

A comparative study of oxygen pick-up of TiHDH powder during press and sinter and loose sintering processing

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Abstract: Press and sinter is considered to be the most cost effective powder metallurgy process for producing parts. However, loose powder sintering shows to be a more promising cost effective powder metallurgy process as it entails pouring powder into a mould followed by sintering. The differences in their behaviour with respect to densification, maintaining dimensional stability and their oxidation behaviours determine the choice of their industrial applicability. Titanium has a high affinity for oxygen which in turn makes it difficult to process components from powder. It also affects the mechanical properties of products significantly; particularly in applications where ductility is imperative. The focus of this study was therefore to evaluate the oxygen pick-up of the two cost effective powder metallurgy processes (press and sinter and loose sintering). A 100 Mesh TiHDH powder was used for sintering. Sintering was performed at 1500 °C for 4 hours. The oxygen contents of the green and sintered compacts were then compared. High oxygen contents were observed in tap density powder and pressed samples. The loosely sintered components showed high oxygen pick-up after sintering while oxygen pick-up decreased with increasing pressure in pressed samples. These results show that press and sinter is advantageous over loose sintering where oxygen control is critical.

1. Introduction

Titanium (Ti) is a structural metal that is used mostly for its light weight and corrosion resistant characteristics [1]. Powder metallurgy (PM) of titanium alloys was established in the 1980s [2]. It is a particularly attractive manufacturing process for titanium components [3]. This is due to its potential for true net shape capability combined with mechanical properties that are equivalent to or exceed cast and wrought products [4]. PM is a near-shape and solid state method which significantly limits the need for machining [5]. The main driving force behind PM processing is cost reduction [2]. So far, the most cost effective powder metallurgy process (for parts production) is press and sinter [6], [7]. This process involves compaction of powders and sintering stages [8]. However, loose powder sintering of Ti shows to be a more promising innovative cost effective process of producing powder metallurgy parts as it eliminates the compaction stage. Loose powder sintering is a process which entails pouring or mechanically vibrating powder into a mould of a desired shape followed by sintering [9].

One of the critical parameters in powder metallurgy of titanium is the selected process' ability to possess minimal oxidation behaviour. The oxidation process occurs through oxygen adsorption, oxide nucleation, lateral growth of the oxide and compact oxide scale formation [10]. Oxygen adsorption involves the attachment of oxygen on the metal surface through chemisorption or physical adsorption. After adsorption, the oxygen molecules dissociate and get adsorbed as atoms. During the oxide



nucleation process, oxide nuclei form after the metal surface is saturated with adsorbed oxygen. Lastly, the lateral nuclei growth result in the formation of a compact oxide scale that covers the metal surface.

Small amounts of oxygen, nitrogen and carbon can significantly alter the mechanical properties of Ti, particularly its ductility [5]. To prevent or minimise oxidation [11], sintering of titanium is usually carried out in high-vacuum [12] or flowing argon gas [13]. The authors could not find literature on work done to compare the amount of oxygen pick up during sintering of loosely packed and tightly packed titanium powder. This work therefore aims at studying and comparing the oxidation behaviour of TiHDH 100 mesh during press and sinter and loose sintering processes.

2. Experimental procedure

TiHDH 100 mesh (-150 μm) powders were supplied by Baoji Lihua Non-ferrous Metals Co., Ltd in China. The powder and pressed compacts were analysed for oxygen content using the ELTRA ONH 2000 Oxygen Nitrogen Hydrogen Determinator PC controlled machine. The powder was pressed using a 17.5 mm high-speed tool steel die at three different nominal pressures of 120, 440 and 1170 MPa. The mass of powder per sample was approximately 7 g. Cold compaction was carried out using an Enerpac 100 T press. Densities were determined from the mass and dimensions of the samples. The masses were measured using an Ohaus explorer mass balance while dimensions were measured using the Vanier calliper. The theoretical densities (%TD) were determined using Equation 1.

$$\text{Theoretical density (\%TD)} = \left(\frac{m}{\pi h \left(\frac{d}{2}\right)^2} / 4.51 \right) * 100 \quad (1)$$

where m is the mass (g), h is the height (cm) and d is the diameter (cm) of the compact.

