# TITANIUM MIM: PERFORMANCE AND CAPABILITY

Jobe Piemme and Joseph Grohowski

Praxis Technology

Queensbury, NY 12804

## ABSTRACT

Praxis Technology has overcome the hurdles of qualifying a titanium MIM production line. Performance of the process will be examined from the perspective of contamination control, mechanical performance, microstructure and dimensional precision. Results on the performance and capability of the process will be discussed.

## INTRODUCTION

Praxis Technology, a PM manufacturer exclusively focused on high performance components manufactured using titanium powder metallurgy routes, has commercialized titanium metal injection molding (TiMIM) under the rigorous requirements of the medical industry.

TiMIM continues to be a focal point for both academia and industry. A recent publication provides a comprehensive overview of the progress and challenges.[1]

There are many variants of TiMIM in current production, most of which are for decorative or mechanical applications using either commercially pure Ti grades or Ti-6Al-4V. Targeted markets of high performance applications that demand ASTM adherence require stringent control of chemistry and mechanical properties.

Although numerous groups have published results meeting chemical and mechanical requirements for Ti-6Al-4V [2-3], capability of their technology remains unstated. This article provides some insight into the performance and capability of a validated TiMIM process in relation to ASTM F2885.

## BACKGROUND

Overcoming the challenges of TiMIM is critical when developing and commercializing the technology. The most relevant of those challenges are meeting the chemical and mechanical requirements of the Grade 5 alloy in a commercial setting as opposed to a laboratory.

In 2011, ASTM adopted a standard for metal injection molding of titanium for surgical implant applications (ASTM F2885). The standard focuses solely on Ti-6Al-4V Grade 5 and contemplates two material classifications: Type 1 being a densified version having higher ultimate and yield strength requirements and Type 2 being less dense and having lower mechanical requirements. The interstitial chemical requirements for both classifications are the same. Development efforts focused on Type 1 because this specification is more similar to other ASTM specifications used for titanium implantable devices and presents less adoption challenges to the device OEM's.

One of the well-known challenges of TiMIM is interstitial chemistry. Numerous groups have discussed and published chemical results meeting ASTM requirements; the challenge is not necessarily meeting the requirements, but qualifying and commercializing the process to meet the requirements.

During validation, the robustness of TiMIM was evaluated at many points throughout the process by testing the outputs of the process from the perspective of interstitial content and mechanical properties.

Because both of these characteristics are destructively inspected, they must be monitored by a statistical sampling plan to ensure quality during production. In order to develop a sampling plan that meets the quality requirements of the customer, it is necessary to determine the capability of the process.

## CAPABILITY AND PERFORMANCE

*Interstitial Contamination*

With respect to interstitial contamination of Ti-6Al-4V, oxygen and carbon are widely understood to be the most challenging to control in the MIM process. The limits of oxygen and carbon for this material are 0.2 wt% and 0.08 wt% respectively. Contamination can stem from numerous sources throughout the MIM process; special consideration must be made to start out with low oxygen powder and minimize the increase of oxygen during thermal processing.

In order to evaluate the ability to control these elements a sample size for the capability must first be established. Sample size calculations were based on historical data that was collected during engineering studies performed prior to validation; the data was based on a furnace cycle at nominal sintering conditions. One sample was tested per tray using a 44 tray capacity, 0.13 $m^3$ vacuum furnace. A summary of the data used to determine sample sizes is presented in Table 1.

**Table 1**: Data set for basis of sample size determination.

| | Oxygen (wt%) | Carbon (wt%) |
|---|---|---|
| Average | 0.174 | 0.0375 |
| Standard Deviation | 0.007 | 0.005 |
| Difference | 0.0052 | 0.0085 |
| *Based on 95% confidence and a power of .95* | | |
| Calculated Sample Size | 25 | 5 |

The oxygen and carbon content proved to be quite consistent throughout the furnace with averages of 0.1740 wt% and 0.0375 wt%, respectively, and standard deviations of 0.0070 wt% and 0.0050 wt%, respectively. A one-sample Z test was used to calculate sample sizes used in subsequent capability testing; this method was chosen to detect a mean shift in elemental contents from run to run. The difference is the amount of detectable shift of a mean value. There are many accepted approaches to calculating difference; the mean shift difference was selected to be 20% of the span between the average and the upper specification limit. This yields roughly a 0.0050 wt% mean shift for oxygen and a 0.0085 wt% mean shift for carbon. In order to increase the accuracy of detecting a true mean shift, power was increased to 0.95 from the widely used value of 0.80. Based on 95% confidence, the samples sizes for both oxygen and carbon were 25 and 5 respectively.

