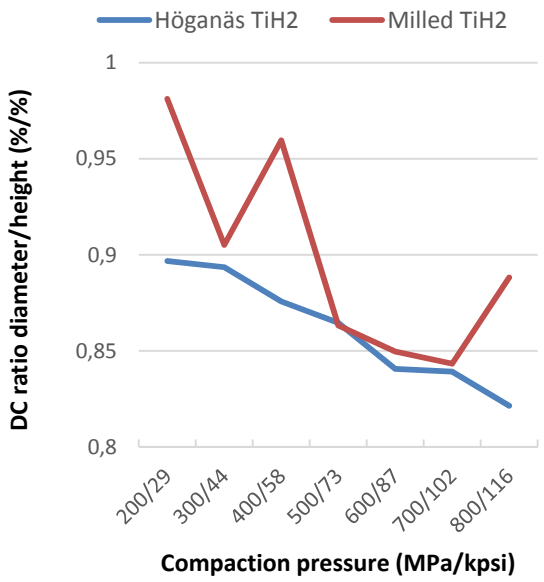


Figure 6. Dimensional change ratio, diameter/height, for Höganäs TiH_2 and milled TiH_2.

In Figure 7 micrographs of pore structure after sintering at 1300°C (2372°F) can be found. The specimens were compacted at 600 MPa ($87x10^3$psi). For both types of TiH_2 a fine evenly distributed porosity is observed. For the milled TiH_2, with lower sintered density, the pores are larger and more frequently occurring.

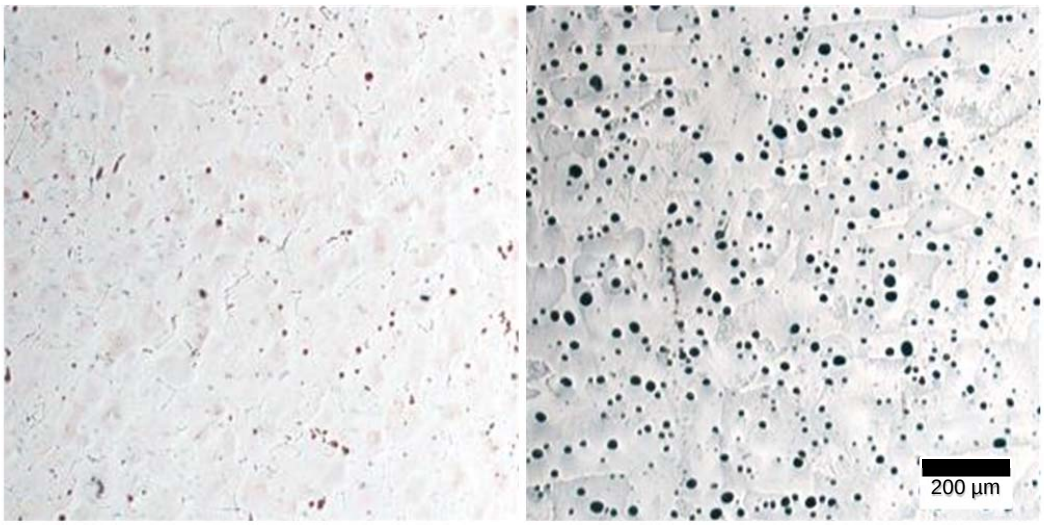


Figure 7. Porosity of specimens compacted at 600 MPa ($87x10^3$psi) and sintered at 1300°C in vacuum. Höganäs TiH_2 (left) and milled TiH_2 (right).

Figure 8 shows etched microstructure of the TiH_2 + 60Al-40V mix after sintering at 1300°C (2372°F). The mix was made from milled TiH_2 and compacted at 600 MPa ($87x10^3$psi). The alloying elements are homogeneously distributed after sintering, and the figure displays a α+β microstructure. The size of the colonies of parallel α-lamellae is relatively large, indicating relatively large primary β-phase grain size. To reach high mechanical performance, it is good to have a fine microstructure, with small colonies of α-lamellae. This can be a challenge when sintering Ti alloys; to reach high mechanical performance also high density is necessary, requiring high temperature sintering. But a consequence of high temperature is grain growth, which in turn reduces performance. From microstructure point of view it can therefore be beneficial to have a small powder particle size. With small powder particles, sintering activity increases, and sintering temperature could be reduced with finer microstructures as a result. In this study all sinterings were performed at 1300°C (2372°F). For future trials it could be very interesting to investigate the effect of lower sintering temperature on density and microstructure for the fine powders of this investigation.

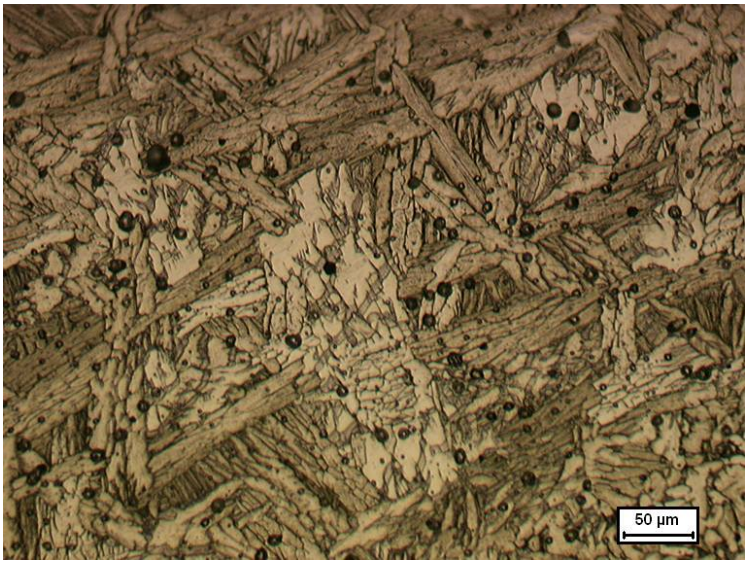


Figure 8. Microstructure of TiH_2+60Al-40V master, with composition Ti-6Al-4V, after sintering.

CONCLUSIONS

Comparison of compaction and sintering behavior of a TiH_2 powder produced by Höganäs AB and a milled "conventional" TiH_2 powder was performed.

The Höganäs powder has a small particle size and irregular shape. The milled powder is coarser and more angular in shape.

The highest green density was reached with the milled TiH_2; 89% of theoretical at 800 MPa ($116x10^3$psi), for the Höganäs powder 83% was reached.

Compared to a milled TiH_2, with more angular powder particle shape, the sintering activity of the Höganäs powder is higher, leading to higher sintered density.

Density levels, after sintering at 1300°C (2372°F) for 2h, are relatively unaffected by green density for the Höganäs powder, which shows density levels above 99% of theoretical for all compaction pressures tried. The sintered density of the milled powder shows a dependence on green density, with levels 95-98% for 200-800 MPa ($116x10^3$psi) compaction.

Addition of 60Al-40V master alloy powder to achieve Ti-6Al-4V results in a homogeneous distribution of alloying elements, and a relatively coarse microstructure after sintering.

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