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Investigation of the experiment and simulation on TiH₂ powder packing by a novel irregular 3D model

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Abstract
Density and porosity have an important influence on powder metallurgy products, and it is feasible to predict the tap density of powder by simulating the packing of powder. Analysis models of spherical and simple geometric have been developed to predict the packing density of the powder. In this study, a novel particle model with complex three-dimensional (3D) morphology was established to simulate the packing process of titanium hydride powder with binary particle size distribution. The results have indicated that when the particle size ratio and the volume ratio of fine powder to coarse powder were 1:3 and 1:1, respectively, the sintered sample reaches its optimum sintered density of 99.24%. Compared with these samples sintered by single-scale powder, the size and distribution of residual pores reduced significantly with the application of mixed powders, which is beneficial to the mechanical properties of powder metallurgy products.

1. Introduction

As one of the most excellent lightweight structural materials, titanium alloys have been widely applied in aerospace and bio-medical industries due to their advanced specific strength, distinctive corrosion resistance and excellent bio-compatibility [1–3], but the high price is the main issue that hinders their application. Recently, powder metallurgy (PM) has attracted wide attention due to its near-net forming characteristics, which might be a potential way to reduce the cost of titanium alloy products [4]. In PM of titanium alloys, pure titanium powder and titanium hydride powder (TiH₂) were used as raw materials. But titanium hydride powder is brittle and can be easily obtained by mechanical ball milling. In addition, the titanium alloys prepared by using TiH₂ powder has the characteristics of surface self-cleaning during the sintering process, which can effectively increase the sintered density of the titanium alloys while reducing its oxygen content [5, 6]. However, the traditional vacuum pressure-less sintering process is always difficult to achieve a higher sintering density, and many pores exist in the samples. The size and distribution of these pores will affect the mechanical properties of the alloy [7]. Hence, it is necessary to reduce the porosity and pore size in powder metallurgy products.

According to the powder packing theory, the use of powders with different particle sizes can increase the final density of powder metallurgy products and reduce the size of pores [8–10], so the packing state and compactness of the powder during the sintering process will affect the final sintering performance. Numerous experiments and simulations have been done on powder packing. For example, Bosman et al [11] used two commercial pure (CP) titanium powders with different particle sizes (～100 and ～200 mesh) and 60Al-40V master alloy (～200 mesh) powder to prepare Ti-6Al-4V (TC4) alloy, and the results showed that the sintering density of TC4 alloy increased with the increasing volume ratio of fine powder. However, in order to obtain the optimal volume ratio and particle size ratio, further refinement of the initial powder particle size distribution and expansion of the volume ratio research range were required, which led to a sharp increase in experimental workload. With the development of computer science, the discrete element method can be used to simulate the packing experiment, and the best parameters can be obtained through the relationship between the particle size ratio and packing density or the volume ratio and packing density, which greatly reduced the workload of the experiment [12, 13]. Currently, in numerical simulation experiments, the commonly applied particle models
include spheres [14, 15] and simple geometric bodies [16, 17], such as cubes and discs. Ye et al [18] used spherical particle model to predict porosity, and the results indicated that porosity and particle volume ratio showed a V-shaped trend. When the volume fraction of small spheres accounted for about 25%, the most densely packed state was accomplished. Yu et al [19] adapted the equivalent spherical diameter method to simulate the packing system of nonspherical particles, and the results showed that the application of this method is capable of improving the reliability of the simulation results of irregular particles to a certain extent. Later, Hussein et al [20] used the specific surface area ratio of coarse particles and fine particles to replace the particle size ratio used in the previous spherical packing model, since the specific surface area contains the morphological characteristics of the particles. In comparison with Yu et al, this method considers the effect of particle morphology on the packing, so it is more suitable irregular-shaped particle packing systems. However, those methods and particle models have only been verified on simple geometric shapes, which are not suitable for particle systems with complex shapes.

In this work, a novel particle model was established based on real morphology of TiH₂ powder, and the powder packing was simulated by the discrete element method. At the same time, by analyzing the simulated and experimental results of the binary particles system with different particle size ratios and volume ratios, the reliability of the powder packing results predicted by using this new particle model was systematically studied. After that, by observing the microstructure of the sintered samples, the influence of the particle size ratio and volume ratio on the sintered density and pore size was further discussed.