Consistent with performance qualification (PQ) requirements, the capability study for oxygen and carbon was based on three full, consecutive furnace runs. Oxygen content was determined using inert gas fusion according to ASTM E 1409-08 and carbon content was determined using combustion according to ASTM E1941-10. A summary of the results of oxygen and carbon contents are shown in Table 2.

**Table 2**: Summary of oxygen and carbon values from three consecutive furnace runs.

| Sinter Run | Oxygen (wt%) | Carbon (wt%) |
|---|---|---|
| Run 1 | 0.1715 | 0.0375 |
| Run 2 | 0.1698 | 0.0346 |
| Run 3 | 0.1744 | 0.0388 |

Prior to the capability analyses, normality, equal variance, and one-way ANOVA tests were conducted on the three data sets. All three were normally distributed with equal variance and the population means tested statistically equal. Figure 1 shows the results of Minitab analysis for oxygen capability. Analysis of the oxygen data indicated the process had a Ppk of 1.42, exceeding the objective of 1.33.

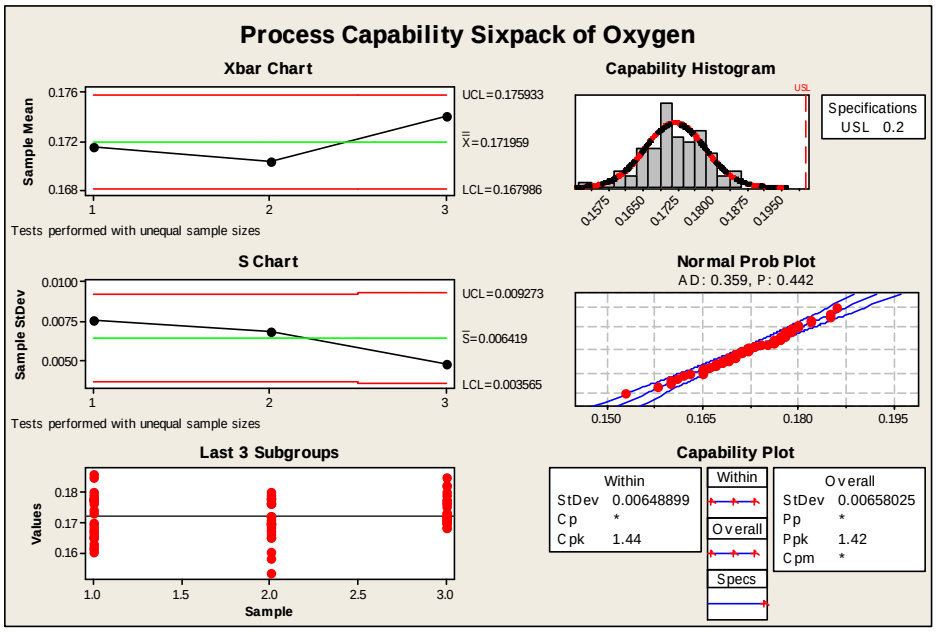


**Figure 1**: Results of a Minitab analysis for oxygen capability.

Samples for carbon capability were randomly selected from the same sample sets used for oxygen capability. Figure 2 shows the results of the Minitab analysis for carbon capability. The capability analysis provided us with a Ppk of 2.61, exceeding the objective of 1.33.

