

DENSIFICATION OF TITANIUM (Ti) FROM TITANIUM HYDRIDE (TiH₂) POWDER THROUGH DEHYDROGENATION AND PRESSURELESS SINTERING PROCESS

Jimoh, A. ¹, Sigalas, I. ² & Hermann, M. ³

¹Department of Chemical Engineering,
School of Engineering and Engineering Technology,
Federal University of Technology Minna, Nigeria.

²School of Chemical and Metallurgical Engineering,
Faculty of Engineering and the Built Environment,
University of the Witwatersrand.
Private Bag 3, Wits 2050 Johannesburg,
Republic of South Africa.

³IKTS (InstitutKeramischeTechnologien und Systeme, Germany).

*Corresponding author: Engr. Dr. A. Jimoh,
Phone No: +2348139682944;
E-mails: fatai2011@yahoo.com,

Abstract

Dehydrogenation of TiH₂ powder and compact with subsequent pressureless sintering of Ti obtained was successfully carried out in argon controlled atmosphere. A Complete dehydrogenation of TiH₂ powder was achieved at 680°C in 120min using a heating rate of 2°C/min. Lower onset pressureless sintering temperature and early full densification of Ti from TiH₂ were obtained in comparison to commercially obtained Ti powder sintered under the same conditions. This further confirmed the fact that Ti obtained from TiH₂ is of better purity, which subsequently enhanced the level of densification achieved with pressureless sintering process.

Keywords: Titanium, Titanium Hydride, Dehydrogenation, Pressureless sintering, Microstructure.

Introduction

Titanium is a light metal with a melting point of 1668°C, a density of 4.51 g/cm³ (at 293K) and it undergoes a phase transformation from hexagonal close-packed (hcp) to body-centered cubic (bcc) at 882°C (Panigrahi *et al.*, 2005). Titanium together with other group IVB elements exhibit diffusion anomalies and also shows anisotropy in the hcp range (Panigrahi *et al.*, 2005).

Titanium and titanium alloys are used for highly demanding applications such as static and rotating gas turbine engine components and fabrication of some of the most critical and highly-stressed civilian and military aircraft parts (Yamada, 1996). Recent findings show that the use of titanium has expanded to include applications in chemical processing, nuclear power plants, food processing plants, oil refinery, construction of heat exchangers, and in medical prostheses (Leyens and Peters, 2003; Larsson *et al.*, 1996; Seagle, 1996).

These numerous applications of Ti have been attributed to its excellent properties like low density, high specific strength, heat resistance, corrosion resistance, and excellent biocompatibility (Abdallah, 1996; Groszoge *et al.*, 1999; Han *et al.*, 2000; Odwani *et al.*, 1998;

Schmidt *et al.*, 1998; Yu, *et al.*, 1999). Despite these excellent properties, titanium is yet to make a significant breakthrough into the broad field of engineering applications as it is the case with steel and aluminium products. High cost of production had been identified as the major constraint militating against wide industrial application of titanium and its alloys. This high cost of finished Ti products is in part due to the cost of the primary production processes as well as several costly downstream processing steps involved in converting the titanium sponge to usable product forms (Leyens and Peters, 2003; Jackson and Dring, 2006). Besides, the commercially obtained titanium powder also contains impurities that include oxygen, manganese, chlorine, nitrogen, iron, silicon, magnesium etc., which raises fundamental questions on the overall quality (purity) of the final composites.

In a study carried out by Saito (2004), it was pointed out that titanium hydride (TiH_2) powder is more cost-effective and also has very little impurity when compared to commercially obtained hydride-dehydride titanium powder. Bhosle *et al.* (2003) reported in their work that although different titanium hydrides have been reported but the most common phases available include TiH_2 , $\text{TiH}_{1.924}$, TiH , and $\text{TiH}_{0.71}$. They also reported that few research findings on the dehydrogenation of the highest hydrogen-containing titanium phase had shown that the sequence of processes that leads to the formation of Ti is still not completely understood.

The present study therefore attempts to investigate the feasibility of producing Ti powder and products from titanium hydride through dehydrogenation and subsequent densification by using cost-effective pressureless sintering in a controlled argon environment. Comparison of densification and microstructures of commercially obtained titanium and titanium produced from titanium hydride would be carried out.