2. Experimental procedure and methodology

2.1. Methodology and model

Particle Flow Code (PFC) software is used to simulate powder packing because it provides a universal method including a discrete element model framework and a graphical interface, and can simulate the movement and interaction of finite-size particles in large quantity. At the same time, these particles are assigned with certain mass and are able to independently execute translational and rotational movements. In order to improve the reliability of the simulation results, a novel three-dimensional model was created by Autodesk CAD software according to the actual microscopic morphology of TiH₂ particles (figure 1(a)). The three-dimensional model (figure 1(b)) constructed with 69 spheres was fitted by PFC, since the accuracy of the simulation can meet the needs of the experiment. In addition, the mechanical behavior of the particle packing process adopts the Hertz contact model [21, 22], where the input material parameters of TiH₂ are shown in table 1 [23, 24].

In the simulation experiment of binary powder packing, the particle size ratios of the fine and coarse powders are 1:2, 1:3, and 1:5 respectively, and the volume fraction ratio of coarse particles and fine particles is 100:0, 75:25, 50:50, 25:75 and 0:100. In addition, a cylindrical container with a diameter of 3 mm and a height of 2.5 mm was constructed, and the mixed powders were randomly generated and dropped according to the free fall method. Then the cylindrical container drove the particles to vibrate for 10 seconds with the amplitude of 0.5 mm and a frequency of 5 Hz, and the porosity of binary particle system after packing is automatically calculated by the program.

2.2. Verification experiment

In order to verify the reliability of the simulation results, it is necessary to test the tap density of the binary powder packing system. Here, TiH₂ powder was divided into four groups, which were 120–170 mesh,

Figure 1. SEM images of a single TiH₂ (a) and particle model (b).
250–325 mesh, −325 mesh and −400 mesh respectively (figures 2(a)–(d)). Then, the particle size distribution was measured by laser particle size analyzer (JL-1155, Chengdu Jingxin Co. LTD.), as shown in figure 2(e), and the median particle sizes (D50) of the four groups were 106 μm, 50 μm, 29 μm and 18 μm, respectively. According to the particle size ratio (1:2, 1:3, 1:5) and volume ratio (100:0, 75:25, 50:50, 25:75, 0:100), the binary powder systems were mixed in the V-type mixer for 2 h to ensure uniform mixing. The green compacts with a height and a diameter of 10 mm were obtained by uniaxial cold pressing at 400 MPa for 60 s. Finally, the green compacts were sintered at 1300 °C in a high vacuum molybdenum wire furnace with the vacuum degree less than $5 \times 10^{-3}$ Pa, the heating rate 5 °C min$^{-1}$ and holding 2 h, and then cooled with furnace.

2.3. Experimental tests

The oxygen content of titanium hydride powder was detected by oxygen analyzer (LECO, TCH600). The tap density of the powder is measured by a tap density meter (JZ-7, Chengdu Jingxin Co., Ltd.) according to the national standard GB/T5162–2006. Both the green density and the sintered density were measured by the Archimedes drainage method, and the green compact needs to be covered with a layer of paraffin before testing. Microstructure evolution of the sintered sample and powder was observed by optical microscope (OM, JX-2000B) and scanning electron microscope (SEM, Hitachi S-3400N), while the size and distribution of the pores

![Figure 2. SEM micrographs of TiH₂ and particles distribution in this study: (a) 120–170 mesh (b) 250–325 mesh (c) −325 mesh (d) −400 mesh (e) volume cumulative distribution and frequency distribution of TiH₂.](image-url)
3. Results and discussion

3.1. Particle model

The PFC program approximates the imported geometric model by generating a large number of balls with different sizes. The sides and corners of the model are formed by the generated balls. In order to ensure the irregular shape and polygonal shape of the model, and to avoid the increase in calculations caused by excessive number of balls consisting each particle (BCEP), it is necessary to study the influence of the BCEP on packing density. The complexity of the geometric model is expressed by the specific surface area. Here, it is defined that the specific surface area of the model composed of 100 balls is equal to the specific surface area of the created geometric model, and the relationship between the number of balls and the relative specific surface area was established. As shown in Figure 3(a), the relationship between the number of BCEP and the relative specific surface area is non-linear. The relative specific surface area increases rapidly with the increase of the number of balls, and the increase rate slows down when it approaches 100. In Figure 3(b), as the number of balls increases, the porosity of the packing gradually decreases and stabilizes after 69. When the number of BCEP is small, the high porosity may be due to the unevenness of the geometric model and the existence of gaps between the constituent balls. Therefore, taking into account the specific surface area and effective pores of the geometric structure and the amount of computer calculations, a geometric shape consisting of 69 spheres was selected in the model to simulate TiH₂ powder.