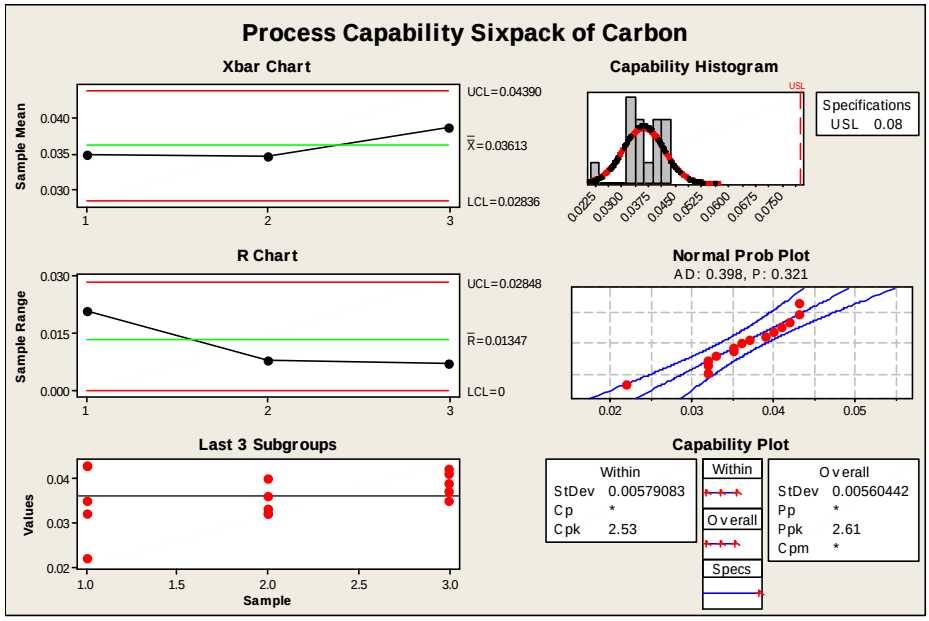


**Figure 2**: Results of a Minitab analysis for carbon capability.

*Mechanical properties*

Developing a sintering process window and proving capability at the boundary conditions is critical to meet the stringent requirements of the medical industry. Sintering process parameters have proven to be detrimental or enabling for establishing capability in TiMIM.

Although sintering time and temperature are set-point parameters in a furnace program, there is always temperature variation within any furnace (i.e. hot and cold spots). When qualifying equipment and processes, not only is it important to quantify the temperature variation but more importantly the effect the variation imparts on final product properties. Once the peak temperature variation is quantified, work can be conducted to determine the effect of the temperature range on final properties.

Although the determination of the sintering window is based on numerous characteristics, capable mechanical properties are paramount. Once a target sintering temperature was established, peak temperature variation was determined. Boundary condition tests were then conducted 5°C above and below the temperature range to determine mechanical property capability. Sample sizes were selected based on the baseline Cpk's for tensile strength, yield strength and elongation which were determined from the target sintering temperature window; the lowest baseline Cpk exceeded 1.41 but was less than 1.55. Using Wayne Taylor's sampling plan tables a minimum sample size of 20 is needed for variable data, one-sided, applying 95% confidence and 99% reliability assuming high risk.[4] Tensile tests were conducted on a sample size of 25 at both low and high peak sintering temperature set-points to determine capability just outside worst case conditions in the furnace hot zone.

Data and results from the two sinter runs are listed in Table 3. The individual data groups were tested for normality and equal variances prior to testing; data from the two sintering temperatures showed equal variance and the strengths were normally distributed but the elongation values were not, this is more than likely due a lack of resolution in the measurement. Since the ultimate and yield strengths were normally

distributed, two-sample t-tests were conducted on the groups and found that an increase temperature can have a statistically significant impact on the mean tensile strength properties. Using a non-parametric Kruskal-Wallis median test, it was determined that although increased sintering temperature did significantly affect impact strengths, it did not have a significant impact on elongation.

