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ARTICLE

New Insights into Change Rate of Pore Volume - Taking Titanium Foam for Example

Xiao Jian[1], Liu Jinping[1], Wang Zhixiang[1], Qiu Guibao[2]

[1] *Jiangxi University of Science and Technology, Ganzhou 341000, China*; [2] *Chongqing University, Chongqing 400044, China*

Abstract: The space holder technique is widely used to fabricate metal foams, especially titanium foam. However, how to obtain the desired porosities is a big challenge for this technique, because they are not always equal to the expected ones. The results of the previous study (i.e., $P=ax+b$, where $a=1/(1+\delta)$, $b=\delta/(1+\delta)$) give a very interesting conclusion that is the change rate of pore volume (δ) is an indefinite mathematical constant. Based on the research work, we obtains a new result by establishing a mathematical model, which can be expressed as equation $\delta=\varphi-1$. Here,φ is the length index product of the ratio between the actual length and the designed length of the sintered metal foam. It reveals that the length index product (φ) is also an indefinite mathematical constant and we can measure its value. Therefore, solving δ means both a and b are solved, so the porosity (P) of titanium foam can be predicted by the equation $P=ax+b$, depending on the spacer content (x). This indicates that in the absence of porosity measurements, the macroscopic dimensions of the sintered metal foam can be measured to obtain a controlling equation for porosity.

Key words: metal foam; titanium alloy; powder metallurgy; space holder technique; structure control

Titanium foam is a novel type of lightweight titanium material which has been developed rapidly in recent years because it has the properties of ultra-light metal. It has many prospects in the fields of aerospace, marine engineering and biomedical than aluminum foam, due to the comprehensive properties of titanium, especially its corrosion resistance, high temperature resistance, and biocompatibility[1]. In addition, titanium foam with surface modification can also be used in the field of emerging technologies such as battery pack fluids[2] and photocatalyst carriers[3].

Since the melting point of titanium is close to 1670 °C, titanium at high temperature and oxygen and nitrogen in the air have a strong chemical affinity. In order to solve the preparation problem, some scholars have turned to powder metallurgy because its sintering temperature requires only 2/3 of the titanium melting point. However, it was until 2000 that M. Bram first made a titanium foam with a porosity between 60%~80% and a pore size between 0.1~2.5 mm by space holder technique[4]. Space holder technique, just as its name implies, is to add space holder to the titanium powder ingredients, use space holder to occupy a space in the body, and then heat or dissolve the material to form a hole to prepare the titanium foam. Therefore, this method is also based on powder metallurgy. Compared with the porous titanium made by traditional loose sintering, the titanium foam has a higher porosity and a larger pore diameter. These structural features can not only greatly reduce the weight of porous titanium, but also improve the performance of porous titanium.

However, it is regrettable that the research on titanium foam is still in the laboratory stage and has not yet achieved real industrialization application. The main reason lies in the difficulty in forming a stable relationship between the process and the structure of the process, especially the relationship between the process and the pore structure. To this end, the author conducted a series of in-depth studies. In terms of technology, the author's two latest reviews show that the

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Corresponding author: Qiu Guibao, Ph. D., Professor, College of Materials Science and Engineering, Chongqing University, Chongqing 400044, P. R. China, Tel: 0086-23-65112631, E-mail: qiuguibao@cqu.edu.cn

method is the main preparation method for titanium foam[5], urea, ammonium bicarbonate and sodium chloride are the three main directions[6]. Among them, urea is the most important. In the aspect of pore structure, the authors' latest research shows a linear relationship between porosity and spacer content. These two parameters are designed to be equal, but this is not the case. For example, the results show that the porosity is lower than the spacer content whenever the content or size of space holder changes[7-9]. The works of other scholars have shown equal or greater experimental results. The difficulty of predicting the deviation from expectations has been the sword of Damocles, suspended in the head of every titanium foam researcher. To solve this problem, the author first thought about why the porosity would deviate from the expected value. After establishing the mathematical model, a new theory has been developed: there is a physical phenomenon that the macropores generated from the removal of space holder will shrink their volume during the sintering process[10]. When the volume shrinkage of the macroscopic pores is larger than that of the microspore in the skeleton, the theoretical porosity is less than the experimental result of the pore volume. By a further investigation, the relationship between the porosity and the spacer content is linear through the bold hypothesis, that is $P=ax+b$[11]. Its derivation is as follows:

