Journal of Metals, Materials and Minerals, Vol.20 No.1 pp.63-68, 2010

Study of Covering Conditions for Sintering of Metal Injection Moulded Commercially Pure Titanium

Nattapol MUENYA and Anchalee MANONUKL*

National Metal and Materials Technology Center,
114 Thailand Science Park, Phaholyothin Rd.,
Klong 1, Klong Luang, Pathumthani.12120

Abstract

In metal injection moulding process, sintering for some specific materials is different from general materials. Titanium is a material that is not easy to sinter because it is a very reactive metal at high temperature. The high quality of the titanium component is difficult to control, especially so in point of the levels of carbon and oxygen, which have large effects on the mechanical properties. Commercially pure titanium was injected, debinded and sintered at 1150°C and 1250°C in high vacuum without a cover, and with a quartz cover, a mullite cover and an alumina cover, respectively. From the physical and mechanical properties of the sintered parts, it can be summarised that it is necessary to protect commercially pure titanium sintered parts from contamination. The cover must be made of a material that is stable at the sintering temperature. Quartz and alumina are possible candidates as both can be used to sinter good quality titanium. However, alumina is a better choice considering the cost and toughness.

Key words: Pure titanium, Covering conditions, Oxygen content, Sintering, Metal injection moulding

Introduction

Titanium and titanium alloys have a high-strength-to-weight ratio, impressive mechanical properties and excellent corrosion resistance. There are many possible applications associated with titanium, which are aerospace, energy and chemical industries. The application of titanium and its alloys has expanded to medical application since it is the most biocompatible metallic material. However, the cost of titanium-base components limits their usage. The relatively high cost of titanium parts is a result of the intrinsic raw material cost and the cost of forming to final products. Although wrought product forms of titanium and its alloys constitute more than 70% of the market share, cast and powder metallurgy (P/M) products are also available for applications that require complex shapes.(5) In addition, P/M can be used to obtain microstructures not achievable by conventional ingot metallurgy.

Metal injection moulding (MIM) is one of the P/M processes that can fabricate small and highly complex metallic parts. There are four main steps in MIM, which are mixing, injection, debinding and sintering.(4,7) In the mixing step, metallic powder and binder are blended homogenously together. The mixture is then granulated into small pallets, called “feedstock”, suitable for injection. The feedstock is injected using an injection moulding machine to obtain a “green” part. The binder within the green parts is removed using heat in a step called thermal debinding. Finally, the skeleton of metallic powders is thermally bonded in a step called sintering. Sintering for some materials, for example titanium and its alloys, requires more attention than for others.(4)

Early works on developing a viable titanium MIM process was plagued by the unavailability of suitable powder, inadequate protection of titanium during elevated-temperature processing, and less-than-optimum binder for a material as reactive as titanium, particularly oxygen pick-up.(1) However, some MIM practitioners have now learned what the titanium community has long known – that titanium is the universal solvent and must be treated accordingly.(2) In this work, the

*Corresponding author Tel.: +66 2564 6500 ext. 4707; Fax.: +66 2564 6403;
E-mail: anchalm@mtec.or.th

means of protecting titanium was investigated. Covering specimens is one of many methods of titanium protection by reducing undesirable reaction between sintered material and burnt binder that still remained within the furnace chamber during debinding and sintering processes. The physical and mechanical properties of specimens after sintering with three different covers, namely quartz, mullite and alumina, and without cover are reported.

Materials and Experimental Procedures

In this work, gas atomised commercial pure (CP) titanium powder was used. The CP titanium powder has an average powder size of 45 µm and was supplied by Sumitomo Titanium Co., Japan. Furthermore, the chemical compositions of CP titanium are shown in Table 1. It was homogeneously mixed with polyacetal-based thermoplastic binder supplied by Mold Research Co., Japan. The mixing ratio was 90%:10% by weight of CP titanium powder to the binder. The CP titanium powder and the binder have densities of 4.5 and 1.0 g/cm^3, respectively; this is equivalent to 65%:35% by volume of CP titanium powder to the binder as tabulated in Table 2.