**Table 3**: Summary of mechanical property data from two sintering temperatures.

| Property | ASTM F2885 Limit | Population analysis p-value (method) | Low Temperature | | High Temperature | |
|---|---|---|---|---|---|---|
| | | | Average | Cpk | Average | Cpk |
| UTS, MPa (ksi) | 900 (130) | 0.000 (two-sample t-test) | 983 | 9.80 | 964 | 5.70 |
| YS, MPa (ksi) | 830 (120) | 0.000 (two-sample t-test) | 871 | 1.42 | 860 | 1.47 |
| Elongation, % | 10 | 0.911 (kruskal-wallis) | 19.9 | 3.13 | 19.8 | 2.74 |

According to Wayne Taylor's sampling plan tables, the acceptance criteria for a minimum sample size of 20 is a Ppk = 1.10. Boundary condition tests conducted 5°C above and below the temperature range produced capable mechanical property results. Table 3 shows the results of the capability analyses displaying Cpk all values exceeding 1.33.

*Microstructure*

Orthopedic devices are often cited as an application that could benefit from commercially viable TiMIM. There are several barriers to TiMIM being widely adopted in the orthopedic industry; among these is high cycle fatigue (HCF) performance.

A major challenge in using TIMIM to manufacture orthopedic devices is that conventional TiMIM components do not have adequate fatigue strength for load bearing applications. When measured in rotating beam fatigue (ASTM E468-11) typical fatigue strength are around 480 MPa (70 ksi) at 10 million cycles. The commonly accepted minimum for load bearing applications is around about 620 MPa (90 ksi) at 10 million cycles.

In order to overcome this limitation, a processing route was developed to improve the final microstructure of the sintered titanium that does not rely on the addition of boron. The process provides fatigue strengths in excess of 620 MPa while meeting the chemical and mechanical requirements of ASTM F2825. Figure 3 compares the rotating beam fatigue performance of the improved microstructure material versus conventional TiMIM material.

