

Using a Helium Pycnometer as a Quality Tool in Powder Metal Injection Molding

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Abstract

The helium pycnometer is a simple method for maintaining quality during the entire powder metal injection molding (MIM) process. The feedstock manufacturer uses it to validate incoming raw materials and their end products. The part manufacturer can use it to verify proper molding of the green part, how many regrinds he can use, whether the correct primary debinding has been achieved and the attainment of the desired sintered density. The paper shows how the helium pycnometer may be used to monitor quality during each step of the MIM process to prevent poorly molded parts from being processed all the way through sintering to be rejected.

Introduction

Some time ago we visited a MIM house where the incoming material is qualified by a test on a small section MIM tensile bar. The molded bars were debound and then sintered in two different furnaces using basically the same program. Parts sintered in Furnace A all met specifications but the results had a wide scatter. Furnace B resulted in uniform tensile values between 474 MPa to 485 MPa and 65 to 80% elongations from all areas of the furnace. The specifications called out a minimum tensile strength value of 500 MPa.

We did not find an explanation for this difference until we looked at the fracture surface of the tensile bars. Figure 1 shows the fracture surface of one of the bars.

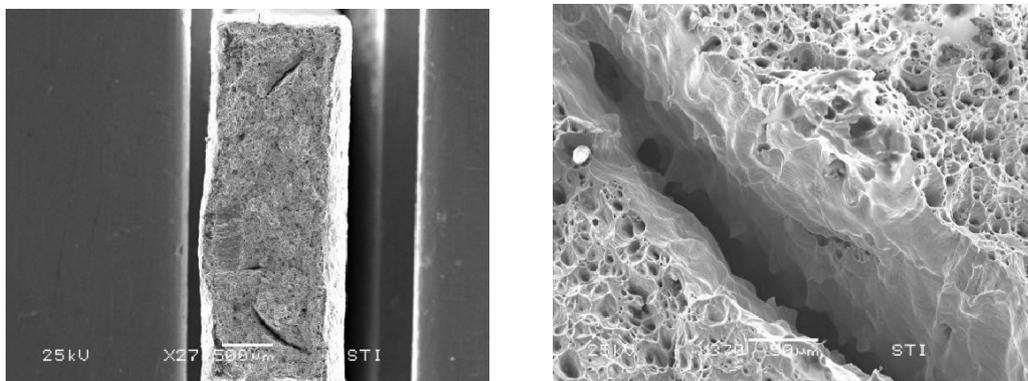


Figure 1: Fracture Surface of Tensile Bars

Every tensile bar, whether sintered in Furnace A or Furnace B showed the same cracks as shown in Figure 1. The first picture in Figure 1 shows a low magnification overview, showing two large voids and a few smaller ones. The second picture is one looking inside the larger void in the bottom. The surface inside is similar to the outside surface, confirming that the voids were pre-existing and did not form during debinding or sintering.

This example shows that there is a real need to check for defects during the MIM process and part makers should not have to wait until the part is sintered to find out that the part is defective and that these defects are formed in the green stage. Such defects need to be caught as they are formed and the paper shows that this can be achieved by measuring density using a helium pycnometer.

The Helium Pycnometer

The helium pycnometer is probably **the most important tool** for the MIM industry and one no MIM manufacturer should do without. A typical pycnometer with three different cup sizes that may be used

in this equipment for different sized parts is shown in Figure 2. It is essential for the manufacture of feedstock to validate incoming raw materials such as metal powders¹ as well as binder materials. It is then used to determine whether the feedstock made is a homogeneous mixture which is suitable for molding to produce MIM parts with the desired shrink factor.



Figure 2: A typical helium pycnometer is shown on the left. The picture on the right shows three different cup sizes that may be used in this pycnometer for different sized parts

The density of the feedstock is easily measured by the helium pycnometer. The density of the molded green part, if molded properly, should closely match that of the feedstock. After primary debinding, the brown density should match the theoretical density of the feedstock minus that of the primary binders, a number that can easily be calculated and supplied by the feedstock maker or manufacturer. And the final density of the part relative to the actual density of the powder used to make the feedstock is the percent density of the part. All these values are easily measured by the helium pycnometer, which makes it an invaluable tool to build in and monitor quality at every step of the process.