Materials and Methods

Materials

High purity powder of titanium and titanium hydride obtained from M/S Alfa Aesar (Germany) were used for this investigation. Detailed chemical analysis of the powders as per the manufacturer's specification showed that the titanium powder (99.5% purity, $-44\mu\text{m}$) contained impurities of O = 0.2353wt. %, Fe = 0.033wt. %, C = 0.0093wt. %, N = 0.0183wt. %, P = <0.0023wt. %, S = <0.0013wt. %, Mn, Cl, Si, Mg = 0.013wt. % (each), Na, Al = <0.013wt. % (each) and H = 237ppm. The titanium hydride (99% purity) contained H = 3.7wt. %min, N = 0.3wt. %max. The average particle size distribution of the commercial titanium powder was $d_{10} = 15.672\mu\text{m}$, $d_{50} = 30.492\mu\text{m}$, $d_{90} = 55.166\mu\text{m}$, while that of the titanium hydride powder was $d_{10} = 1.925\mu\text{m}$, $d_{50} = 4.473\mu\text{m}$, $d_{90} = 9.409\mu\text{m}$. The Ti powder used had a larger particle size than the titanium hydride because finer powders were not available and comminution methods not effective due to the ductility of the Ti which makes milling very difficult. The particle morphology of the starting powders are given in figure 1a, b.

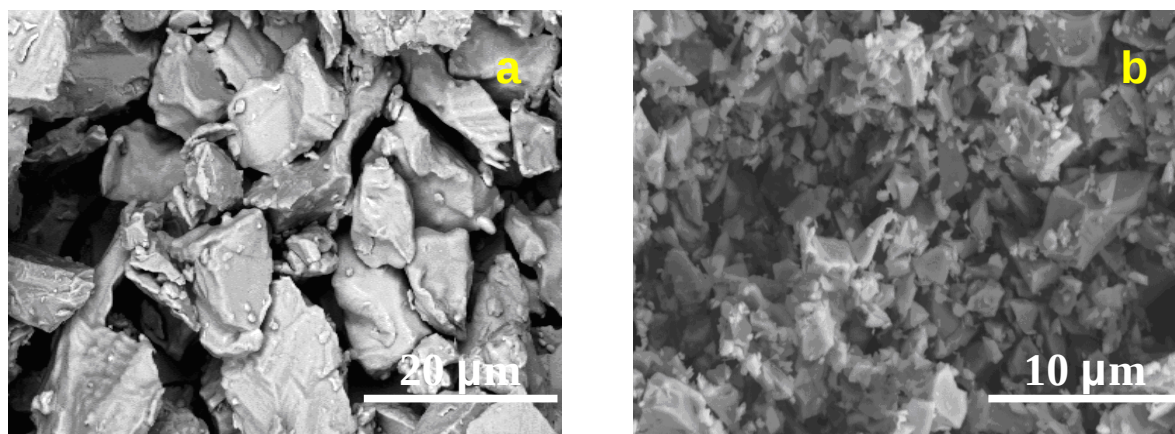


Figure 1: SEM micrograph of (a) commercial powder ($-44\mu\text{m}$) and (b) commercial TiH_2 powder

Methods

Compaction of Powders

Compaction of the commercially obtained Ti and TiH_2 powders was carried out in a uniaxial press using a hardened steel die of 18mm diameter. Cylindrical compacts of about 5mm in height were prepared at pressures up to 393MPa from the two powders.

Pressureless Sintering of Compacts

Compacts produced from commercial titanium powder were pressureless sintered at temperatures ranging from 750°C to 1400°C in an alumina tube furnace. The sintering was carried out in a tube furnace preceded by an oxygen getter furnace with a glass bubbler at the other end. The oxygen getter furnace was packed with copper turnings which were kept at 700°C . The compacts were heated at a rate of $6^\circ\text{C}/\text{min}$ to a fixed sintering temperature, maintained at this temperature for 90min and allowed to cool to ambient temperature under argon at a cooling rate of $6^\circ\text{C}/\text{min}$. The compact was placed on a zirconia tray surrounded by alumina boats containing commercially pure titanium on either side in order to avoid oxidation from any untrapped oxygen in the inert gas from the oxygen getter furnace. The ends of the alumina tube were sealed using brass fittings with rubber viton o-rings. The gas tightness of the seals was checked using a gas sniffer leak detector to detect any gas leaks.

