The investigation of die-pressing and sintering behavior of ITP CP-Ti and Ti-6Al-4V powders

W. Chen a, Y. Yamamoto a,*, W.H. Peter a, M.B. Clark a, S.D. Nunn a, J.O. Kiggans a, T.R. Muth a, C.A. Blue a, J.C. Williams b, K. Akhtar c

a Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
b Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA
c Cristal US Inc./International Titanium Powder, Woodridge, IL 60157, USA

A R T I C L E   I N F O
Article history:
Received 5 December 2011
Received in revised form 22 May 2012
Accepted 26 June 2012
Available online 5 July 2012

Keywords:
Titanium alloys
Die-press
Sinter
Powder metallurgy

A B S T R A C T
This paper investigated the die-pressing and sintering behavior of ITP CP-Ti and Ti-6Al-4V powders produced by the Armstrong Process™. The ITP powders have an irregular coral-like, dendritic morphology, with a dendrite size of approximately 2–5 μm. As-received as well as milled powders were uniaxially pressed at designated pressures up to 690 MPa to form disk samples with different aspect ratios. In the studied pressure range, an empirical powder compaction equation was applied to linearize the green density − pressure relationship, and powder compaction parameters were obtained. The ITP Ti-6Al-4V powder exhibited a significantly higher sinterability than the CP-Ti powder. This was explained to be due to the higher diffusivity of V in β-Ti at the sintering temperature. The Ti-6Al-4V samples with a green density of 71.0% increased to 99.6% after sintering at 1300 °C for 1 h. An ex-situ technique was used to track the powder morphology change before and after sintering.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Powder metallurgy (PM) processes such as press-and-sinter, injection molding, and hot isostatic pressing are viable methods for producing near-net-shape components that require minimal machining, thus reducing manufacturing costs and increasing the material yield, which is commonly referred to as the “buy-to-fly ratio” in the aerospace sector [1–3]. PM methods have been used to make steel- and copper-based alloy parts for a wide range of applications [1]. However, in the case of titanium (Ti), the high cost of good quality powder (e.g. gas-atomized powder) has been a major stumbling block and has limited the commercial viability of Ti PM processing [4–7].

The Armstrong Process®, developed by Cristal US Inc./International Titanium Powder, Inc. (Woodridge, IL), produces high purity Ti and Ti-alloy powders in a one-step, continuous process [8–10] (The powder produced by this process will be referred to as ITP powder hence force). As Fig. 1 shows, metal chlorides are mixed and injected into a flowing stream of liquid sodium (Na) for reduction. The reaction by-product, NaCl, can be washed away by water. The Armstrong Process® has the potential to make Ti and Ti-alloy powders affordable, and has stimulated research at Oak Ridge National Laboratory (ORNL) to better understand Ti powder consolidation. Preliminary research has been performed on evaluating fabrication processes for near-net-shape forming of components using ITP CP-Ti and Ti-6Al-4V (Ti-64) powders. These processes include: die-pressing, cold isostatic pressing (CIP), sintering, hot isostatic pressing (HIP), and pneumatic isostatic forging (PIF) [11–13]. Fig. 2 shows a comparison of the buy-to-fly ratio for an aircraft component fabricated by conventional machining of a wrought Ti alloy block vs. a press-and-sinter PM method using ITP Ti-64 powder. In this example, the buy-to-fly ratio was reduced from 33:1 for standard processing to 4:1 for the PM approach. Powder produced by the Armstrong process®, used in combination with existing and developing PM technologies, has the potential to reduce the cost of finished Ti components by up to 50% [9].

This paper focuses on understanding the press-and-sinter behavior of ITP CP-Ti and Ti-64 powders. The relationship between green density and die pressure was evaluated and the sintering behavior of the two powders was compared.

* This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the US. Department of Energy. The United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

* Corresponding author. Tel.: +1 865 576 7095; fax: +1 865 574 4357.
E-mail address: yamamotoy@ornl.gov (Y. Yamamoto).

Available online 5 July 2012
Accepted 26 June 2012
Received 5 December 2011
Received in revised form 22 May 2012

Article history:

© 2012 Elsevier B.V. All rights reserved.