Quality

The concept of total quality breaks down each process step into suppliers and customers. For example, the metal powder and binder polymer vendors are suppliers to the feedstock manufacturer, who is their customer. The feedstock manufacturer is the supplier to the molder, who is the customer. Note, that the feedstock manufacturer may be an outside company or may be a group in the same building in the same company as the molder.

The same is true for any portion of the steps. The molder is then the supplier to the debinder their customer, while the debinder is the supplier to the sinterer. At the end of the process the final requirements for the part per the needs of the end customer is checked. But before it gets to this stage, each (internal or external) supplier must meet certain requirements before the materials or parts may be passed on to the next (internal or external) customer.

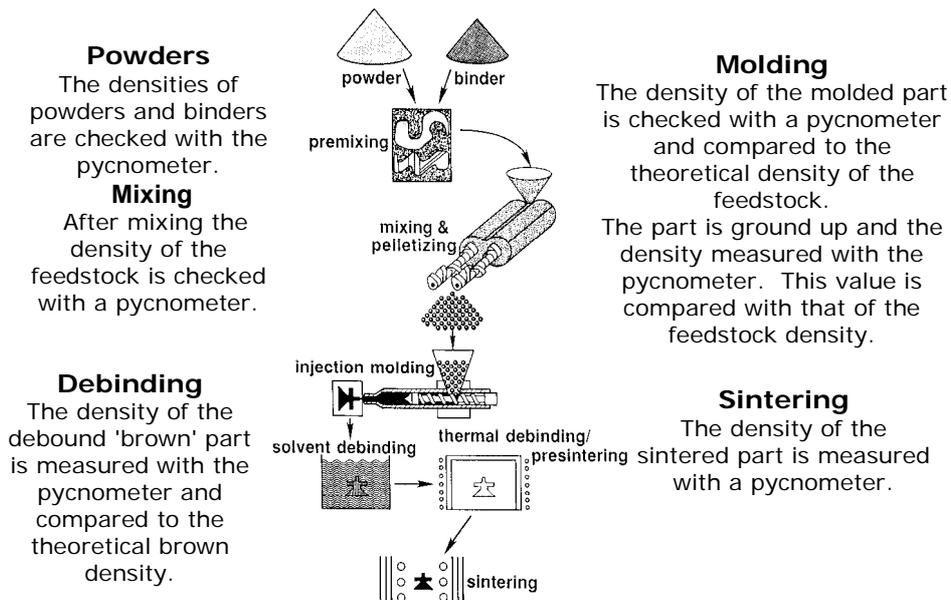


Figure 3: The MIM Quality Process

Figure 3 shows how the pycnometer may be used to monitor quality during each of the process steps. Each process step in MIM has many variables. Hence adhering to this principle helps in rejecting parts in process so that these parts do not end up through each and every process step and is sintered and then have to be thrown away because these do not to meet the final requirements.

Feedstock

In preparing a Feedstock, it is important first to measure the actual density of each lot of both the metal powders and binders. This is extremely important especially for the metal powders in that each lot will be different based on the actual chemistry of that grade of powder. For example, 316L is comprised of several elements, such as Fe, Cr, Ni, Cu, Mo, P, Si, S and C. In order to be rightfully called a 316L, each of these elements must meet a minimum and maximum percentage weight requirement as called out in the relevant specification. Hence the variation in the chemistry within the specification results in a significant density variation within the acceptable composition range.

Depending on the lot received from the powder producer, the density will vary depending on the actual chemistry received. Tests have shown that the density of these powders can vary several g/cm^3 .