$$\begin{aligned} P &= \frac{V_1+\Delta V_1+V_3}{V_1+V_2+(\Delta V_1+V_3)} \\ &= \frac{V_1}{V_1+V_2+(\Delta V_1+V_3)}+\frac{\Delta V_1+V_3}{V_1+V_2+(\Delta V_1+V_3)} \\ &= \frac{V_1+V_2}{V_1+V_2+(\Delta V_1+V_3)}\cdot\frac{V_1}{V_1+V_2}+\frac{\Delta V_1+V_3}{V_1+V_2+(\Delta V_1+V_3)} \\ &= \frac{1}{1+\frac{\Delta V_1+V_3}{V_1+V_2}}\cdot S_c+\frac{\frac{\Delta V_1+V_3}{V_1+V_2}}{1+\frac{\Delta V_1+V_3}{V_1+V_2}} \\ &= \frac{1}{1+\frac{\Delta V}{V}}\cdot S_c+\frac{\frac{\Delta V}{V}}{1+\frac{\Delta V}{V}} \\ &= \frac{1}{1+\delta}\cdot S_c+\frac{\delta}{1+\delta} \end{aligned}$$

where, P porosity, V_1 the volume of space holder, V_2 the volume of titanium powder, V_3 the volume of micropores in the cell-walls, ΔV_1 the volume change of macropores during sintering process, S_c spacer content ($S_c=V_1/(V_1+V_2)$), V the volume of the raw material ($V=V_1+V_2$), ΔV the volume change of pores ($\Delta V=\Delta V_1+V_3$), and δ the change rate of pore volume ($\delta=\Delta V/V$). Order that:

$a=\frac{1}{1+\delta}$, $b=\frac{\delta}{1+\delta}$, $x=S_c$, then:

$$P = ax + b \quad (1)$$

Boldly assume that the change rate of pore volume (δ) is a constant. That is, its value will remain unchanged with the change in the content of space holder. So a and b are constants. Thus, Eq.(1) is a linear equation in theory. Use the data in the existing literature to carefully verify. The results show that although the parameters of powder composition, size and type of space holder, pressing pressure, sintering temperature and time will affect the final porosity of titanium foams, this does not prevent the linear relationship between the porosity and the spacer content. This not only proves that the assumption is true, but also calculates the value of δ by the linear equation. Moreover, the values of δ vary under different technological parameters, which ranges from −0.03 to 0.76. Hence, δ is not just a constant, it is still an indefinite mathematical constant. Similarly, a and b are also two indefinite mathematical constants, whose value ranges are 0.57~1.03 and −0.03~0.43, respectively. Besides, $a + b=1$. From the point of application, Eq. (1) is also applicable to other foam metals prepared by space holder technique, such as aluminum foam. In this work, the spacer contents (%) and porosities (%) are 52, 58, 63, 67, 71, 75, 79, 83, and 52, 59, 64, 68, 73, 77, 80, 84, respectively[12]. As a result, the porosity can be expressed as $P=1.033x-0.011$ with linear fitting. In addition to the porosity, the mechanical properties can also be predicted via the spacer content, which only needs the combination of the Gibson-Ashby model equations between pore structure and properties[13]. For example, the relationship between relative Young modulus and porosity in Esen's work is $E/E_s=1.589(1-P)^{4.72}$[14]. According to our theory, the relationship between porosity and spacer content can be taken as $P=0.796x+0.141$. Putting it into the former equation, $E/E_s=0.54(x-1.08)^{4.72}$ can be obtained. For the yield strength, it can also be obtained that $\sigma/\sigma_s=0.94(x-1.08)^{3.57}$.

