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Volume change of macropores of titanium foams during sintering

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Abstract: The porosity of titanium foams obtained from the space holder technique was theoretically analyzed in the cases of volume shrinking, retaining and expanding during sintering. The relationship between porosity and spacer content was compared under different conditions. The kind of volume change of macropores during sintering was discussed. The results indicate that the relationship between porosity and spacer content depends on the decreased volume of macropores and the volume of micropores in cell-walls in the first case, while the porosity will be greater than the spacer content for the other two cases. It proves that the volume change of macropores during sintering decreases based on theory and practice.

Key words: porous material; titanium foam; space holder technique; sintering; volume change; porosity

1 Introduction

Titanium foams are a kind of novel functional materials. They combine the advantages of porous structure and titanium. Compared with traditional dense titanium, they are attractive for aerospace, automobile, biomedical and chemical catalytic applications, due to their excellent mechanical properties, superior corrosion resistance and good biocompatibility [1]. It is well known that all these properties directly depended on their pore structure. Hence, it is important to study the pore structure of titanium foams.

The salient structural features of a metal foam are its porosity, cell topology (open cells, closed cells), cell size and cell shape and anisotropy [2]. Among them, the porosity was considered as the most important feature [3]. Its value is always designed to be equal to the spacer content when the titanium foams were obtained from the well established space holder technique. This method utilizes a fugitive solid material to create the desired macropores. The fugitive solid material was the so-called space holder such as familiar carbamide [4], ammonium bicarbonate [5] and sodium chloride [6]. Recently, there have been new space holders as starch [7], saccharose [8] and cenosphere [9]. In the authors' previous work, titanium foams with porosity in the range of 50.2%−71.4% were successfully prepared by using acicular carbamide as a space holder when the spacer content was in the range of 60%−80% [10]. However, the results show that the final porosity of the foams was lower than the spacer content. It is similar to the cases when the spacer size was varied in Ref. [11]. However, there is still a lack of a further study to provide a more detailed analysis from the point of view of the volume change of macropores during sintering. TORRES et al [12] speculated that it was the consequence of metallic framework shrinkage during sintering. Furthermore, this view was referenced from Ref. [13], which showed axial and radial shrinkages of the measured titanium foams after sintering. As a result, the porosity was lower than the spacer content. On the other hand, while this work puts forward that the macropores remain nearly unchanged or even tend to grow during the sintering process, the other researchers' work indicated that the macropores shrink their volume during sintering with the result of the porosity lower than the spacer content [14]. However, it is unknown by far that what kind of volume change of macropores would occur during sintering and what kind of relationship between the porosity and the spacer content will be obtained.

Therefore, the aim of the study was to determine the volume changes of macropores that occur during sintering when using the space holder technique. Given

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that a considerable number of experiments had been conducted in the authors' previous work, part of their results will be used in this work instead of conducting new experiments and other authors' works will also be combined to provide a detailed analysis.

2 Processing and characterization of titanium foams

Initially, the pre-calculated amount of titanium powders and spacer particles (Fig. 1 in Ref. [10]) was mixed using a mortar for 2−3 min. Then, the mixture was uniaxially cold pressed at ~200 MPa using a cylindrical steel die (diameter 16 mm; height 50 mm) to obtain green compacts. The dwelling time is set to be a fixed value of 45 s. Subsequently, two steps of heat treatment were applied to these compacts in a carbon vacuum furnace as follows: Firstly, a low heating rate was used to remove spacer particles at 460 °C under vacuum (10^{-1}−10^{-2} Pa), followed by furnace cooling. Secondly, with argon of 99.99% purity protective atmosphere to avoid oxidation, the scaffolds were sintered at 1250 °C for 2 h, followed by furnace cooling (for details, Figs. 2 and 3 in Ref. [10]). Figure 1 shows the relationship between the porosity and spacer content in the case that the content or size of space holder particles varied in Refs. [10,11].