It is essential to use the exact density of the powder lot to calculate the volume requirement of the binder or the powder loading and to determine the theoretical densities of the feedstock in order to obtain its correct desired shrinkage. This information is also critical in determining the proper mixing techniques required to produce a homogenous mix.

The definitions and formulae for theoretical powder loading, theoretical green density and theoretical brown density are presented in Appendix 1.

The helium pycnometer is used to measure the densities and validate incoming metal powders and binders from suppliers. It is then used to measure the density of the feedstock made to determine whether a homogenous mix has been attained.

If the feedstock producer does not follow this procedure, it will affect not only the flow of the feedstock, but more importantly the shrinkage of the final part. When the feedstock is not made in-house, the feedstock supplier **MUST** supply this information to the end user. Without it, there is no easy way to gauge the quality of the final part achieved. Most feedstock producers do provide a pycnometer density of their feedstocks.

With this information, you now have a tool that can validate each step in your manufacturing process. Knowing that the feedstock is 99.8% of theoretical, the density is given in a value of g/cm^3 . The pycnometer gives you a way to validate the density on the feedstock the MIM customer receives.

Manufacturing MIM Parts

Customers who receive feedstock from their suppliers now have a tool to test incoming material and can determine before they start molding as to whether the Feedstock will sinter to correct dimensions.

Molding

Many MIM companies will mold a part until they feel that the cavity has been filled. Just because a part looks "good" does not mean that the molding is optimum. Both mold design factors such as runner and gate size, gate placement, venting and molding parameters set on the molding machine affect the molded part. A helium pycnometer can determine if there are voids trapped inside the parts. During molding, you have a tool that can be used to measure the percent of theoretical density achieved on the "Green" or molded part. By crushing the measured "green" molded part back to powder, you can now confirm the percent of air (or voids) trapped in the molded part.

To measure this, the density of the molded part should be measured in the helium pycnometer and compared to the theoretical density of the feedstock. Then, take the same molded part that was used in the density test and crush it back to powder. Figure 4 shows a typical hand grinder used to grind the part of feedstock into a finer powder. Place this crushed powder back into the helium pycnometer and measure the density again. Figure 5 shows pelletized feedstock, a molded part which in this case is a dog-bone or tensile bar and the ground up feedstock from a molded part.



Figure 4: Typical hand grinder that may be used to crush and grind parts back to a granular form

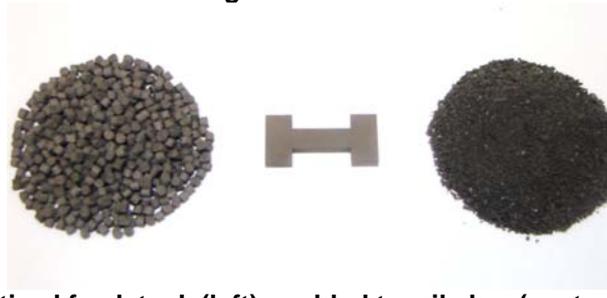


Figure 5: Pelletized feedstock (left), molded tensile bar (center) and tensile bar after granulation in the grinder shown above

Table 1 shows a typical example. The tensile bar (dog-bone) was molded from the feedstock shown beside it and the bar looked completely filled. The molded part however measured at 96.72% of theoretical density. After the part was ground up a density of 99.70% of the theoretical was obtained. This means that there is about 3% air trapped inside this tensile bar and the molding may be improved.

Condition	Measured Density g/cm ³	Theoretical Density g/cm ³	% Density g/cm ³	Remarks
Feedstock	5.0896	5.1044	99.71	Typical Feedstock
Dog-Bone 103007	4.9368	5.1044	96.72	Molded Part
Dog-Bone 103007 Ground after Molding	5.0893	5.1044	99.70	Ground up Molded Part

Table 1: Molding Characterization by Density Measurement

The molded part needs to be ground up and the resulting granules tested in the pycnometer for another purpose. If this granulate shows a density of more than 100% of that of the feedstock, then some of the primary binders have been lost during the molding process. The molding process needs to be corrected because using this process with a degraded feedstock will result in a larger shrinkage and result in a part smaller than that desired.