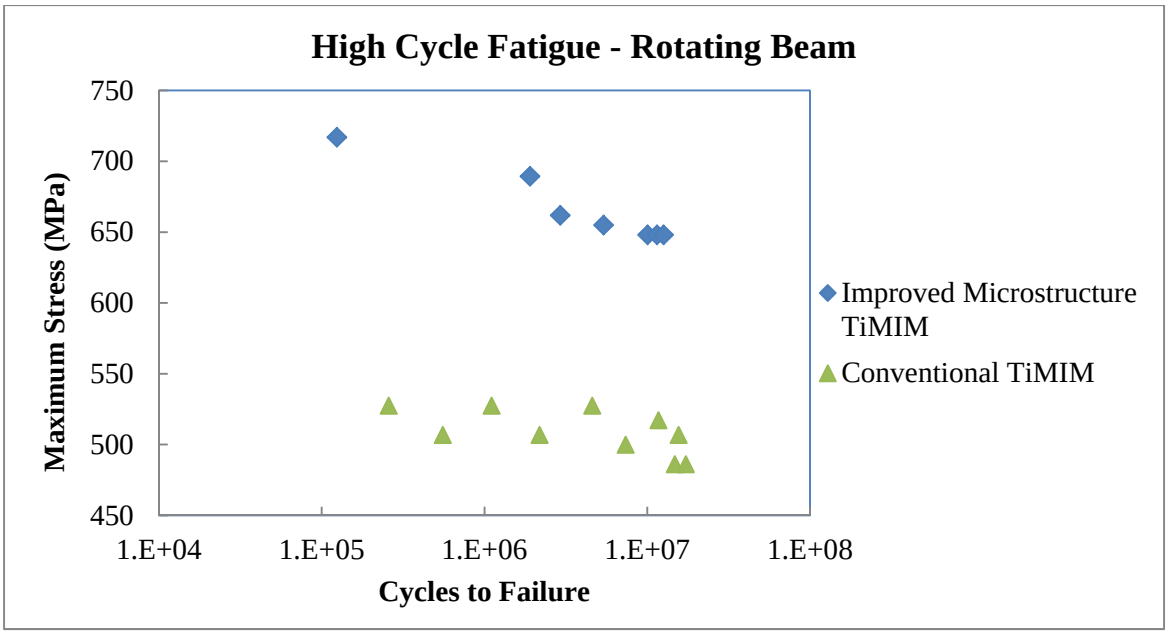


**Figure 3**: Comparison of high cycle fatigue performance for improved microstructure versus conventional TiMIM

An advantage of the process is that it increases the static mechanical properties as well as the fatigue performance. Table 4 summarizes mechanical properties of Ti-6Al-4V materials with improved microstructure, one without and one with the addition of 0.5 wt% boron.[5] Note that the yield strength of the material without boron is higher than the ultimate tensile strength of Ti-6Al-4V with boron. In addition to the diminished tensile properties, the addition of 0.5 wt% boron creates additional difficulties from a material conformance perspective. Adopting this alloy for implant applications creates additional FDA acceptance hurdles since the material differs from predicate devices.

**Table 4**: Summary of mechanical properties of high fatigue Ti-6Al-4V with and without the addition of 0.5 wt% boron.

| Material | YS - MPa (ksi) | UTS – MPa (ksi) | Elongation - % | HCF – MPa (ksi) |
|---|---|---|---|---|
| Ti-6Al-4V-0.5B | 787 (114) | 902 (131) | 12 | 640 (93) |
| Ti-6Al-4V* | 930 (135) | 1034 (150) | 15 | 640 (93) |

* Ti-6Al-4V material without boron addition with an improved microstructure.

*Dimensional Precision*

Although MIM dimensional precision has been widely published and ranges dramatically based on material and processing conditions, documentation of the dimensional precision of TiMIM is scarce. The powder size of most TiMIM is larger than the average powder size of conventional MIM; powder size can have an impact not only on surface finish but also dimensional precision.

Typically, MIM dimensional precision is stated two ways: an actual tolerance span for size ranges and a percentage based on coefficient of variation, meaning one standard deviation divided by the mean. Although both methods are informative, the main question is whether the technology can meet capability requirements

for a given component feature tolerance. To better understand the impact on capability, we have chosen a modified method based on dimensional capability. Assuming the tolerance range represents +/- 3 standard deviations, a modified percentage based on three standard deviations divided by the mean was calculated.

Table 5 summaries the conventional MIM dimensional capability versus TiMIM capability based solely on feature size. The first two columns of Table 5 include size ranges and conventional MIM tolerances.[6] Based on the size range and tolerance, an average dimensional capability percentage for conventional MIM was calculated and is shown in the column titled Conventional MIM (%).

The fourth column is a summary of the TiMIM dimensional precision results to date, based on +/- 3 standard deviations normalized over the mean values per size range. The data set is comprised of averaged tolerance percentages from multiple features from multiple components. To date, TiMIM precision is quite comparable to conventional MIM dimensional precision. By closely monitoring and controlling TiMIM process parameters, the impact on dimensional precision using larger particle size powder for TiMIM can be overcome.

**Table 5**: Dimensional precision of conventional MIM versus TiMIM.

| Size - mm (inches) | Tolerance – mm (inches) | Conventional MIM (%)* | TiMIM (%)** |
|---|---|---|---|
| < 3 (0.12) | +/- 0.05 (0.002) | 1.7 | 1.4 |
| 3 – 15 (0.12 – 0.58) | +/- 0.08 (0.003) | 0.5 | 0.5 |
| 30 – 60 (1.17 – 2.34) | +/- 0.25 (0.010) | 0.5 | 0.3 |

* Results based on +/- 3 standard deviations representing ~99% of the population; it is not represented as coefficient of variation (i.e. one standard deviation divided by mean size).

** TiMIM % based on average values from numerous components and feature sizes.

## SUMMARY

The work presented in this paper shows the performance and capability results of a commercialized Ti-6Al-4V MIM process; these results are not meant to represent the entire work involved in qualifying TiMIM. The results demonstrate that commercializing a TiMIM process under stringent requirements to meet ASTM requirements similar to wrought material is achievable but only under the most careful processing conditions. Contamination control is paramount when dealing with TiMIM; starting with powder and binder choice and proceeding all the way through thermal processing. All factors can have an impact on final part chemistry and mechanical properties.

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