The mixture was granulated and injected into "green" tensile specimens. The binder in the green parts was thermally removed in argon atmosphere at 500°C for 1 hour. This proceeding resulted in a skeleton of titanium powder, which was sintered at 1150°C and 1250°C in high vacuum atmosphere (< 10^{-4} Pa) for 2 hours.[8] The heating rate was relatively slow and the total debinding and sintering time was 30 hours. During sintering, three different covers were used and the results were compared with results obtained by sintering without cover as a reference sample. The three covers were made from quartz, mullite and alumina. The density of green and sintered parts was measured using the Metal Powder Industrial Federation (MPIF) standard no. 42. The microstructures were investigated using optical microscopy. In addition, the mechanical properties, such as the macroscopic hardness test, were examined using the MPIF standard no. 43, and the tensile test was conducted using the MPIF standard no. 10.

Table 1. Chemical compositions of CP titanium powder

Material	Chemical composition (%)					
	Fe	O	C	N	H	Ti
CP Ti powder	0.026	0.120	0.005	0.007	0.007	Balance

Table 2. Density and percentage by weight and by volume of CP titanium powder and binder in feedstock

Composition	Density (g/cm^3)	% by weight	% by volume
CP Ti powder	4.5	90	65
Binder	1	10	35

Results and Discussion

Sintering Temperature 1250°C

CP titanium green parts were debinded and sintered at 1250°C with a quartz cover and without cover. The sintered density and mechanical properties are shown in Table 3 and Figure 1. Parts produced with a quartz cover or without cover reached the same sintered density of 4.32 g/cm^3. However, the mechanical properties are different. The hardness of specimens sintered without cover was slightly lower than those sintered with a quartz cover. Parts that were sintered without cover had significantly lower elongation to failure (4%) than those sintered with a quartz cover (11%). The usage of quartz cover improved the elongation to failure significantly, while the modulus of elasticity remained nominally the same and the yield stress of parts sintered without cover was noticeable higher than that of parts sintered with a quartz cover.

Table 3. Comparison of sintered density and hardness of CP titanium sintered at 1250°C with a quartz cover and without cover

Covers	Sintered density (g/cm^3)	Hardness (HRB)
No cover	4.32	94
Quartz	4.32	100

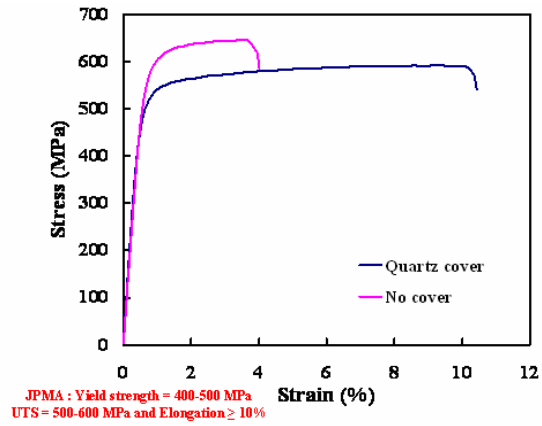


Figure 1. Stress-strain response of CP titanium sintered at 1250°C with a quartz cover and without cover

The oxygen and carbon contents of sintered parts without cover were slightly higher than those sintered with a quartz cover. Both groups of sintered parts gained more oxygen and carbon when compared with the original oxygen and carbon contents shown in Table 1. In addition, the oxygen content of parts sintered without cover was above the maximum allowable level of 0.3% according to the Japanese Powder Metallurgy Association (JPMA) standard. Furthermore, the level of carbon, yield stress and ultimate tensile strength conform suitably to the JPMA standard. However, the elongation to failure of parts sintered without cover is also less than the required minimum level 10% according to the JPMA standard. Hence, CP titanium cannot be sintered without cover to conform to the JPMA standard. In addition, the slightly higher oxygen and carbon significantly reduced the elongation to failure. Thus, titanium is very sensitive to oxygen and carbon contants.