Our theory equation was experimentally validated by peer scholars from Delft University of technology in the Netherlands, shortly after the publication of the paper[15, 16]. The relationship between porosity and spacer content is linear for the sintered foams ($P=1.070x-13.747$), as well as for the green compacts ($P=1.145x-15.381$). Our theory can lead to more interesting experiments, and there are also some scholars who cited our paper when introducing the method for space holder technique[17, 18].

In fact, the key to solving the problem is the change rate of pore volume, namely δ. The previous work has revealed that δ is an indefinite mathematical constant, but the reason is unknown. If we can obtain δ value in other ways without measuring the porosity, we can also derive the prediction equation for the porosity, because both the slope and intercept in Eq.(1) are directly dependent on δ. However, if x is known but P is unknown, δ can not be solved by Eq.(1).

1 Derivation of Model Equation

It is well known that the size control of the sintered body is very important in the design and fabrication of powder metallurgy products. Normally, the size of the parts and the blank modulus should be the same or proportional. Changes in size often lead to changes in shape. In order to reduce the size change and the shape change, the sintered body should have a uniform linear shrinkage. For titanium foam, the macropores exacerbates the size change and shape change of the sintered body, but the shrinkage mechanism is unchanged. If the variable x in Eq.(1) and the calculation formula of the dependent variable P change with size and shape change, there may be some relationship between δ and the linear shrinkage of the sintered body. To facilitate the study, we take the cube as an example.

When we prepare titanium foam with a cubic shape, we can use Fig. 1 to describe the size change and the shape change brought about by the sintering process.

As can be seen from the diagram, the skeleton of the designed model is completely compact and contains only macropores. It has an equal length and width, denoted by the capital L. Assuming that its mass is m and the density of the frame material is ρ_s, the spacer content x is calculated as follows:

$$x = S_c = 1 - \frac{m}{L^3 \rho_s}$$

Compared with the designed model, the shape of the sintered model may be rectangle or square, depending on whether the line shrinkage rate in x, y and z directions is equal. If equal, it is a square, otherwise a rectangle. We use squares to represent the shape of the sintered model, and the length is denoted by the lowercase l. In the x, y and z coordinates, the length, width and height are l_x, l_y and l_z, respectively. The mass of the sintered model and the density of the skeleton material are equivalent to those of the designed model, which are denoted as m and ρ_s, respectively. The calculation formula of the porosity P is as follows:

$$P = 1 - \frac{\rho}{\rho_s} = 1 - \frac{m}{l_x l_y l_z \rho_s}$$

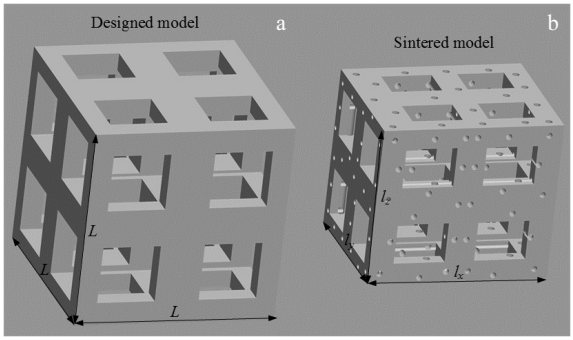

Fig. 1 Designed model (a) and sintered model (b) of titanium foam with cube shape

Substituting the two into Eq.(1), we obtain:

$$1 - \frac{m}{l_x l_y l_z \rho_s} = a\left(1 - \frac{m}{L^3 \rho_s}\right) + b$$