3.2. Simulation results

In binary powder packing experiment, the effect of particle size ratio on density was also considered in addition to discussing the different volume ratio of coarse powder and fine powder. Figure 4 shows the relationship between the volume fraction of fine powder and the packing density. Apparently, the packing density of the binary particle system will increase as the powder particle size ratio increases. Meanwhile, as the volume ratio of fine powder increases, the packing density of the system will gradually increase, and reaches the maximum when the volume ratio of fine powder is 50%. However, in the traditional spherical packing experiment, the binary particle system will reaches the maximum packing density when the volume ratio of fine powder is 25%,
indicating that the morphology of particles has a significant impact on the simulation results [25]. According to the results in figure 4, an empirical formula (equation (1)) between volume ratio (x) and bulk density (ρ) was obtained by second-order polynomial fitting [12]. η and λ are quadratic polynomial coefficients and have a linear relationship with the particle size ratio. Therefore, the function of η and λ with the particle size ratio was obtained by linear fitting (equations (2) and (3)). Substituting equation (2) and (3) into equation (1), the functional relationship between volume ratio and packing density under different particle size ratios can be established, where Pr represents the particle size ratio (the correlation values and correlation coefficient of equation (1) is shown table 2, the correlation coefficient of equation (2), R = 0.991; the correlation coefficient of equation (3), R = 0.987).

\[
\rho = \eta x^2 + \lambda x + 59.621 \quad (1)
\]
\[
\eta = -0.00144 \times \Pr + 0.173 \quad (2)
\]
\[
\lambda = 0.0803 \times \Pr + 0.0441 \quad (3)
\]

Figure 5 shows the distribution of particles in the longitudinal section of the cylinder after packing simulation. There are large gaps between the particles when the packing system only exist coarse particles (figure 5(a)). With the addition of fine particles, the gaps between large particles will be filled with small particles (figures 5(b), (d), (f), (h)). When the volume fraction of fine particle is 25%, the gaps between the large particles are only partially filled (figures (b), (f)). After that, when the volume fraction of the fine powder reaches 50%, the coarse and fine particles are packed tightly, with hardly any large gaps detectable (figures 5(c), (g)). At this time, the binary particle packing system obtains its maximum packing density. However, as the volume ratio of fine powder continues to increase, more arch bridge structures will be formed between small particles, resulting in an increase in porosity (figures 5(d), (e), (h), (i)). It is worth noting that when the particle size ratios is relatively small (2:1), fine particles will wedge into the large particles, resulting in an increase in the system gap. Therefore, the particle size ratio (3:1) can be increased to obtain higher packing density.

3.3. Experimental verification results

In order to verify the above simulation results, the coarse powder of 120–170 mesh was mixed with the fine powder of 250–325 mesh, –325 mesh and –400 mesh in different proportions, and the tap density of the binary powder system was measured (figure 6(a)). It can be found that with the addition of fine powder, the tap density

| Particles size ratio | η     | λ     | R value |
|----------------------|-------|-------|---------|
| 2:1                  | -0.00144 | 0.173 | 0.966   |
| 3:1                  | -0.00272 | 0.316 | 0.998   |
| 5:1                  | -0.00408 | 0.459 | 0.980   |
| 7:1                  | -0.00540 | 0.590 | 0.989   |
of the binary powder system gradually increases, and reaches the maximum when the volume fraction of fine powder is 50%, which is consistent with the simulation results. Figure 6(b) shows the matching relationship between simulation and experimental results. When the particle size ratio is 2:1 (120–170 mesh to 250–325 mesh), the match between the simulation and the experimental results is the best. The reason is that the powder distribution in the range of 120–170 mesh and 250–325 mesh is more concentrated, which is closer to the size range of particle model in the simulation experiment. However, when the particle size ratio rise to 3:1 (120–170 mesh to −325 mesh) or 5:1 (120–170 mesh to −400 mesh), the fine powder has a large size distribution range, leading to a certain difference between the simulated results and the experimental results. In addition, although the tap density of the binary
system increases with the increasing particle size ratio (the fine powder changes from −325 mesh to −400 mesh), it is inconsistent with the trend of the simulation results (figure 5(b)). Due to the wide particle size distribution of −325 mesh and −400 mesh powder (figure 2(e)), the particle size distribution of these powders has a large overlap, which leads to insignificant changes in the tap density. At the same time, the tap density of the verification experiment are 11% lower than simulated data, the reason is that the particle model is completely dense while the titanium hydride powder has many grooves and holes on the surface and inside (figure 1(a)), which leads to certain differences between the simulation and experimental data.