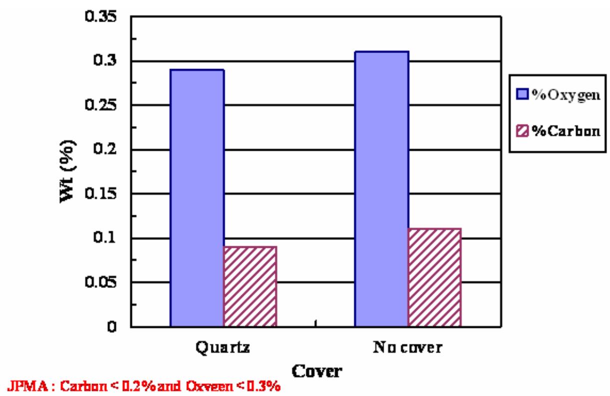


Figure 2. Bulk oxygen and carbon contents of CP titanium sintered at 1250°C with quartz cover and without cover

Sintering Temperature 1150°C

It was clear from the results of CP titanium sintering at 1250°C that covering is necessary to produce good titanium sintered parts. Quartz is an expensive material and difficult to handle since it is very brittle and lacking in toughness. Mullite and alumina (Al_2O_3) were other possible candidates. The previous study on the effect of the sintering temperature showed that sintering at 1150°C can provide better mechanical properties, especially the elongation to failure.[6] Three sets of tensile test bars were sintered at 1150°C using a mullite cover, an alumina cover, and no cover. Densities obtained after sintering were similar, and the hardness was slightly higher for specimens using a mullite cover as shown in Table 4. All specimens were sintered at the same sintering temperature. Hence, the density was expected to be similar because sintering is a thermally activated process.[3] In addition, the stress-strain curves of these three sets of specimens are shown in Figure 3. All three sets of specimens had a similar modulus of elasticity and ultimate tensile stresses, which complies with the JPMA standard. However, the elongation to failure of specimens without cover and with a mullite cover (3%) was significantly shorter than of those with alumina cover (17%).

Table 4. Comparison of sintered density and hardness of CP titanium sintered at 1150°C with mullite and alumina covers, and without cover

Covers	**Sintered density (g/cm^3)**	**Hardness (HRB)**
No cover	4.30	87
Mullite	4.27	90
Alumina	4.28	87

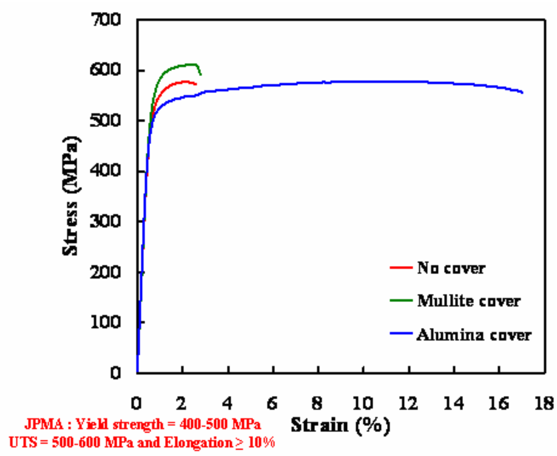
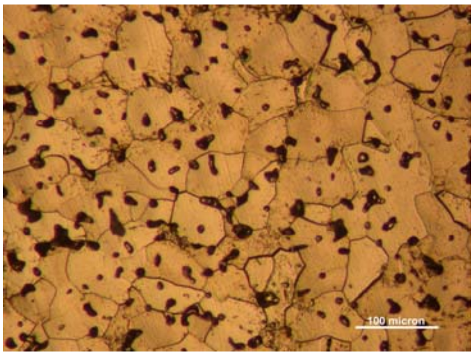
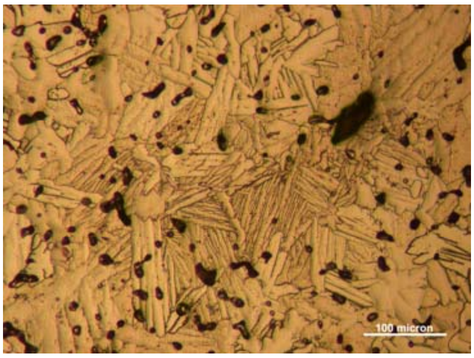