The loose sintering samples were achieved by sintering powders in their aerated (untapped) and tapped states using alumina crucibles. Each powder sample was poured into the crucibles and left untapped or tapped before sintering. The tapped state was obtained after 60 taps. Each tapping consisted of lifting the crucible containing the powder to a height of approximately 10 mm from the working surface. Equation 1 was used to calculate both bulk densities.

The sintering of the powders (aerated and tapped) and green compacts was carried out at 1500°C for 4 hours. Ceramic reef discs were used to close the tops of the alumina crucibles. Sintering was done in a Carbolite tube furnace using a heating rate of 10°C/min in an inert argon atmosphere at a flow rate of 1 L/min and the experiment was terminated by a furnace cool. The ends of the work tube were fitted with gas-tight end seals to keep out air from the atmosphere.

The densities of the sintered samples were determined as for the green compacts, from their masses and dimensions. For overall oxygen content analysis, and in order to accommodate location differences, approximately 100 mg sections of the sintered compacts were cut from the top, middle and bottom of the compacts using a BRILLANT 221 abrasive cutter. The sections were analysed for oxygen content using the ELTRA ONH 2000 and the overall oxygen pick-up (from the top, middle and bottom sections of the samples) was reported as an average. The ELTRA ONH 2000 was calibrated using standards. The level of deviation in the oxygen content of the three standards tested was 0.00168/1.18775 %.

3. Results and discussion

3.1 Initial oxygen content

Table 1 gives the oxygen contents of the powders used in this work. The tested oxygen contents were found to be higher than those given by the suppliers on the supplier certificates. The tested oxygen content of TiHDH -150 μm was found to match that of the ASTM Ti grade 2 [4].

Table 1. The starting oxygen contents of TiHDH with varying starting densities.

| TiHDH 100 mesh | | wt. % O ₂ |
|----------------|----------|----------------------|
| Powder | Supplier | 0.10 |

Tested

0.19

3.2 Visual examination

Photograph in figure 1 shows a change in colour of the sintered compacts with increasing density from the aerated state (1) to a pressure of 1170 MPa (2). Compacts sintered in the aerated state were gold in colour as compared to those sintered after pressing at 1170 MPa which were silver in colour. The colour change observed is due to oxidation and nitridation which is commonly observed during sintering of titanium powders [10]. Another interstitial that can be picked up, besides oxygen and nitrogen, is carbon [14]. However, it should be noted that the focus of this study is on oxygen pick-up of titanium during sintering. The source of oxygen and nitrogen could have been the oxygen on the particle surface, air in the pores of the loose powder “compacts”, air that leaked into the furnace or the argon gas. Loosely packed powders have greater porosity, and therefore, more entrapped air, as compared to tightly packed or compacted powders. This resulted in high discolouration in the aerated sample (1) with the highest porosity as compared to samples pressed at the highest nominal pressure of 1170 MPa (2), which had the least porosity. Oxygen and nitrogen studies were carried out using the ELTRA ONH 2000.

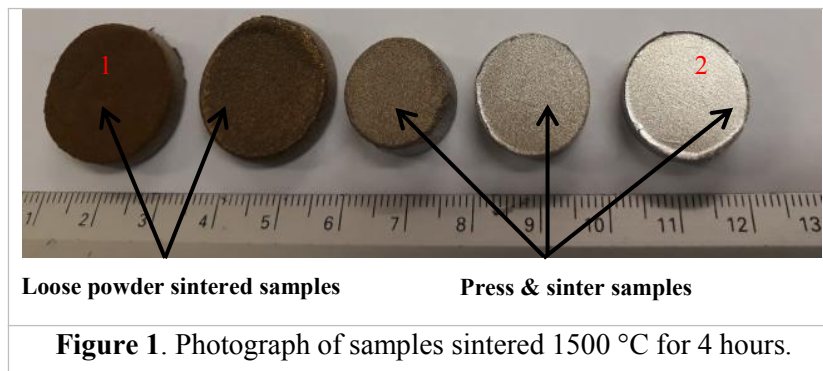


Figure 1. Photograph of samples sintered 1500 °C for 4 hours.

