Effect of particle size distribution on green properties and sintering of Ti-6Al-4V

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Abstract: In this study, the conventional powder metallurgy route of pressing and sintering was employed to study the effects of the particle size of blended elemental Ti-6Al-4V powders on the properties of powder mixtures, green and sintered densities. The -45 µm and -150 µm 60Al-40V master alloy powder were blended with the titanium powder to produce the -45 µm and -150 µm Ti-6Al-4V blend. Powders were pressed at 580 to 870 MPa and sintered in a tube furnace. Taguchi method was used to optimise the sintering parameters, temperature and time, and ANOVA was employed to determine the significant parameters and their contribution to the sintered density. The optimum parameters maximising the density were found to be sintering temperature of 1300 °C and sintering time of 180 mins, for both particle sizes. The green density was higher for the coarser powder and the sintered density was higher for the finer powder.

1. Introduction
Titanium is the 4th abundant structural metal in the earth’s crust. Titanium and its alloys have received interest in a lot of applications such as aerospace, chemical industry, biomedical, and many more because of their high specific strength and excellent corrosion resistance and biocompatibility. They possess the weight half of steels and Ni-based super-alloys. However, because of the extraction and processing costs, titanium and its alloys are expensive and their use is only limited to areas where cost is not an issue. The high cost of titanium-based components can be reduced by changing component production to powder metallurgy [1,2].

The microstructure and properties of sintered powder compacts depend strongly on the quality of the green compacts [3] and in turn, the quality of the green compact is strongly determined by the powder morphology, particle size and size distribution, impurities [4,5] and the densification mechanism [6].

Several authors have studied and established relationships between the compaction pressure, the powder characteristics (such as impurity levels and particle size shape), different compaction route (cold, hot, or dynamic compaction), and the obtained properties of the compacts (density, sinterability and strength) with varying degrees of success [4,5,7,8,9]. Among these, particle size distribution (PSD) is one of the most important, easiest to control and has a direct impact on green compacts and sintering. Properties such as apparent density, tapped density flowability, and compressibility of the powder depend on PSD. Green compacts properties such as porosity, surface roughness and green strength all depend on the PSD [10]. Fine particles generate interparticle friction than coarse powders and this restricts the powder from flowing [10,7]. Moon and Choi [11], have found that the green strength increases with decreasing particle size of the powder due to the larger surface area available for bonding. It is well known that reducing the particle size increases the rate of sintering and densification [5,8].
In this study the effects of the particle size on the green and sintered densities of blended elemental Ti-6Al-4V were investigated. Taguchi method was employed for the design of sintering experiments and analysis of variance (ANOVA) for the optimization process of sintering.

2. Experimental Procedure

2.1. Materials

The starting powders used in this work were Ti Hydride-Dehydride (TiHDH) -150 µm and -45 µm and 60Al40V (60 wt.% Al and 40 wt.% V) -150 µm and -45 µm master alloy (MA) both from Baoji Lihua Non-Ferrous Metals Co., Ltd.

2.2. Powder characterisation and mixing

The particle size of the used powders was determined using the Microtrac Bluewave laser particle analyzer (Microtrac Inc, Bluewave, USA) using distilled water as the dispersant. The morphology of all the starting powders was investigated by the JEOL JSM-6510 scanning electron microscope (SEM).

Two Ti4Al6V powder fractions -150 µm and -45 µm were prepared by mixing TiHDH with 10 wt.% 60Al40V master alloy for 30 minutes in a TURBULA® Mixer. The apparent and tapped density of the two powder mixtures was determined according to ASTM D7481-09 and the flowability of powder mixtures was determined according to ASTM B213–03 using a hall flow.

To study the compressibility behaviour of the 2 powder blends, uniaxial die pressing was used as the method of compaction. Powder mixtures were compacted into cylindrical specimens using a 17.5 mm diameter steel die in a single action mode press from 290 MPa – 1160 MPa. No lubricant was applied on the die wall or added in the powder mixture during mixing. The green density of the compacts was calculated from the volume and mass of the pressed compacts. The pressed samples were weighed with a precision mass balance. The volume of the compacted samples was calculated from the diameter and height measured with a vernier calliper. From the mass and calculated volume, the samples’ densities were calculated.

Two compaction loads, 580 and 870 MPa were then selected to press compacts for sintering. Taguchi L9 (2³) orthogonal array was used to design the sintering experiments followed by ANOVA to determine the significant level and contribution of each variables to the sintered density.