Figure 2 shows the macromorphology and micro morphologies of sintered foams and green compact. The three sintered foams were the parallel samples (i.e., the same starting materials and preparation process). It can be seen that the external heights of sintered foams were lower than those of green compact, regardless of whether the direction is parallel or perpendicular to that of compact pressing (Fig. 2(a)). It is assumed to be a consequence of metallic framework shrinkage during sintering. The SEM image of surface morphology of a green compact show that it contains titanium powders and spacer particles (Fig. 2(b)). The compact with spacer particles completely removed was called scaffold. The experimental results indicated that providing an accurate characterization of a spacer particle and its removal hole

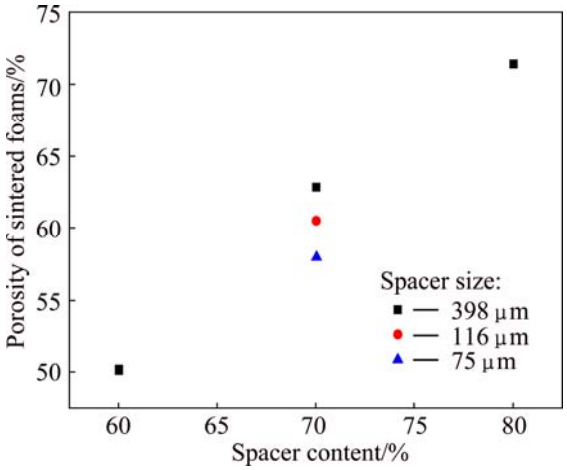

Fig. 1 Porosity of titanium foams prepared with different spacer contents and sizes in Refs. [10,11]

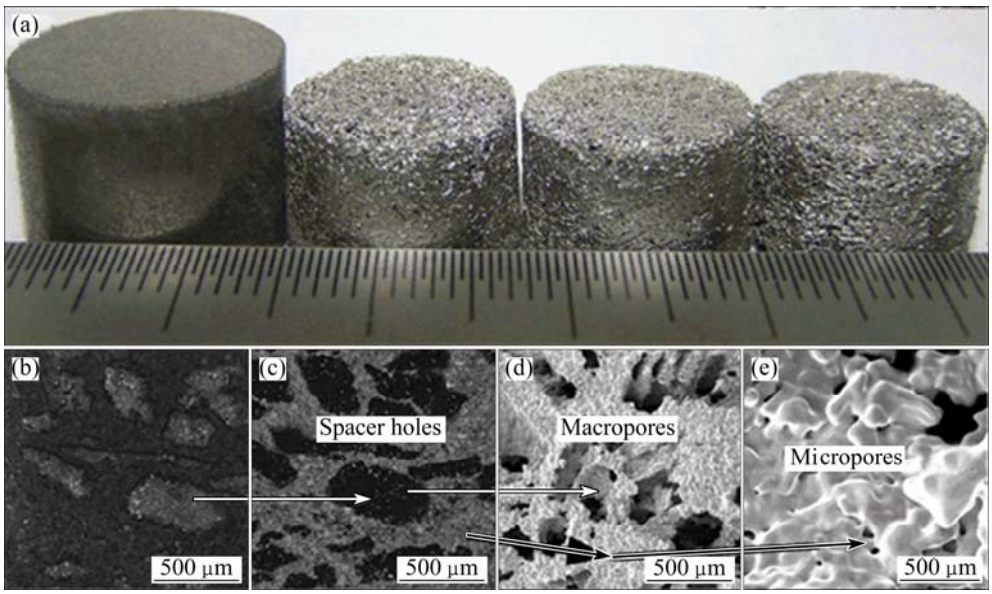

Fig. 2 Macromorphology and micromorphology of titanium foams before and after sintering: (a) One green compact and three sintered parts with same spacer content; (b) SEM image showing surface morphology of green compact; (c) BES image showing surface morphology of green compact; (d, e) SEM images of foam sample structures from surface (Directions of white and black arrows represent formation of macropores and micropores in sintered foams, respectively. SEM and BES images of green compact well depict morphology of hole generated from spacer particle removal)

is difficult because the former is in a green compact, whereas the latter is on a scaffold, which resulted in a different position of the two images. However, the BSE image can well characterize the process (Fig. 2(c)). The large black holes, white zone, and small black points represent the spacer particles, titanium powders and microvoids, respectively. The large black holes are the spacer holes in scaffolds obtained from the removal of spacer particle. The spacer holes and microvoids were then sintered into macropores (Fig. 2(d)) and micropores (Fig. 2(e)) in foam samples, respectively. Figure 3 vividly describes the aim of the present study.