This paper investigated the die-pressing and sintering behavior of ITP CP-Ti and Ti-6Al-4V powders produced by the Armstrong Process®. The ITP powders have an irregular coral-like, dendritic morphology, with a dendrite size of approximately 2–5 μm. As-received as well as milled powders were uniaxially pressed at designated pressures up to 690 MPa to form disk samples with different aspect ratios. In the studied pressure range, an empirical powder compaction equation was applied to linearize the green density − pressure relationship, and powder compaction parameters were obtained. The ITP Ti-6Al-4V powder exhibited a significantly higher sinterability than the CP-Ti powder. This was explained to be due to the higher diffusivity of V in β-Ti at the sintering temperature. The Ti-6Al-4V samples with a green density of 71.0% increased to 99.6% after sintering at 1300 °C for 1 h. An ex-situ technique was used to track the powder morphology change before and after sintering.

© 2012 Elsevier B.V. All rights reserved.
Materials and methods

The materials used in this study were CP-Ti and Ti-64 powders produced by the Armstrong Process\(^\text{TM}\) (Fig. 1a). The powders were used either in the as-received condition or after milling. For the milling operation, powders were ball-milled in ethanol for 1 h in a polyethylene jar containing ~13 mm diameter yttria stabilized zirconia (ZrO\(_2\)) media. After the milled powder was dried, it was screened to minus 100 mesh (~140 μm), before being used for the current study. The powder chemistry was analyzed using inert gas fusion for oxygen (ASTM E 1409-08) and combustion infrared detection for carbon (ASTM E 1941-04). The morphology of the ITP powders was characterized using a JSM-6500F (JEOL, Inc.) scanning electron microscope (SEM). The specific surface area of the ITP powders was measured using the BET method with nitrogen gas as the adsorbate.

A cylindrical steel die with an inner diameter of 1.27 cm (0.5 in) was used for powder pressing, which was done at room temperature. The CP-Ti and Ti-64 powders were uniaxially pressed (double-action) over a range of pressures: 17, 34, 69, 172, 345, and 690 MPa (2.5, 5, 10, 25, 50, and 100 ksi). For the powders in the as-received condition, 2 g of powder was used for each sample. The milled powders were used to study the effect of the aspect ratio of pressed pellets on the green density, so the amount of powder used varied from 2.5 to 10 g depending on the specific aspect ratio. Cylindrical samples with nominal aspect ratios (thickness to diameter) of 0.5, 1, and 2 were obtained at each pressure. The density of the as-pressed samples was determined by measuring the mass with a balance and calculating the volume after measuring the dimensions with calipers.

The as-pressed samples were then sintered in vacuum (<5 × 10\(^{-3}\) Pa) at 1300°C for 1 hour with heating and cooling rates of 10°C/min. The density of the sintered samples was determined by means of Archimedes' principle (buoyancy method) using ethanol. An ex-situ SEM technique was used to examine the powder morphology before and after sintering. Selected as-pressed samples were broken to expose a fracture surface and a specific area on the surface was imaged using a HITACHI-S3400 (HITACHI, Inc.) SEM. The samples were then sintered and the same area was located to observe the powder morphology change after sintering.

3. Results and discussion

3.1. Powder characterization

Secondary electron-scanning electron microscopy (SE-SEM) photomicrographs of the as-received ITP CP-Ti and Ti-64 powders are shown in Fig. 3. The morphology of the two powders is similar. Both have an irregular coral-like, dendritic morphology, with a dendrite (primary particle) size of approximately 2–5 μm. The specific surface area for the as-received ITP CP-Ti and Ti-64 powders is 0.18 and 0.36 m\(^2\)/g, respectively. Because of the irregular, agglomerated structure of the powders, the tap density of the as-received powder is 6–8%. The particle size distribution of the powders after ball milling is shown in Fig. 4. The milling process breaks up the agglomerates and significantly reduced the powder size, which increases the tap density to 30–32% [11]. The specific surface area also increased to 0.36 and 0.5 m\(^2\)/g for the CP-Ti and Ti-64 powders, respectively. The chemical composition of the as-received powders is listed in Table 1.

3.2. Powder compaction and density-pressure relationships

Fischmeister and Arzt [14] suggested a three-stage model for the densification of spherical powders during die pressing:

Stage I: particle rearrangement, which occurs at the very beginning of compaction and does not contribute significantly to the densification of spherical powders.

Stage II: particle plastic deformation, in which particles are flattened and brought closer to form additional contacts.

Stage III: particle impingement, in which neighboring contacts on one particle impinge, making an increasing fraction of the volume harder to compress.