Taguchi method is a statistical method for improving the quality of products and process optimization. It provides a simple, efficient and systematic approach to determine optimum conditions with reduced number of experiments. Taguchi identified that there were three specific goals in an experiment, either to i) : minimize the response, The smaller, the better, ii) maximise the response - The larger, the better, or iii) achieving a given target value - target is best. Taguchi uses a performance criteria known as signal-to-noise (S/N) ratio that takes into account both the process mean and the variance. For each of the different goals, the aim is to maximise the S/N ratio [12]. In this study the aim was to maximise the response, larger the better type characteristics was selected and the SN Ratio was determined by:

\[
SN = 10 \log \left( \frac{1}{n} \sum_{i=1}^{n} y_i \right) \quad (1)
\]

Where \(y\) is the measured response and \(n\) is the number of trial runs. Sintering temperature and time were considered as input parameters and the sintered density was considered as the output parameter (the response). The levels at which they were tested is shown in Table 1. Sintering of the pressed compacts was performed in a tube furnace in flowing argon gas and all the runs were conducted at a constant heating rate of 10 °C/min. The sintered density of the specimens was determined by Archimedes principle according to ASTM B311−13. The relative density was calculated as the ratio of the bulk density to the theoretical density and the theoretical density of Ti-6Al-4V was taken as 4.43 g/cm³.

| Table 1: Process parameters and corresponding levels |
|----------------|-----------|-----------|-----------|
| **Factors**    | **Unit**  | **1**     | **2**     | **3**     |
| Time           | min       | 60        | 120       | 180       |
| Temperature    | °C        | 1200      | 1250      | 1300      |

3. Results and discussion
The results of the particle size distribution of the starting powders is shown in Figure 1. The TiHDH 150 μm and MA -150 μm were found to have bimodal powder particle distributions (containing both the fine and coarse particles) and the TiHDH -45 μm and MA -45 μm were unimodal. The measured particle size distribution is in agreement with the observed SEM images as presented in figure 2. The PSD of powders is also presented as D_{10}, D_{50} and D_{90} in Table 2.

![Particle size distribution of starting powders](image)

Table 2: Particle size distribution of starting powders

| Powders   | d_{10} (µm) | d_{50} (µm) | d_{90} (µm) |
|-----------|-------------|-------------|-------------|
| Ti -150 μm| 54.86       | 100.2       | 151.4       |
| Ti -45 μm | 11.3        | 26.68       | 47.74       |
| MA -150 μm| 32.19       | 114.8       | 194.9       |
| MA -45 μm | 15.16       | 33.86       | 59.44       |

Figure 2 shows the SEM images of the starting materials. The particles of the powders have an angular morphology and for TiHDH, this is consistent with the production process which includes hydrogenation and milling [9].
Figure 2. Powder morphology (a) -45 μm Ti HDH (b) -150 μm Ti HDH (c) -45 μm 60Al4V master alloy (d) -150 μm 60Al4V master alloy.

After blending the TiHDH with the master alloy, the properties of the two size fraction were determined and the results are given in Table 3. It can be observed that the decreased size of powders was accompanied with decreased apparent densities and tapped density. The fine powder, Ti6Al4V -45 μm could not flow in the Hall flow meter. This could be attributed to the fact that smaller particles generate greater interparticle friction and thus particles pack tightly while restricting to flow.

Table 3: Properties of the blended powders

|              | Apparent Density | Tapped Density | Flowability |
|--------------|-----------------|----------------|-------------|
| Ti6Al4V -150 μm | 1.682           | 2.099          | 60.12 s     |
| Ti6Al4V -45 μm  | 1.371           | 1.924          | -           |

Figure 3 shows the compressibility curves of the investigated powder mixtures. It can be seen in the diagram that the green density of powders increased with the increase in the applied pressure. From 290 MPa to 870 MPa, the green density increases rapidly with the increase in the applied pressure. At this point, the two powders had attained the green densities of 87% for the -45 μm and 92% for the -150 μm. The green density then increased gradually with the increase in compaction pressure up to 1170 MPa, indicating a lower compressibility at higher pressure in the range of this study. The green density increased slightly as the particle size increased. This was expected for the bimodal PSD as the finer particles fill the interstitial voids between coarse particles leading to the reduced porosity and increased green density [13]. Also, there is more interparticle friction between the -45um powders than the -150um powders. The maximum density obtained at the highest pressure for both powders was 89.9% for the -45 μm and 93.3 % for the -150 μm.
In this study 9 sintering trials were done as per Taguchi L9 orthogonal array to study the effects of sintering time and temperature on density at 3 levels on two Ti6Al4V powder mixtures. The effect of sintering time and temperature on density is shown in figure 4. The sintered density was influenced by the sintering temperature and time for both -45 μm and -150 μm particle size at all compaction pressures used, 580 and 870 MPa, but the fine particle size (-45 μm) resulted in higher sintered density despite their low green density as compared to the -150 μm. A comparison of the sintered density for a particular powder pressed at different pressures shows that increasing the compaction pressure increased the sintered densities.