Because $a + b = 1$, therefore:

$$\frac{m}{l_x l_y l_z \rho_s} = \frac{am}{L^3 \rho_s}$$

Dividing out the same parameters, we obtain:

$$\frac{1}{l_x l_y l_z} = \frac{a}{L^3}$$

Because $a = \frac{1}{1+\delta}$, therefore:

$$\delta = \frac{l_x}{L}\frac{l_y}{L}\frac{l_z}{L} - 1$$

Line shrinkage refers to the percentage of the length of the material after processing. Obviously, there is no easy way to apply the line shrinkage. For this purpose, we define the length index (θ) as the ratio between the actual value and the designed value of the length of sintered foam, namely $\theta = l/L$. In the x, y and z directions, we have:

$$\theta_x = \frac{l_x}{L},\ \theta_y = \frac{l_y}{L},\ \theta_z = \frac{l_z}{L}$$

Substituting them into the last one, we obtain:

$$\delta = \theta_x \theta_y \theta_z - 1$$

Define the length index product (φ) as the product of the length index (θ) in three-dimensional coordinates, we get:

$$\varphi = \theta_x \theta_y \theta_z$$

substituting it into the last one, we obtain:

$$\delta = \varphi - 1$$

Because δ is an indeterminate mathematical constant, φ is also an indefinite mathematical constant. In other words, the value of δ can be solved by φ. The value of φ can be calculated by θ, and the value of θ can be solved by l/L. This means that δ can be calculated by measuring the actual length (l) of the sintered bubble, because L is a known designed value. When the value of δ is known, the slope a and the intercept b in Eq.(1) can be calculated. In this way, a regulation equation for porosity can be achieved without measuring porosity.

In the same way, we can use Fig. 2 to describe the dimensional change and the appearance of the sintering process when the mass and the skeleton material remain unchanged and the cube design model becomes a cuboid.

As shown in Fig. 2, the length, width and height of the designed model are no longer equal, which are L_x, L_y and L_z, respectively. Then the calculation formula for the spacer content x is as follows:

$$x = S_c = 1 - \frac{m}{L_x L_y L_z \rho_s}$$

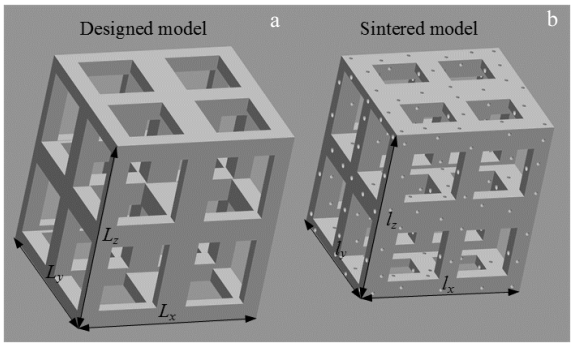

Fig. 2 Designed model (a) and sintered model (b) of titanium foam with cuboid shape

The length, width and height of the sintered model are also expressed by l_x, l_y and l_z. Because the calculation method for the porosity is the same, so:

$$\delta = \frac{l_x}{L_x}\frac{l_y}{L_y}\frac{l_z}{L_z} - 1$$

In this model, the value of θ in the x, y and z directions are:

$$\theta_x = \frac{l_x}{L_x},\ \theta_y = \frac{l_y}{L_y},\ \theta_z = \frac{l_z}{L_z}$$

respectively. So, the result is the same as the designed cube model, also:

$$\delta = \varphi - 1$$

We know that the cube and the cuboid are both square. The above two results can be attributed to the same kind of shape. In addition to the square body, the designed model of the titanium foam can be a cylinder. In the same way, we can use Fig. 3 to describe the dimensional change and appearance of the sintering process.