3 Theoretical proposition

Spacer content was determined using an ideal titanium foam with a specific height (H) and diameter (D), in which the cell walls are fully dense. Its 3D physical model is shown in Fig. 4(a). The volumes of the macropores and skeleton are equal to those of the spacer particles and titanium powders, respectively. Thus, spacer content can be calculated using Eq. (1), where S_c is spacer content, V_1 and V_2 represent the volumes of the spacer particles and titanium powders, respectively, and ΔV is defined as the volume change of macropores during sintering. Therefore, the porosity of a prepared foam can be calculated using Eq. (2), where P is porosity and V_3 with positive value is the volume of micropores. If ΔV values show negative, zero and positive results, the volumes of macropores are shrinkage, constant and expansion, respectively. The difference ($d=P-S_c$) between porosity and spacer content was obtained using Eq. (3):

$$S_c = \frac{V_1}{V_1 + V_2} \tag{1}$$

$$P = \frac{V_1 + \Delta V + V_3}{V_1 + \Delta V + V_2 + V_3} \tag{2}$$

$$d = \frac{V_2(\Delta V + V_3)}{(V_1 + V_2)(V_1 + \Delta V + V_2 + V_3)} \tag{3}$$

We firstly assume that the macropores shrink their volume during sintering, that is $\Delta V<0$. Figure 4(b) shows the 3D physical model of the obtained ideal foam. Compared with the foam in Fig. 4(a), its height and

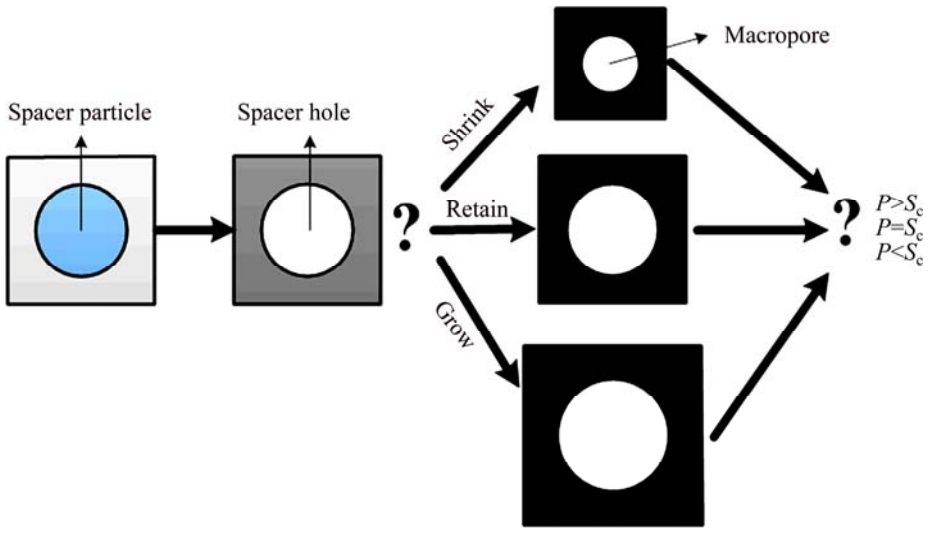

Fig. 3 Schematic illustration of aim of present study

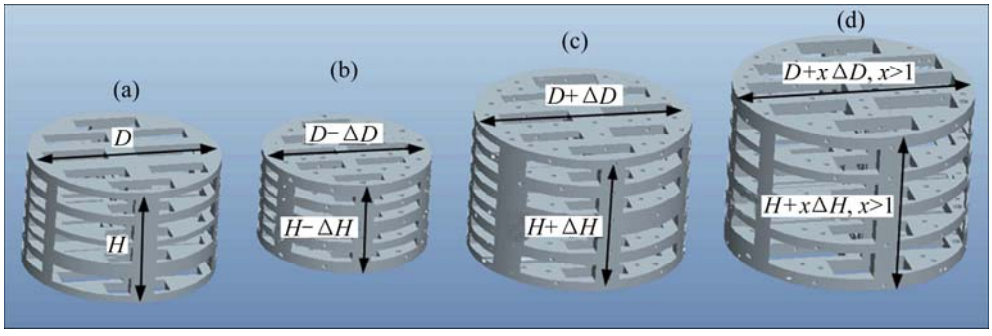

Fig. 4 3D physical models for designed ideal titanium foam with fully dense cell-walls to determine spacer content (a), obtained ideal foams with micropores in cell-walls and macropores with shrinked (b), retaining (c) and expanded (d) volume during sintering process, according to expected foam in (a)