Figure 3. Stress-strain response of CP titanium sintered at 1150°C with mullite and alumina covers, and without cover

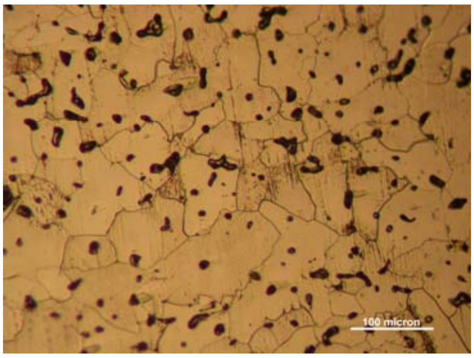
The microstructures of all three specimens are illustrated in Figure4. The level of porosity was similar because they were sintered using the same sintering temperature and this resulted in a similar sintered density as shown in Table 4. However, the microstructure obtained from sintering with a mullite cover was unique. There were several areas that had the Widmanstatten structure, which in titanium had on several occasions been described as the transformed alpha phase. In the other area, where the structure was not Widmanstatten, the microstructure was similar to other cases. The large difference in the elongation to failure is due to the contaminations during sintering.



No cover



Mullite cover



Alumina cover

Figure 4. Microstructures of CP titanium sintered at 1150°C with mullite and alumina covers, and without cover

Figure 5 shows the oxygen and carbon contents of specimens sintered using different covers. The carbon content was slightly different. Parts sintered without cover had the highest carbon content, while parts sintered using a mullite cover had lower carbon contents. The lowest carbon content was observed in parts sintered using an alumina cover. Similarly, the oxygen content is lowest in parts sintered using an alumina cover. Parts sintered without cover and with a mullite cover contained noticeably more oxygen content, which was higher than the minimum limit specified by the JPMA standard. This resulted in a significant small elongation to failure for parts sintered without cover and with a mullite cover, and large elongation to failure for parts sintered with an alumina cover.

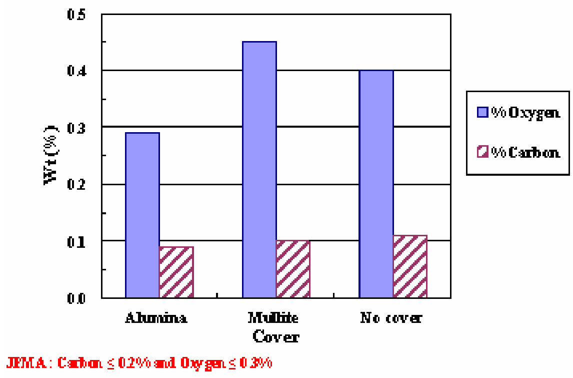
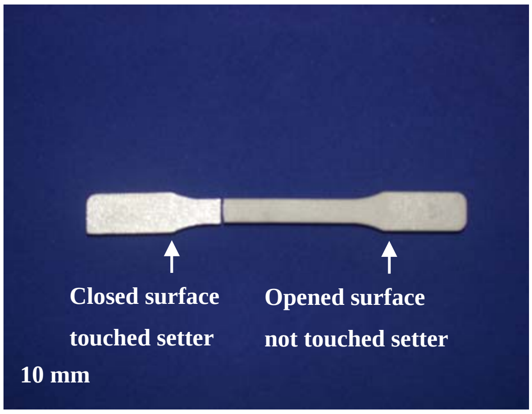


Figure 5. Bulk oxygen and carbon contents of CP titanium sintered at 1150°C with mullite and alumina covers, and without cover