In this paper, we use capital L to represent the length. So, for the designed model, the diameter is L, and the height is L_z. The density and the mass of the frame material are also m and ρ_s, respectively. Then the formula for calculating the spacer content x is as follows:

$$x = S_c = 1 - \frac{4m}{\pi L^2 L_z \rho_s}$$

The cross section of the sintered model may be elliptic and the axial lengths are l_x and l_y, since the shrinkage rate of the cross sections along the x and y lines is not necessarily consistent. Therefore, we use the shape of the elliptic cylinder to describe the sintered model with a height of l_z. The calculation formula for porosity P is as follows:

$$P = 1 - \frac{\rho}{\rho_s} = 1 - \frac{4m}{\pi l_x l_y l_z \rho_s}$$

Substituting the two into Eq. (1), we obtain:

$$1 - \frac{4m}{\pi l_x l_y l_z \rho_s} = a\left(1 - \frac{4m}{\pi L^2 L_z \rho_s}\right) + b$$

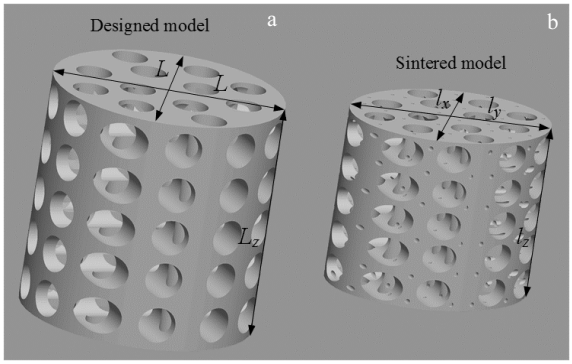

Fig. 3 Designed model (a) and sintered model (b) of titanium foam with cylinder shape

Because $a + b = 1$, therefore:

$$\frac{4m}{\pi l_x l_y l_z \rho_s} = \frac{4ma}{\pi L^2 L_z \rho_s}$$

Dividing out the same parameters, we obtain:

$$\frac{1}{l_x l_y l_z} = \frac{a}{L^2 L_z}$$

Because $a = \frac{1}{1+\delta}$, therefore:

$$\delta = \frac{l_x}{L}\frac{l_y}{L}\frac{l_z}{L_z} - 1$$

In this model, the value of θ in the x, y and z directions are:

$$\theta_x = \frac{l_x}{L},\ \theta_y = \frac{l_y}{L},\ \theta_z = \frac{l_z}{L_z}$$

respectively. Substituting them into the last one, we obtain:

$$\delta = \theta_x \theta_y \theta_z - 1$$

Because $\varphi = \theta_x \theta_y \theta_z$, therefore $\delta = \varphi - 1$.

As you can see, the results of the cylinder model are the same as the square model. The equation of $\delta = \varphi - 1$ can be obtained whether the designed model of the titanium foam is a cube, a cuboid or a cylinder. If other metals are used instead of titanium, it works the same way. Therefore, as long as the metal foam is prepared by the space holder technique, the same results can be obtained. To sum up, the new theory derived from this paper is shown in Eq. (2):

$$\delta = \varphi - 1 \quad (2)$$

Where, the symbols of δ and φ stand for change rate of pore volume and length index product, respectively.

Its physical meaning is that the volume change of the pore volume (δ) is equal to the length index product (θ) minus 1. Because δ is an indeterminate mathematical constant, so φ is also an indefinite mathematical constant. In other words, the value of δ can be solved by φ, and the value of φ can be calculated by θ, because $\varphi = \theta_x \theta_y \theta_z - 1$. Meanwhile the value of θ can be solved by l/L, because $\theta_{(x,y,z)} = l_{(x,y,z)}/L_{(x,y,z)}$.

Since L is a known designed value, the change rate of pore volume (δ) can be calculated by measuring the actual length of the sintered bubble(l), thereby obtaining the slope (a) and the intercept (b) in Eq.(1). For the cylindrical model, similarly to the square model, we can also implement a regulation equation for porosity without measuring porosity.