In the case of titanium hydride, the compacts were subjected to two heat treatment processes, dehydrogenation and pressureless sintering. The dehydrogenation process was carried out by heating the compact to a temperature of 715°C at a rate of $2^\circ\text{C}/\text{min}$ in Argon stream. This temperature was maintained for 120min and afterwards the sample was allowed to cool to ambient temperature under argon at a cooling rate of $6^\circ\text{C}/\text{min}$. Sintering was also carried out immediately after dehydrogenation. The temperature was ramped up to the sintering temperature at a rate of $6^\circ\text{C}/\text{min}$, maintained for 90min and allowed to cool to ambient at a rate of $6^\circ\text{C}/\text{min}$. A stream of Argon was used to protect the compacts from oxidation during the sintering process.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) analyses of the powders and sintered samples were carried out using a Philips PW1710 diffractometer with monochromatic Cu K α - radiation at 40 kV and 20 mA.

Diffraction patterns were collected over a range of 2θ angles between 10° and 80° with a step size of 0.02° .

Scanning Electron Microscopy (SEM/EDX) Analysis

SEM/EDS analyses of the powders and sintered samples were carried out using A LEO 1525 FE-SEM Scanning Electron Microscope coupled to an Oxford Link Pentafet Energy Dispersive X-ray (EDS) spectrometer in the SE2 secondary mode. Sintered samples for optical microscopy (OM) and SEM/EDS analyses were prepared using conventional grinding and mechanical polishing techniques. The polished samples were etched in Kroll's reagent (composition: 1–3 ml HF, 2–6 ml HNO_3 , 100 ml water). Density was determined using the Archimedes technique.

Results and Discussion

Compaction curves for both powders were generated and compared as shown in Figure 2. In terms of the green relative densities, the compaction curves of Ti and TiH_2 show that the commercial Ti compacted better than TiH_2 powder. For the purpose of heat treatment, powder samples were compacted at 393 MPa and these resulted to green densities of 79.3 and 72.1% theoretical for commercial Ti and TiH_2 powder respectively.

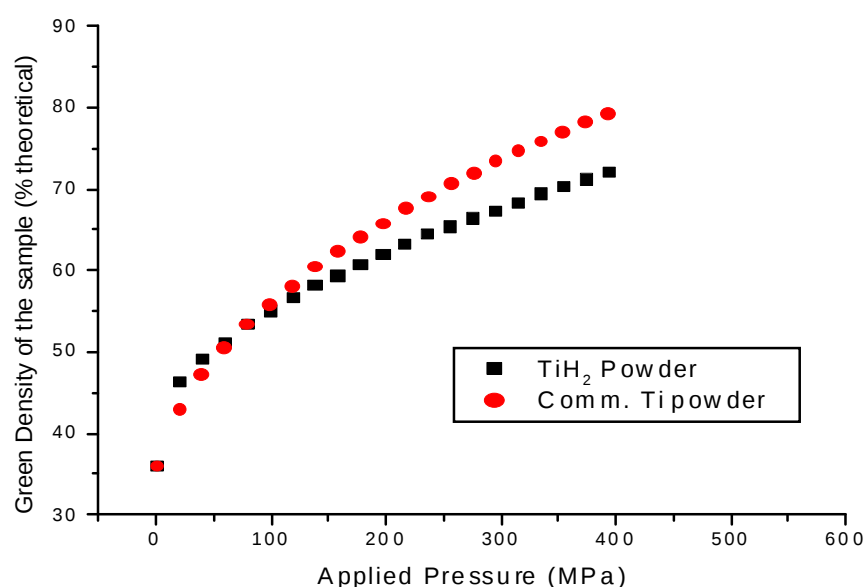


Figure 2: Compaction graph of commercial TiH_2 and Ti powders.

Porosity generated in the green compact is obtained by subtracting the value of green relative density from 100%. It can be seen from figure 2 that although the value of porosity generated in the titanium hydride green compact is low but not lower than that of Ti green compact as was reported by Robertson and Schaffer (2009). However, the relatively high green density, 72.12%, achieved by green compact from Ti hydride may be attributed to the fragmentation of hydride particles (Adamset *al.*, 2008; Ivasishin *et al.*, 2005; Ivasishin *et al.*, 2007) and reduced cold welding between hydride particles that allowed more particles rearrangement (Bhosle *et al.*, 2003). The low green porosity recorded in the Ti hydride compact is suspected to have also contributed to the observed increase in the sintered density (Table 1) of pressureless sintered TiH_2 compacts as would be shown later.

The pressure required to eject the green compact from the die was significantly higher for the Ti powders than for the hydride powders. After compaction at 393MPa, the average of maximum ejection pressure for each compact was 88MPa for Ti and 13MPa for Ti hydride. These results suggest that there is a greatly reduced friction and cold welding to the die wall for hydride powder than for the Ti metal powder. This could be attributed to the effect of low particles deformability of the Ti hydride. Reduced cold welding could also be responsible for the lower strength of green Ti hydride compact as was observed during the ejection of the compacts from the die with evidence of broken corners (Figure 3) even at higher compaction pressures (>393MPa).