Poquillon et al. [15] studied the cold compaction behavior of a spongy iron powder which is quite similar in morphology to the ITP Ti-64 powder. Three deformation stages were clearly observed for the iron powder, with particle interlocking being the dominant factor, which increased with compaction pressure. In a previous study, the current authors used an in-situ SEM technique to observe the deformation of CP-Ti powder [16]. A powder compression test was performed using a screw-driven tensile stage placed inside an SEM. The observed compression process consists of three stages: 1. Powder cluster rotation; 2. Powder cluster broken down to fill in large spacing; 3. Powders being squeezed to fill in the inter-particle spacing. The corresponding stresses for the first two stages were below 10 MPa. In the final stage of compression, the powders were deformed and individual particles were brought closer to each other. The lowest pressure in the current study was 17 MPa (2.5 ksi), hence the compaction behavior described in this study corresponds to stage III.

Density-pressure curves have been widely used to study the compaction behavior of powders [1,17]. There are four widely used empirical compaction equations which have been developed by Heckel [17], Kawakita [18], Ge [19], and Panelli [20]. A critical review of these equations [21] showed that the Panelli equation best represented the density-pressure relationship for the 22 different
powders studied. The density-pressure data for the ITPCP-Ti and Ti-64 powders were plotted using the Panelli equation:

\[
\ln \left( \frac{1}{1-D} \right) = A\sqrt{P} + B
\]

in which \(D\) is the relative density of the compacted material and \(P\) is the applied die pressure. \(A\) is a constant which represents the compressibility (powder’s ability to densify by plastic deformation).

\[
B = \ln \left( \frac{1}{1-D_0} \right)
\]

\(B\) is the Y-intercept, where \(D_0\) represents the loose powder density (tap density).

Fig. 5 shows the density-pressure data for the as-received ITP CP-Ti and Ti-64 powders fitted to Eq. (1). Fig. 6a and b show the curve fitting for the milled powders pressed to three different aspect ratios. Note that the data of ITP Ti-64 powders were reported previously [13]. The curve fitting parameters are also listed in Tables 2 and 3. The linear correlation coefficient was greater than 0.99 in all cases, indicating good agreement between Eq. (1) and the experimental data. The compressibility (\(A\) value) for the CP-Ti powder is always higher than the Ti-64 powder.

For the milled powder, as the aspect ratio increased from 0.5 to 2, the \(A\) value decreased from 0.062 to 0.050 for the CP-Ti powder, and from 0.040 to 0.034 for the Ti-64 powder. The increased
die–wall friction due to the higher aspect ratio reduced the pressure transferred to the powder bed and caused the apparent decrease in compressibility of the powders. Die–wall friction is related to the radial wall stress transmitted by powders through axial stress, so it is a material–dependent value and difficult to measure. Experimental data has shown that a locally induced normal stress causes a significant change in the friction coefficient between a powder and the die wall [22]. From Fig. 6, it can also be seen that the change in slope (compressibility) for the Ti–64 powder (−15%) is slightly smaller than that for the CP–Ti powder (−19%), which could be due to the higher strength of Ti–64 powder lowering the relative effect of die–wall friction. As the applied die pressure increases, the density of samples decreases with increasing aspect ratio due to the higher frictional force between the powder and the die wall. If there is no friction, |a| should be zero. The Y–intercept (b value) is the theoretical density when the aspect ratio equals zero and can be used to estimate the green density when there is no friction. Fig. 7a and b can also be used to estimate the green density as a function of compaction pressure for CP–Ti and Ti–64 samples with different aspect ratios.

3.3. Green density – aspect ratio analysis

Fig. 7a and b illustrate the effect of aspect ratio on the green density at six different applied die pressures for the ITP CP–Ti and Ti–64 powders, respectively. Due to the physical limit of the die, samples with an aspect ratio of 2 are not obtainable at 690 MPa. The detailed density data are included in Tables 4 and 5. In Tables 4 and 5, the |a| value is the slope of the linear regression fit to the data plotted in Fig. 7 and also an indication of the extent of die–wall friction. However, there was an abnormal increase of |a| value in the CP–Ti powder and the die wall. At low die pressure, the |a| value increased rapidly, indicating a fast increase of die wall friction and the percentage of stress transferred from punch to powder bed decreased significantly. However, as the die pressure increased, the rate of friction increment became mild. It is likely that the increased die pressure was dissipated by the deformation of the powder agglomerates and only a small portion was transferred to the die wall. However, there was an abnormal increase of |a| value for CP–Ti powder at pressure between 517 and 690 MPa. Janssen–Walker differential slice analysis [23] has been used to predict the value of the mean axial stress across a horizontal plane at a certain height [24,25]. In those studies, only an estimated value of stress transmission coefficient was used for density prediction. It is noticed that the |a| value for CP–Ti is always higher than that for Ti–64, indicating higher friction between the CP–Ti powder and the die wall. At low die pressure, the |a| value increased rapidly, indicating a fast increase of die wall friction and the percentage of stress transferred from punch to powder bed decreased significantly. However, as the die pressure increased, the rate of friction increment became mild. It is likely that the increased die pressure was dissipated by the deformation of the powder agglomerates and only a small portion was transferred to the die wall. However, there was an abnormal increase of |a| value for CP–Ti powder at pressure between 517 and 690 MPa. At this pressure range, the CP–Ti has yielded (yield stress is 520 MPa) and the plastic deformation of the powder increased the hydraulic pressure against the die wall, which resulted in the rapid increase of friction. The die pressure is always below the yield stress of...
Ti-64 (917 MPa), thus there was not such an increase of |a| value for ITP Ti-64 powder.