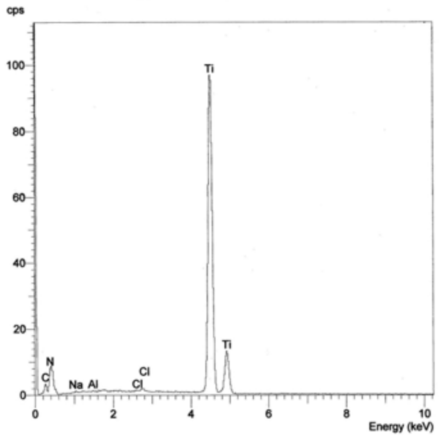
In addition, the contaminations could also be observed from external appearance as shown in Figure 6. Figure 6 displays the photograph of a failed tensile specimen sintered using a mullite cover. The part on the left hand side demonstrates the closed surface that touched the substrate, and the part on the right hand side shows evidence of the open surface that did not touch the substrate. The closed surface has a metallic silver color, was not exposed to atmosphere and had a lower risk of contamination. In contrast, the opened surface was exposed to atmosphere, and was consequently contaminated as can be seen from the dull grey surface.



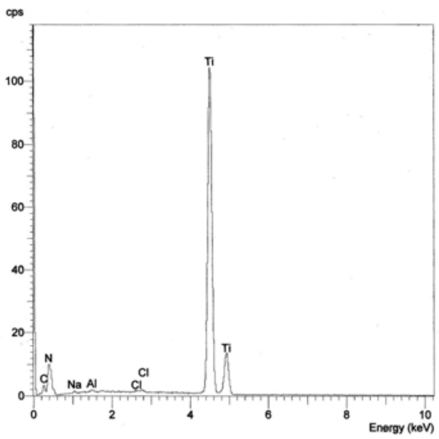
Figur 6. Closed and opened surface of sintered specimen using mullite cover

The energy dispersive spectrometer (EDS) analysis of the scanning electron microscope (SEM) was used to identify the contaminated substances on the surface of the specimens shown in Figure 6. The comparison of EDS results for sintered parts using different covers is shown in Figures 7-9. For specimens sintered using an alumina cover, similar trace elements were found in the titanium matrix of both open and closed surface as shown in Figure 7.

In Figure 8, on the other hand, for specimens sintered using a mullite cover, traces of potassium and silicon were observed on the opened surface, but not on the closed surface. Potassium and silicon contamination resulted from the mullite cover. The mullite cover was not stable at the sintering temperature used (1150°C). The composition of mullite is shown in Table 5. It can be seen that SiO_2 and P_2O_5 from mullite had become unstable and contaminated sintered CP titanium. Figure 9 shows the traces of chromium, iron and copper on both open and closed surface of specimen sintered without cover. However, no traces of potassium and silicon were observed. It is possible that certain amounts of chromium, iron and copper were present in the furnace chamber because the furnace had been used to sinter several grades of stainless steel including 316L and 17-4PH. The reaction of titanium with these contaminated elements originated at the surface and was detrimental to the ductility of the sintered parts. Hence, most mechanical properties remained similar apart from a significantly lower level of elongation to failure.

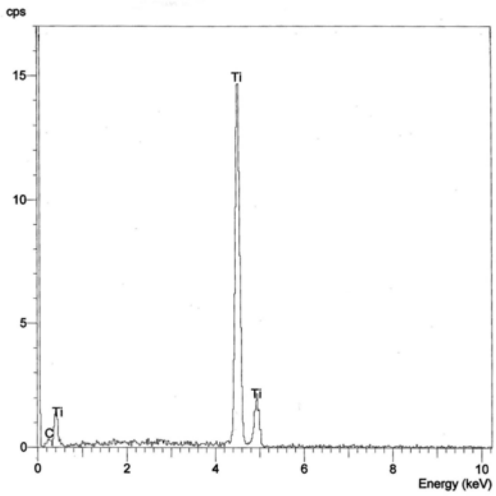


Closed surface touched setter

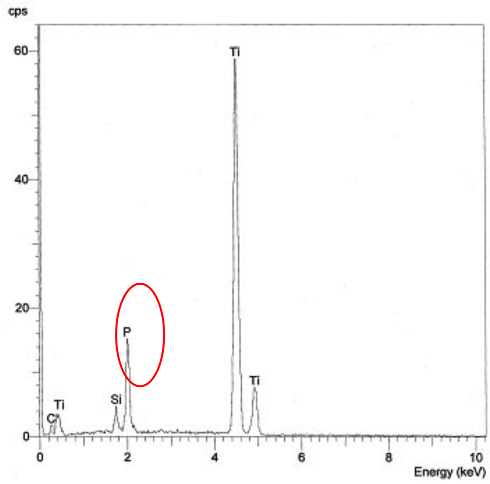


Opened surface not touched setter

Figure 7. EDS analysis of chemical components on the closed and opened surface of sintered specimen using alumina cover