Figure 7(a) shows the green density of the binary powder system. When the particle size ratio of the powder is 3:1 and the volume fraction of fine powder is 50%, the green density reaches the maximum. After that, the green density of the system decreases with the increasing particle size ratio or the volume fraction of fine powders, which is due to the larger contact point and contact area between the fine powders. Then, the friction resistance of the entire system increases with the increasing number of fine powders, resulting in an increase loss in compact pressure [26].

Figure 7(b) shows the sintered density of the samples. When the particle size ratio of the binary powder system is 3:1,
with the increase of the volume fraction of the fine powder, the change trend of sintered density is basically consistent with the green density, and the maximum value is 99.24%. After that, the sintered density of the system gradually decreases with increasing particle size ratio or volume fraction of fine powders. The reason is that the activity of powders increases with the increase of specific surface area, which promotes the densification behavior during the sintering process. However, more oxygen will be absorbed on the surface of the particle and a surface oxide layer forms due to the increased activity, so the oxygen content of the powder will increase sharply as the particle size decreases (table 3). Since high oxygen content will hinder the sintering and densification process [27–29], the sintered density of the sample will decrease as the particle size ratio and volume ratios of fine powders increase. Therefore, it is necessary to select the appropriate powder size ratio and volume ratio to achieve the highest sintered density of the product.

3.4. Microstructure
Figures 8(a)–(e) shows the microstructure and the pore distribution of the samples when the powder particle size ratio is 3:1. With the addition of fine powder, the size of the pores is significantly reduced (the diameter of most pores is less than 9 μm), but the number of pores has a tendency to firstly decrease and then increase, and reach the minimal value when the volume fraction of fine powder is 50% (the number of pores is 65% less than that of the alloy sintered by fine powder), which shows that the sintering effect of the binary powder system is better than that of single-scale powders. This is due to the fact that the fine powder can be filled into the voids of the coarse powder to increase, the contact area between particles and improve the diffusion of atoms during the sintering process, then increase the sintering density [30].

Figure 9 shows the changes in Vickers hardness of these sintered samples. The overall trend of the hardness increases firstly and then decreases, which is consistent with the trend of sintered density. When the volume fraction of the fine powder is 75%, the maximum hardness is 307HV, which is greater than the hardness at the volume fraction of 50% and 100%. This behavior is caused by the dual effects of solid solution strengthening and increased sintered density. Oxygen atoms will act as a stabilizing element of the Alfa phase in the titanium alloy, and play a solid solution strengthening effect to increase the strength of the alloy [31]. Therefore, the binary system titanium hydride powder can not only increase the density, but also can be strengthened by the higher oxygen contained in the fine powder.

4. Conclusions
In this study, a novel 3D model of irregular titanium hydride powder with complex geometric was established, and the packing simulation of binary system powders with different particle size ratios and volume ratios was carried out by the discrete element method. By applying vibration to the powder, the packing density of the binary powder system was calculated and the empirical formula between tap density and volume ratio and particle size ratio was established. The results show that when the particle size ratios remain unchanged, the relative density firstly increases and then decreases with the increasing volume fraction of fine powder, which is consistent with the experimental conclusion of tap density, indicating that the novel irregular 3D particle model
is suitable to simulate the packing of polygonal particles. In addition, the density and microstructure of the sintered samples were analyzed. When the volume fraction of the fine powder was 50% and the particle size ratio was 3:1, the relative sintered density of the samples reached the maximum value of 99.24%, which is 1.7% and 0.55% higher than that of the samples sintered by coarse powder and fine powder, respectively. Therefore, in the powder metallurgy titanium alloy industry, selecting the appropriate powder size ratio and volume ratio can effectively promote the densification during the sintering process and improve the mechanical properties of the alloy.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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