The SN equation was used to determine the parameter levels that maximize the density (%) in the sintering of blended elemental Ti6Al4V. SN values were found from equation (1) to determine the parameter levels that maximize the performance response. The results obtained are shown graphically in Figure 5. For both materials, the parameter levels maximising the SN ratio are a sintering temperature of 1300 °C and sintering time of 180 minutes.
To statistically analyse the significance of process variables the ANOVA was done using Minitab 17 software. Parameters such as P-value, F-value and R-Squared were used to determine the significance of each model parameter. The larger the value of F and the smaller the value of p (< 0.05), the more significant the corresponding coefficient is. Table 4 shows the results of ANOVA analysis for density of the sintered compacts.

From the table of the ANOVA it can be seen by looking at the p-value that for the -150 μm particle size, both temperature and time are significant to maximise the sintered density for all compaction pressures studied, since the p values were very low. However this was not the case for the -45 μm as the p value for temperature increased with the compaction pressure with a p value of 0.681 at 870 MPa and a very low F-Value with a mere contribution of 4.49 to the response. The ANOVA % contribution was supported by the Taguchi Delta value. The Delta Value indicates the relative effect of each factor on the response. It can be seen from Table 4 that the Delta Value for temperature is very small for the -45 μm particle size. The significance of temperature on the sintered density over the ranges investigated could be explained by the fact that sintering densification takes place faster as the particle size decreases because the diffusion distances between particles are shorter and the corresponding curvature stresses are larger [14] and that the samples prepared using fine powder can be sintered at lower temperature than ones prepared by conventional powder no matter by gas-pressure sintering or pressureless sintering techniques [15].

Regression equations were obtained relating input process parameters and the output response Density. The equations are shown in Table 5 with the respective $R^2$ and Adjusted $R^2$ values. A model with a good ability to fit the data is required to have the highest $R^2$ and adjusted $R^2$ ($R^2$-adj). This means that the closer the value of $R^2$ is equal to 1, the model can accurately describe the relationship between the variables and the response variables. Generally, $R^2$ should be required to be at least 0.8 for the models with well-fitted data [16]. The $R^2$ and Adjusted $R^2$ values shown in Table 5 prove that the Taguchi accurately correlates the experimental data for both materials and therefore the regression equations can be used for the prediction of sintered density for confirmation experiments.
Table 4: ANOVA Results

|                  | F-Value | p-value | Contribution (%) | Taguchi Delta Value |
|------------------|---------|---------|------------------|---------------------|
| 150 μm pressed at 580 MPa |         |         |                  |                     |
| Time             | 144.10  | 0.00020 | 43.26            | 1.1                 |
| Temperature      | 187.05  | 0.00010 | 56.14            | 1.3                 |
| 150 μm pressed at 870 MPa |         |         |                  |                     |
| Time             | 67.36   | 0.00080 | 59.50            | 0.64                |
| Temperature      | 43.85   | 0.00190 | 38.73            | 0.5                 |
| 45 μm pressed at 580 MPa |         |         |                  |                     |
| Time             | 33.79   | 0.0031  | 82.55            | 0.97                |
| Temperature      | 5.14    | 0.0785  | 12.56            | 0.36                |
| 45 μm pressed at 870 MPa |         |         |                  |                     |
| Time             | 10.01   | 0.02780 | 79.60            | 0.6                 |
| Temperature      | 0.5648  | 0.60810 | 4.49             | 0.16                |

Table 5 Regression Equations for the two powders pressed at two different pressures.

| Material                  | Regression Equation | R² and Adjusted R² |
|---------------------------|---------------------|--------------------|
| 150 μm pressed at 580 MPa | \( RD \) (%) = 76.26 + 0.00914 \( t \) + 0.01304 \( T \) | R² = 0.994Adjusted R² = 0.988 |
| -150 μm pressed at 870 MPa| \( RD \) (%) = 88.94 + 0.005338 \( t \) + 0.005049 \( T \) | R² = 0.9823Adjusted R² = 0.9647 |
| -45 μm pressed at 580 MPa | \( RD \) (%) = 91.37 + 0.00806 \( t \) + 0.00355 \( T \) | R² = 0.951Adjusted R² = 0.9023 |
| -45 μm pressed at 870 MPa | \( RD \) (%) = 94.66 + 0.00504 \( t \) + 0.00156 \( T \) | R² = 0.8409Adjusted R² = 0.6818 |

*RD is the Relative density

4. Conclusions

In this study, the effects of particle sizes on the green and sintered were investigated and the experimental results reported here confirm some well-known trends for the effects of particle size on the green density and sintered density.

- The coarse powder packed more densely than the fine powder as it was observed by comparing the apparent density, tapped density of the two powders and the coarse powder consistently exhibited a higher green density for the range of compaction pressures evaluated.
- Fine powder result in higher sintered density than that for the coarse powder for a specific press-and-sinter process scenario.
- Increasing the compaction pressure increased both the green and sintered densities.
- The ANOVA analysis revealed that temperature becomes less significant when sintering fine powder for the temperature range evaluated.

Acknowledgements

The authors would like to acknowledge the Department of Science and Technology and CSIR for funding the project.

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