Closed surface touched setter



Opened surface not touched setter

Figure 8. EDS analysis of chemical components on the closed and opened surface of sintered specimen using mullite cover

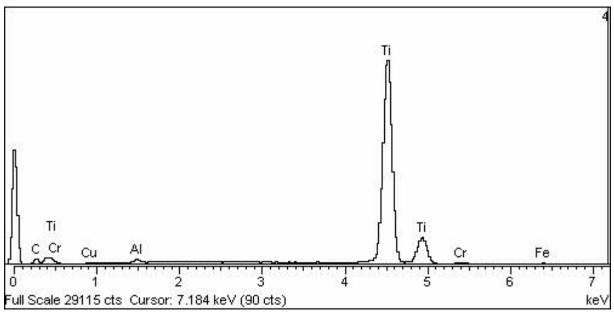


Figure 9. EDS analysis of chemical components on the closed and opened surface of sintered specimen without cover

Table 5. Composition of a mullite cover

Composition (Mass %)									
SiO_2	**Al_2O_3**	**Co_3O_4**	**Fe_2O_3**	**K_2O**	**CaO**	**Na_2O**	**P_2O_5**	**MgO**	**Mn_3O_4**
96	1.53	0.01	0.07	0.76	0.49	0.39	0.20	0.51	0.04

Conclusions

Covering sintered parts could help improve sintering properties of titanium. CP titanium was successfully injected, debinded and sintered. It was sintered at 1150°C and 1250°C in high vacuum using three different covers, which are quartz, mullite and alumna, as well as using no cover for reference. The results show that it is necessary to cover CP titanium during sintering to prevent contamination. The density of parts sintered using all covering conditions were similar. The hardness, the modulus of elasticity, the yield stress and the ultimate tensile stress were also similar. However, the elongation to failure is most sensitive to contamination and the oxygen and carbon contents. Parts sintered using a mullite cover had very poor elongation to failure similar to those using no cover. Parts sintered using a mullite cover were most contaminated because mullite was not stable at the sintering temperature (1150°C). EDS results confirmed that the contaminants were potassium and silicon from the unstable mullite. This resulted in the Widmanstatten structure observed in the parts sintered using a mullite cover. Both quartz and alumina can be used to sinter CP titanium with good elongation to failure. However, alumina is more preferable since it is cheaper and tougher for handling.

References

1. Froes, F. H. and German, R. M. 2004. Titanium powder injection molding (PIM). *Met. Powder Rep.* **55**: 20-23.

2. Froes, F. H., Mashl, S. J., Hebeisen, J. C., Moxson, V. S. and Duz, V. A. 2004. The technologies of titanium powder metallurgy. *J. Miner. Met. Mater. Soc.* **56(11)**:46-48

3. German, R. M. 1996. *Sintering theory and practice.* New York: Wiley.

4. German, R. M. and Bose, A. 1997. *Injection molding of metals and ceramics.* New Jersey: Metal Powder Industries Federation.

5. Leyens, C. and Peter, M. 2003. *Titanium and titanium alloys: fundamentals and applications.* Weinheim: Wiley-VCH.

6. Manonukul, A. 2007. Sintering process optimisation of metal injection moulded pure titanium. In: *Proceeding of International Symposium in Science and Technology*, 31 July – 1 August, Osaka, Kansai University, Japan: 54-59.

7. Chuankrerkkul, N., Messer, P.F. and Davies, H.A. 2007. Powder injection moulding of cemented carbides: Feedstock preparation and injection moulding. *J. Met. Mater. Miner.* **17(1)**:53-57.

8. Takahashi, S., Shimizu, S. and Shimodaira, K. 1999. Method of manufacturing sintered compact. *US Patent 5,911,102.*