2 Results

1) This new theoretical equation is based on the results of previous research. In 2015, the author published two theories. One is that the macropores generated from the space holder particles shrink their volume during sintering[10], and the other is that the relationship between porosity and spacer content is linear[11]. The second theory is based on the first one, and the new theory in present paper is based on the first two theories, especially the second theory. However, the physical meaning of the slope (a =1/(1+δ)) and the intercept (b=δ/(1+δ)) of the equation P=ax + b is not clear. In this study, the change rate of pore volume was studied, and the equation $\delta+\varphi$=1 was derived. Because the length index product (φ) is a physical constant with practical meaning, the change rate of pore volume (δ) is also a physical constant. Similarly, the slope (a) and the intercept (b) are also physical constants.

2) Due to the absence of relevant data, the theoretical equations derived from this study require further experimental verification. The requirement for verification work is that the macroscopic size of the sintered foam must be properly sized so that the measured data can be accurately obtained to reduce the experimental error. The compaction process is the most important factor in determining the regularity of samples. In this step, it is important to keep the green compacts close to complete density and uniform distribution of residual stress. It is difficult to do this either in unidirectional compaction or double compaction. Therefore, the best way is to first unidirectional pre-compaction followed by an isostatic compacting. Laptev et al[19] studied the effects of suppression process on the strength of titanium foam in 2005. According to their research, the smaller the size of the spacer particles, the higher the densification degree of the green compacts and the slightly higher the strength. The larger the volume of the space holder, the lower the yield strength of the green compacts. Arifvianto et al[15] characterized the porous structures of the green body and the sintered biomedical titanium scaffolds with micro-computed tomography. This work mainly tested the author's second theory equation P=ax+b. However, these experimental data cannot be used to verify the new theoretical equations in this paper. Therefore, the physical mechanism of the pressing parameters affecting the macroscopic scale of sintered foam is the difficulty and key to future research work.

3 Conclusions

1) The equation $\delta=\varphi-1$ is established. Here, φ is the length index product, which stands for the ratio between the actual length and the designed length of the sintered metal foam. It reveals that the length index product (φ) is an indefinite mathematical constant whose value can be measured.

2) Solving δ means both a and b are solved, so the porosity (P) of titanium foam can be predicted by the equation $P=ax+b$, depending on the spacer content (x).

3) This study links the macroscopic dimensions to the porosity equation of the sintered foam. It indicates that the porosity control equation can be derived by measuring the macroscopic size of the sintered foam without measuring the porosity. It can be said that the new theory in this paper breaks the shackles of the existing theories, further enriching the basic theory of pore structure control of sintered foam metal.

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新锐洞察孔体积变化率-以泡沫钛为例

肖 健[1]，刘锦平[1]，王智祥[1]，邱贵宝[2]

(1. 江西理工大学，江西 赣州 341000)

(2. 重庆大学，重庆 400044)

摘 要：基于粉末冶金的造孔剂法被广泛应用于制备泡沫金属尤其是泡沫钛。然而，如何获得所需孔隙率是这一技术面临的巨大挑战，因为孔隙率往往偏离期望值。作者前期研究的结果（即，$P=ax+b$。其中，$a=1/(1+\delta)$，$b=\delta/(1+\delta)$）导致一个非常有趣的结论：孔体积变化率（δ）是一个不定数学常数。在研究基础上，通过建立数学模型发现了一个新的结果，即方程 $\delta=\varphi-1$。其中，长度指数积 φ 代表烧结泡沫的实际长度与设计值的比值乘积。这表明长度指数积（φ）是一个数值可测量的不定数学常数。因而，求出 φ 可算出 a 和 b，泡沫钛的孔隙率（P）就可以通过基于造孔剂含量（x）的线性方程 $P=ax+b$ 来预测。这意味着在不测量孔隙率的情况下，可以通过测量烧结泡沫金属的宏观尺寸变化来获得孔隙率的调控方程。该研究为粉末造孔剂法制备泡沫金属的结构调控提供了新思路和新方法。

关键词：泡沫金属；钛合金；粉末冶金；造孔剂法；结构控制

作者简介：肖 健，男，1989 年生，博士，讲师，江西理工大学材料科学与工程学院，江西 赣州 341000，E-mail: xiaojian@jxust.edu.cn