diameter decrease and cell walls contain isolated micropores. The difference between porosity and spacer content is shown as Eq. (4), where subscript S stands for shrink. According to this equation, the porosity was equal to/lower than the spacer content if the decreased volume of macropores was equal to/greater than the volume of micropores. However, it is nearly unable to confirm a positive or negative d_S. This is because on the one hand, the volumes of macropores and micropores were not provided in the published papers. On the other hand, the signs of ΔV and V_3 are negative and positive, respectively. It also shows that it does not mean that the porosity will be lower than the spacer content, though the macropores shrink their volume during sintering. In this case, a mathematical method called "proof by contradiction" was applied, where the volume change is either retained or increased.

$$d_S = \frac{V_2(V_3 - \Delta V)}{(V_1 + V_2)(V_1 - \Delta V + V_2 + V_3)} \quad (4)$$

We again assume that the macropores retain their volume during sintering. Figure 4(c) shows the 3D physical model of the obtained ideal foam. Compared with the foam in Fig. 4(a), its height and diameter slightly increase because of the micropores on the cell walls. The difference between porosity and spacer content can be shown as Eq. (5) since ΔV=0, where subscript R stands for retain. It can be seen that d_R>0 because of the factor V_2V_3>0. This result indicates that, in this case, the porosity will be greater than the spacer content. Although LAPTEV et al [13] claimed that the macropores remain nearly unchanged during the sintering process, the results showed that the porosity was lower than the spacer content. Apparently, their opinions do not tally with the actual case.

$$d_R = \frac{V_2V_3}{(V_1 + V_2)(V_1 + V_2 + V_3)} \quad (5)$$

We have finally assumed that the macropores expand their volume during the sintering process. Figure 4(d) shows the 3D physical model of the obtained ideal foam. Its height and diameter are larger than those of the foams in Fig. 4(a) and Fig. 4(c). Hence, a coefficient x with a value larger than 1 was added in front of the height and diameter. The case difference between porosity and spacer content is shown in Eq. (6), where subscript E stands for expand. Evidently, d_E>0 because of the factor $V_2(\Delta V+V_3)$>0. This result indicates that, in this case, the porosity will also be greater than the spacer content.

$$d_E = \frac{V_2(\Delta V + V_3)}{(V_1 + V_2)(V_1 + \Delta V + V_2 + V_3)} \quad (6)$$

The porosity of a prepared foam will be greater than the spacer content, regardless of whether the macropores retain or expand their volume during sintering based on the two previously discussed assumptions. A proposition of negation is that, if porosity is equal to or less than the spacer content, then the macropores shrink their volume during sintering. Therefore, the reason for the experimental phenomenon that the porosity of titanium foams is lower than spacer content is that the macropores shrink their volume during sintering. It is well known that volume shrinking of micropores during sintering is a significant characterization in powder metallurgy. While does it similar to the shrinkage volume of macropores during sintering for the space holder technique? In this case, further investigations should also be conducted to determine the specific number of cases in which the porosity of prepared foams is lower than or equal to spacer content.

4 Theoretical validation

Figure 5 shows the reported relationship between the foams porosity and spacer content with carbamide and other materials as a space holder. We observed that the porosities were all lower than or equal to spacer contents, except for the part of results in Refs. [15,16]. According to the above derivation, these results were obtained from a shrinkage volume of macropores during sintering. Then, the macropores may retain their volume or tend to expand during sintering instead of shrink in the case where the porosity is greater than the spacer content (i.e., 44%−40%, 53%−50% and 64%−60% in Ref. [15]; 46.3%−40%, 53.2%−50% and 62.3%−60% in Ref. [16]; where the former is porosity and the latter is spacer content). This is because only when the difference between porosity and spacer content is greater than or equal to d_R or d_E (i.e., $d \geq d_R$ or d_E) can it be established, according to Eqs. (5) and (6). However, since these manuscripts do not provide the volumes of macropores and micropores in foam samples, it is unable to calculate the values of d_R and d_E. It is difficult to give a comparison between the experimental and theoretical difference (d) as a result. In fact, more likely, the shrunk volume of macropores was not enough to offset that of micropores, which led to porosities greater than spacer contents based on Eq. (4). And these two papers also showed that the porosity was lower than the spacer content (i.e., 46%−50%, 54%−60% and 62%−70% in Ref. [15] and 69.8%−70% in Ref. [16]). It suggests that the driving force during sintering is unsufficient which results in a slight shrinkage of macropores, for example, a serious oxidation of the surface of titanium powders, a low sintering temperature or short sintering time.