### 3.4. Sintering behavior of ITP powders

The density of the ITP CP-Ti and Ti-64 samples after sintering at 1300 °C for 1hr is shown in Fig. 8. The green density of the samples is also included for comparison. For the CP-Ti sample pressed at 690 MPa, the density increased from 84.0% for the as-pressed powder (Fig. 9a) to 94.1% (Fig. 9b) after sintering and all interconnected porosity was eliminated. The Ti-64 powder exhibited a much higher sinterability than the CP-Ti powder. Although the green density of the Ti-64 sample was only 71.0% (Fig. 9c) after die pressing at 690 MPa, the density increased to 99.6% (Fig. 9d) after sintering. The melting point is 1665 °C for CP-Ti (ASTM Grade-2) and 1604 °C for Ti-64 (ASTM Grade-5) [26], thus the sintering temperature is closer to the melting point of the Ti-64 powder. This may be one reason why the Ti-64 powder has better sinterability than the CP-Ti powder. Various mass transport mechanisms have been shown to contribute to sintering, such as surface diffusion, bulk diffusion, grain boundary diffusion, viscous flow, plastic flow, and vapor transport from solid surfaces [27]. It is suggested that low temperature sintering (below β-transus) of Ti is controlled predominantly by lattice diffusion in the α-Ti [28–30]. When the sintering temperature is above the β-transus, several other mechanisms are suggested, such as pipe diffusion through dislocations [31], lattice diffusion from surface and grain boundary sources [32] and creep [28]. In the initial stage of the sintering, surface diffusion is the dominant densification mechanism, since the mass transportation would take place only at the physical contact of each powder surface. Because the specific surface area of the ITP

---

### Table 4

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Relative density (%)</th>
<th>Linear regression Y = aX + b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nominal sample aspect ratio</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>41.3</td>
<td>41.9</td>
</tr>
<tr>
<td>69</td>
<td>50.0</td>
<td>49.0</td>
</tr>
<tr>
<td>172</td>
<td>62.8</td>
<td>60.3</td>
</tr>
<tr>
<td>345</td>
<td>73.2</td>
<td>71.4</td>
</tr>
<tr>
<td>517</td>
<td>80.4</td>
<td>77.8</td>
</tr>
<tr>
<td>690</td>
<td>84.0</td>
<td>81.4</td>
</tr>
</tbody>
</table>

N/A: not available.

### Table 5

<table>
<thead>
<tr>
<th>Pressure, (MPa)</th>
<th>Relative density (%)</th>
<th>Linear Regression Y = aX + b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nominal sample aspect ratio</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>35.7</td>
<td>36.2</td>
</tr>
<tr>
<td>69</td>
<td>40.6</td>
<td>40.3</td>
</tr>
<tr>
<td>172</td>
<td>51.3</td>
<td>50.6</td>
</tr>
<tr>
<td>345</td>
<td>61.5</td>
<td>58.3</td>
</tr>
<tr>
<td>517</td>
<td>67.9</td>
<td>67.1</td>
</tr>
<tr>
<td>690</td>
<td>71.0</td>
<td>69.4</td>
</tr>
</tbody>
</table>

N/A: not available.

---

Fig. 7. (a) (b) Green density versus aspect ratio plot for the ITP CP-Ti and Ti-64 samples pressed at 6 different pressures, (c) the change of |a| value (line slope) versus the die-pressure.