3.3 Density and oxygen results

The initial (a) densities and (b) oxygen contents are given as grey bars and lines in figure 2 respectively; the grey bars represent the initial densities while the grey lines represent the starting oxygen contents. Tapping led to a statistically significant increase in the bulk density from 38 % TD in the aerated state to 44 % TD for the tapped state. This is in agreement with previous study where tapping led to increased contact area between the particles, resulting in increased bulk density [15].

With the pressed samples, the green density also showed an increase with increasing pressure, increasing from 62 % TD when pressing at 120 MPa to 90 % TD when pressing at 1170 MPa. This was expected as the volume of pores in commercially pure (CP) Ti decreases with the increase in pressure, resulting in the increase of sample theoretical density as observed in other titanium powders [16].

The bulk densities of the loose powders were lower than the densities of the compacted powders, tentatively because of the application of a load during compaction causing the powder particles to move closer and decrease the volume of pores, hence the increased density [16].

The oxygen content of the powder that was loose sintered increased with tapping from 0.19 to 0.23%. This was unexpected as the aerated powder is expected to have more open pores due to increased distance between particles as compared to the tapped and pressed compacts. Oxygen content increases with increase in porosity [17]. There is no significant change in oxygen content of the pressed compacts with the increase in pressure. This is in agreement with the study done by Baril *et al.* where oxygen content does not change with pressing [18].

The lowest oxygen content of 0.19 % was observed in the aerated powder. The highest oxygen content of 0.23 % was achieved with the tapped powder and compacts pressed at 120 and 1170 MPa.

The reason for the increased oxygen content with decreased porosity from aerated to both the tapped powder and cold compacted samples are unknown and still under investigation.