Many companies use the green weight as a benchmark for proper molding. This assumes that the part has been molded correctly and has the same volume which has been filled optimally every time. In most cases, each time the gate is broken off the break is not the same which results in a weight variation. While this is better than no check, it does not provide accurate information.

It is crucial to mold the parts correctly, free of voids without feedstock degradation so as to achieve the highest possible density with the correct dimensions after sintering. It is vital to be sure that your molded parts are completely filled before continuing the manufacturing process for debinding and sintering. The helium pycnometer provides this assurance.

Primary Debinding

Properly debound parts are extremely important to establish the correct sintering profile. The primary binder must be completely removed before attempting to start to remove the secondary binder as the secondary binder will travel through the pores created by the extraction of the primary binder.

Primary debinding techniques depend on the feedstock type used to make the parts. However the feedstock supplier (internal or external) knows the amount of primary binders that have been added and should be removed before proceeding to the next process step. The feedstock supplier should provide you with the minimum "brown density" that must be achieved before the parts can be moved into a furnace for final debinding and sintering. This minimum brown density will take into account that a small amount of the primary binder remnant may be present and could be removed by a suitable hold during secondary debinding and sintering. For example, TCK recommends that a minimum of 92% loss of primary binder is achieved before starting the sintering operation. A higher percentage is better, but the sintering profile should be adjusted to remove this remaining small percent of primary binder before the removal of the secondary binder.

Feedstock Alloy	Measured Brown Density g/cm ³	Theoretical Brown Density g/cm ³	% Brown Density Attained g/cm ³	Remarks
TCK H-11 Mod.	6.1810	6.2576	98.78	Acceptably Debound
TCK H-13 Mod.	6.2015	6.2679	98.94	Acceptably Debound

Table 2: Primary Debinding Characterization by Density Measurement

Table 2 shows primary debinding characterized by density measurement for tensile bars made from H-11 and H-13 feedstocks made by TCK.

Most external feedstock manufacturers provide only a weight loss percent that should be obtained to define suitable debinding. This is not the best option because for certain thermal debinding processes you could also lose some powder during handling a brown part and obtain a weight loss value higher than the actual one.

Solvent debound parts must be thoroughly dried before the helium pycnometer is used to determine the "brown" density so that the remnant solvent in the part does not affect the measured density value.

When the feedstock manufacturer gives you the theoretical density of the "brown" or debound part, you now have a tool that can validate the percent of debinding that has been achieved.

Secondary Debinding and Sintering

Most MIM operations today perform the secondary debinding and sintering in the same operation. The density of the sintered parts² can also be measured against the theoretical density and you now have a method of determining the exact percent of density that was achieved.

Only a few Feedstock manufacturers give this information as part of their standard Certificate of Analysis. It is important to remember that each lot of metal powders and binders will have a different density because of the chemistry tolerances.

Regrinds:

Every MIM molder has gates and runners left over from molding their parts. How many times have you asked if those gates and runners can be granulated and re-used? A helium pycnometer can give you that answer. So, you will be able to now re-use your gates and runners with confidence that they will shrink correctly after sintering.

Since the feedstock producers have given you the actual and theoretical densities of their feedstock, you can easily measure the densities of the gates and runners and compare the results to the values supplied. Once the regrind densities are higher than that required to maintain the part dimensions, the regrinds are no longer reusable. Here is a tool that can make that decision for you. Often, a feedstock producer will state that you can re-grind their feedstock a certain amount of times or they may say that

you need to add in a certain percentage of virgin feedstock with the re-grinds to maintain flow and shrinkage. The use of a helium Pycnometer takes the guess work out and gives you a method to validate your data.

Conclusions

It is clear that the helium pycnometer plays a significant role throughout the entire MIM quality process, making it the most important tool available in the MIM process to determine if each manufacturing step has been correctly processed.