Fig. 8. Change of density for ITP CP-Ti and Ti-64 die pressed powder after vacuum sintering at 1300 °C for 1 h. The nominal aspect ratio of the samples before sintering was 0.5.
Ti-64 powder is larger than the CP-Ti powder (in the milled condition, 0.5 and 0.3 m²/g, respectively), the Ti-64 powder is expected to sinter faster than the CP-Ti powder. In the final stage of the sintering process, when most pores are closed, bulk diffusion processes are the most active. At 1300 °C, the diffusivity of Al in β-Ti is approximately $2 \times 10^{-12}$ m²/s, which is close to the self-diffusivity of Ti ($2.5 \times 10^{-12}$ m²/s) at this temperature [33]. However, the diffusivity of V in β-Ti at 1300 °C is $2 \times 10^{-11}$ m²/s [34], which is an order of magnitude higher than both of the Ti self-diffusivity and Al diffusivity. The high diffusion rate of V atoms facilitates the diffusion of vacancies (in the opposite direction). The combined effect of larger specific surface area and higher diffusivity of V may explain why Ti-64 has significantly better sinterability than the CP-Ti.

An ex-situ technique was used to track the powder morphology change after sintering at 1300 °C for 1 h (see Fig. 10). The ITP powders were pressed to 345 MPa and broken apart to exhibit the powders in the as-pressed condition. Since the ITP powders are in the form of agglomerates, there are two pore sizes in the structure – the larger pores between agglomerates and the smaller pores in the agglomerates. By comparing the SEM images in Fig. 10, it can be seen that all intra-agglomerate pores have closed and only some
inter-agglomerate pores remained open. For the Ti-64 sample (Figs. 10c and d), although the initial inter-agglomerate pores were larger, most of them are closed after sintering.

The sintering shrinkage of ITP powders has also been quantitatively evaluated. Fig. 11 shows the shrinkage in the radial direction and the thickness direction for the samples after sintering at 1300 °C for 1 h. The Ti-64 samples exhibited anisotropic shrinkage, with the shrinkage in the radial direction being larger than in the thickness direction for all of the test samples. This anisotropic shrinkage is typical for a die-pressing and sintering process. During the die-pressing, the pores tend to be flattened to a lenticular shape with the long axis perpendicular to the pressing [27]. When the sintering reaches the final stage, the pores become spherical and finally disappear, thus the shrinkage in the radial direction is higher than in the thickness direction [27]. This phenomenon could be a significant factor because of the large inter-agglomerate pores and the large amount of shrinkage that occurred with the Ti-64 samples (Fig. 11b). However, for the ITP CP-Ti samples, there is no observable anisotropy in the shrinkage (Fig. 11a). This is most likely because of the lower sinterability of the CP-Ti and because the sintering did not enter the final stage. After sintering, there were still a large number of pores that had not been spheroidized, as can be seen in Fig. 9b. In addition, the sintered disk samples were cut for measuring the 2D density (area density) in different directions. The area density perpendicular to the thickness direction is 6.5 ± 0.4%, compared with 5.4 ± 0.3% perpendicular to the diameter direction. This difference confirms that many pores are still in a lenticular shape so the sintering shrinkage of CP-Ti is in general isotropic.

4. Conclusions

The low-cost ITP CP-Ti and Ti-64 powders produced by Armstrong Process™ have an irregular coral-like, dendritic morphology, with a primary particle size of approximately 2–5 μm. The die-pressing behavior of the CP-Ti and Ti-64 powders was studied in the case of disk shape compacts with 3 different aspect ratios, namely 0.5, 1, and 2. In the studied die-pressure range, an empirical powder compaction equation: \( \ln(1/(1 - D)) = A\sqrt{P + B} \), linearized the relationship between the green density \( D \) and die-pressure \( P \) very well for both the as-received and milled ITP Ti-64 powders. The ITP CP-Ti exhibited a significantly better compressibility than the ITP Ti-64 due to its lower yield stress. Pressure dwell during die-pressing effectively increased the green density of the ITP CP-Ti and reduced the localized large pores.

For the ITP CP-Ti sample pressed at 690 MPa, the density increased from 84.0% to 94.1% after sintering at 1300 °C for 1 h and the interconnected pores were eliminated. The ITP Ti-64 exhibited significantly higher sinterability than the ITP CP-Ti. The density of the ITP Ti-64 sample pressed at 690 MPa increased from 71.0% to 99.6% after sintering at the same condition. The higher sinterability of Ti-64 powder is believed to be due to its larger specific surface area and the high diffusivity of V in β-Ti at this temperature, which facilitated the sintering process. The ITP Ti-64 samples exhibited anisotropic shrinkage, while the sintering shrinkage of CP-Ti is in general isotropic. This study will provide guidance for the future development of PM processing for the near-net-shape manufacturing of Ti components using ITP CP-Ti and Ti-64 powders.

Acknowledgments

This research is sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE) Industrial Technologies Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Research supported by ORNL’s Shared Research Equipment (ShARE) User Facility, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

References