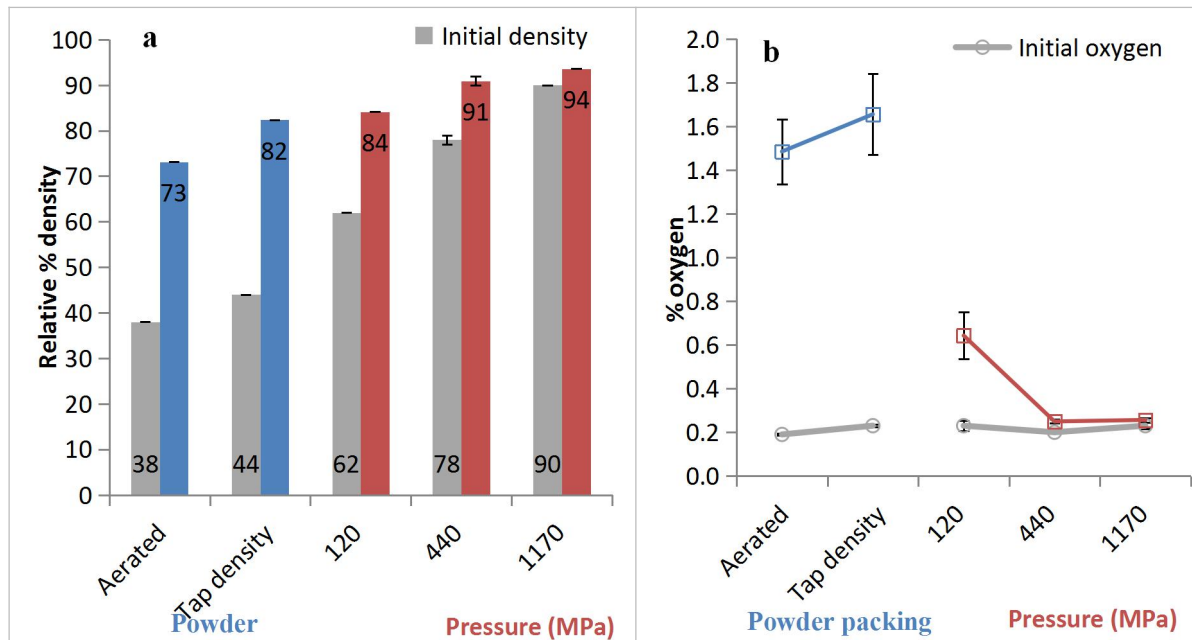


Figure 2. Relative percentage (a) densities and (b) oxygen content of loose powder sintering and press and sinter at 1500 °C for 4 hours.

The final (a) densities and (b) oxygen contents of compacts sintered at 1500 °C for 4 hours are also given in figure 2. These are represented by the blue and red bars, and the blue and red lines respectively. There is an increase in density of loose sintered samples from 73 % in the untapped state to 82 % in the tapped state. This could be due to the higher starting density in the tapped state as compared to the untapped state. The increase in density with tapping after loose sintering is attributed to the increased contact area between the particles, resulting in increased bulk density, hence high sintered density [15].

The brown density of the compacted samples also increases with the increase in pressure. The increase is significant in samples pressed at 120 and 440 MPa, and insignificant between samples pressed at 440 and 1170 MPa. The increase in brown density with increasing pressure could be due to decreased porosity as pressure increases, leading to increased sintered density [16].

The brown densities of the loose powder sintering process (blue bars) are lower than those of the press and sinter samples (red bars). This could be due to the high starting densities in press and sinter as compared to loose sintering as high starting densities lead to high final densities [15].

The final oxygen content of loose sintered samples showed an insignificant difference with the increase in packing; see figure 2 (b), blue line. This behaviour was unexpected as tapped powder has lower porosity, and therefore, less entrapped air compared to untapped powder. Increased porosity/entrapped air will lead to high oxidation [17]. The reason for the insignificant increase in oxygen with the increase in packing (decreased porosity) in loose sintered samples could be due to the high starting oxygen contents of 0.23 % in the tapped powder compared to 0.19 % in the untapped powder.

There is a decrease in oxygen content with the increase in pressure from 120 to 1170 MPa in the press and sinter compacts. This is supported by previous work of others where low porosity samples had low oxygen content as compared to high porosity samples [17]. Looking at the final oxygen content, blue and red lines, there is a significant difference in the amount of oxygen in the two processes. The press and sinter samples picked up less oxygen as compared to the loose sintered samples. The significant difference is observed between the tap density samples and the sampled

pressed at 120 MPa. The difference in the oxygen pick-up of loose sintering and press and sinter of TiHDH 100 mesh was expected as press and sinter samples had less initial porosity/ high starting density as compared to loose sintered samples [17].

The lowest oxygen contents of 0.25 % and 0.26 % are achieved after sintering samples pressed at 440 MPa and 1170 MPa respectively. The highest oxygen content of 1.66 % is achieved with tap density samples. The lowest oxygen results were expected as the compacts pressed at 1170 MPa have the lowest porosity, therefore low oxygen pick-up [17]. The highest oxygen results from tap density components are contradicting what was previously discovered as tap density components have low porosity as compared to aerated components [17]. The high oxygen content could be due to the high initial oxygen content in the tapped samples.

4. Conclusions

It is therefore concluded that, in cases where oxygen control is vital, press and sinter is preferred over loose powder sintering. This is because cold compaction results in decreased porosity, leading to reduced oxygen pick up.

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