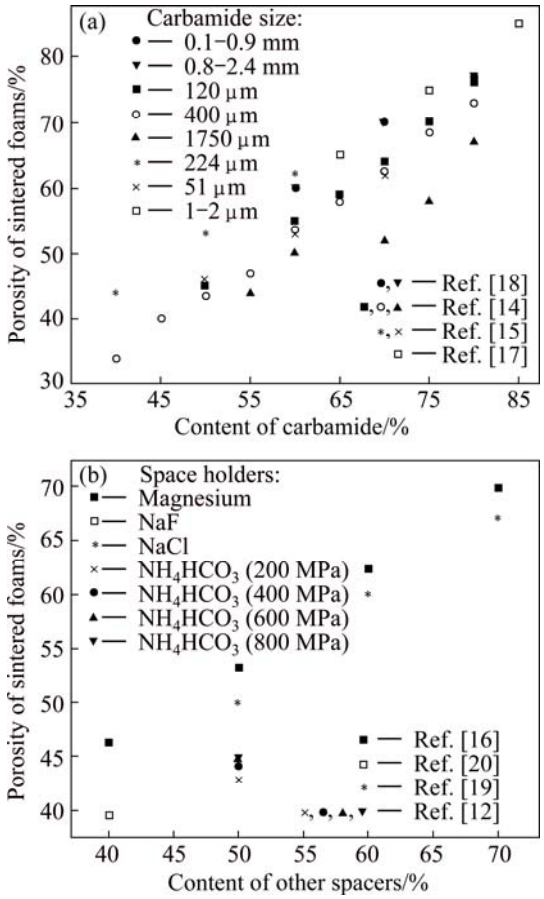

Fig. 5 Reported relationship between porosity of titanium foams and spacer content with spacer as: (a) Carbamide [14,15,17,18]; (b) Other materials [12,16,19,20]

In conclusion, the evidence proves that the kind of volume change of macropores during sintering is shrinkage. In fact, the view that the spacer holes retain their volume even tend to grow violates the principle of surface thermodynamic: spontaneous process results in smaller surface area driven by the reduction of surface tension. The obtained conclusion can be used not only to explain why porosity is lower than spacer content, but also to analyze the effects of parameters, such as spacer size or compaction pressure, on the porosity of titanium foams and even other foams, which has not yet been well explained in literatures [12,21]. More importantly, the present study will be helpful for scientists and engineers to obtain a better design of the desired foam structure in future.

5 Conclusions

1) The relationship between porosity and spacer content of titanium foams during sintering depends on the decreased volume of macropores and the volume of micropores in cell-walls.

2) It proves that the volume change of macropores during sintering is decreased based on theory and practice.

3) This new discovery solves a dispute which baffles the academic circles for a long time and is helpful for people to obtain a better understanding of space holder technique.

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宏观大孔在泡沫钛烧结过程的体积变化

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摘 要：理论分析造孔剂技术制备的泡沫钛中宏观大孔在烧结过程体积减小、不变和增大 3 种条件下所获得的泡沫孔隙率。比较不同条件下孔隙率与造孔剂含量的关系，并对宏观大孔在烧结过程的体积变化进行探讨。结果表明，第一种情况下的孔隙率与造孔剂含量的关系取决于宏观大孔在烧结过程的体积减小量和骨架上微观小孔的体积，而另外两种情况下所获得的孔隙率大于造孔剂含量。理论分析表明所得宏观大孔在烧结过程的体积是减小的。

关键词：多孔材料；泡沫钛；造孔剂技术；烧结；体积变化；孔隙率

(Edited by Yun-bin HE)