The helium pycnometer, which almost every MIM manufacturer owns, is a relatively inexpensive quality tool that is easy to use for evaluating:

- Raw materials during incoming inspection,
- Molding of green parts,
- Primary debinding,
- Drying of debound parts
- Sintering and
- To assess the usability of regrinds.

Acknowledgements

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References

1. R.M. German and Animesh Bose, "Injection Molding of Metals and Ceramics", ISBN: 1-878954-61-X, Metal Powder Industries Federation, Princeton, NJ, 1997, p-66.
2. MPIF standard 35-2007, Metals Powder Industries Federation, Princeton, NJ, 2007, p.-5

Appendix – 1: Definition and Formulae

$$\begin{aligned} \% \text{ Theoretical Powder Loading} &= 100 * (\text{Sum of the volumes of all the powders}) \text{ divided by the } (\text{Sum of all the volumes of the powders plus that of all the binders}) \\ &= 100 * (V_{P1} + V_{P2} + \dots + V_{Pn}) / (V_{P1} + V_{P2} + \dots + V_{Pn}) + (V_{B1} + V_{B2} + \dots + V_{Bn}) \\ &= 100 * \{ (M_{P1}/\rho_{P1}) + (M_{P2}/\rho_{P2}) + \dots + (M_{Pn}/\rho_{Pn}) \} / \{ (M_{P1}/\rho_{P1}) + (M_{P2}/\rho_{P2}) + \dots + (M_{Pn}/\rho_{Pn}) \} + \{ (M_{B1}/\rho_{B1}) + (M_{B2}/\rho_{B2}) + \dots + (M_{Bn}/\rho_{Bn}) \} \end{aligned}$$

Where:	V	=	Volume
	M	=	mass
	ρ	=	density
	P1	=	Metal powder 1
	P2	=	Metal powder 2
	Pn	=	Metal powder n
	B1	=	Binder 1 (Primary)
	B2	=	Binder 2 (Secondary)
	Bn	=	Binder n. (Secondary)

Theoretical green density = (Sum of the mass fraction of all the powders and binders) divided by the (Sum of the volumes of each of these powders and binders)

$$\begin{aligned} &= \{ (V_{P1} * \rho_{P1} + V_{P2} * \rho_{P2} + \dots + V_{Pn} * \rho_{Pn}) + (V_{B1} * \rho_{B1} + V_{B2} * \rho_{B2} + \dots + V_{Bn} * \rho_{Bn}) \} / \{ (V_{P1} + V_{P2} + \dots + V_{Pn}) + (V_{B1} + V_{B2} + \dots + V_{Bn}) \} \\ &= (M_{P1} + M_{P2} + \dots + M_{Pn}) + (M_{B1} + M_{B2} + \dots + M_{Bn}) / \{ (M_{P1}/\rho_{P1}) + (M_{P2}/\rho_{P2}) + \dots + (M_{Pn}/\rho_{Pn}) \} + \{ (M_{B1}/\rho_{B1}) + (M_{B2}/\rho_{B2}) + \dots + (M_{Bn}/\rho_{Bn}) \} \end{aligned}$$

Theoretical brown density = Same as above except that the binder constituents that are eliminated after primary debinding are removed from the above equation

$$\begin{aligned} &= \{ (V_{P1} * \rho_{P1} + V_{P2} * \rho_{P2} + \dots + V_{Pn} * \rho_{Pn}) + (V_{B2} * \rho_{B2} + V_{Bn} * \rho_{Bn}) \} / (100 - VB1) \\ &= (M_{P1} + M_{P2} + \dots + M_{Pn}) + (M_{B2} + \dots + M_{Bn}) / \{ (M_{P1}/\rho_{P1}) + (M_{P2}/\rho_{P2}) + \dots + (M_{Pn}/\rho_{Pn}) \} + \{ (M_{B2}/\rho_{B2}) + \dots + (M_{Bn}/\rho_{Bn}) \} \end{aligned}$$