Figure 3: Macrograph of green compact from TiH_2 powder with broken corners at higher compaction pressure (>393MPa).

Dehydrogenation was carried out using both loose powder and compacts from Ti hydride over temperature range of 450 to 715°C using DTA/TGA literature data (Bhosle *et al.*, 2003; Sandimet *al.*, 2005) in argon controlled tube furnace. Analyses from the present investigation revealed that the conversion of TiH_2 to Ti is a two-step transformation in the sequence: $\text{TiH}_2 \rightarrow \text{TiH}_x \rightarrow \text{Ti}$, where TiH_x is an intermediate confirmed through XRD analysis to be TiH. This is in agreement with the report of Bhosle *et al.* (2003). Further analyses of XRD results and the mass loss during dehydrogenation process indicated that the stoichiometry of the starting Ti hydride is TiH_2 . Mass loss due to the release of hydrogen from TiH_2 was effectively completed for the loose Ti hydride powder at 680°C and at 715°C for Ti hydride compact using the same heating rate of 2°C/min over a period of 120min to form α -Ti. The low pore volume for diffusion of hydrogen of Ti hydride powder particles and reduction in the surface area resulting from compaction could possibly be responsible for the observed retardation and consequent higher temperatures for the dehydrogenation of green compact. This observation agreed with the report of Bhosle *et al.* (2003) however, the temperature where complete dehydrogenation was achieved for both Ti hydride powder and compact is lower in this study compared to theirs of 700 and 800°C respectively. The only reason that may be attributed to this behaviour is the lower heating rate of 2°C/min used in the present study as against 20°C/min and 5°C/min used by Bhosle *et al.* (2003) and Sandimet *al.* (2005) respectively. This however, confirmed the report of Sandimet *al.* (2005) that the lower the heating rates the lower is the onset temperature for dehydrogenation.

The green pellets produced from commercial titanium were subjected to pressureless sintering at different temperatures while pellets of titanium hydride were similarly subjected to heat treatment under the same condition to simultaneously achieve hydrogen removal and densification by pressureless sintering. Both TiH_2 and Ti compacts were pressureless sintered at temperatures between 750°C and 1400°C in argon controlled atmosphere. Summary of the densities obtained for the various sintered materials are given in Table 1.

It can be seen from these results that sintered density increases with increasing sintering temperature (Figure 4). Densification of commercial titanium through pressureless sintering was only noticed at sintering temperatures starting from 1000°C (Figure. 4), this is in a total agreement with the findings of Panigrahi *et al.* (2007). The TiH_2 based materials began to densify at sintering temperature as low as 750°C (Table1, Fig. 4), which indicates that Ti produced from TiH_2 has a better sinterability in comparison to the commercially obtained Ti powder. For example, sinteredTi hydride compact achieved 86.70% relative density (with theoretical density of 4.51g/cm^3) at 750°C and also recorded a 100% relative density at 1200°C , 1300°C and 1400°C respectively compared to 95.34% relative density recorded by commercial Ti compact that was sintered at 1400°C (Figure 4).

Table 1: Density and phase composition of pressureless sintered samples of commercial Ti and Ti from commercial TiH_2 at an Isothermal sintering time of 90min

Sample (Green Compact)	Sintering temperature	Green density (%)	Sintered density (g/cm^3)	% Theoretical density	Phase composition
Commercial TiH_2	750°C	72.1	3.91	86.70	Ti, Ni
Commercial TiH_2	800°C	72.1	4.02	89.14	Ti, Ni
Commercial TiH_2	900°C	72.1	4.17	92.25	Ti, Ni
Commercial TiH_2	1000°C	72.1	4.41	97.78	Ti, Ni
Commercial Ti	1000°C	79.3	3.67	81.37	Ti
Commercial TiH_2	1100°C	72.1	4.49	99.56	Ti
Commercial Ti	1100°C	79.3	4.01	88.91	Ti
Commercial TiH_2	1200°C	72.1	4.51	100	Ti
Commercial Ti	1200°C	79.3	4.18	92.68	Ti
Commercial TiH_2	1300°C	72.1	4.54	100	Ti
Commercial Ti	1300°C	79.3	4.28	94.90	Ti
Commercial TiH_2	1400°C	72.1	4.54	100	Ti
Commercial Ti	1400°C	79.3	4.30	95.34	Ti

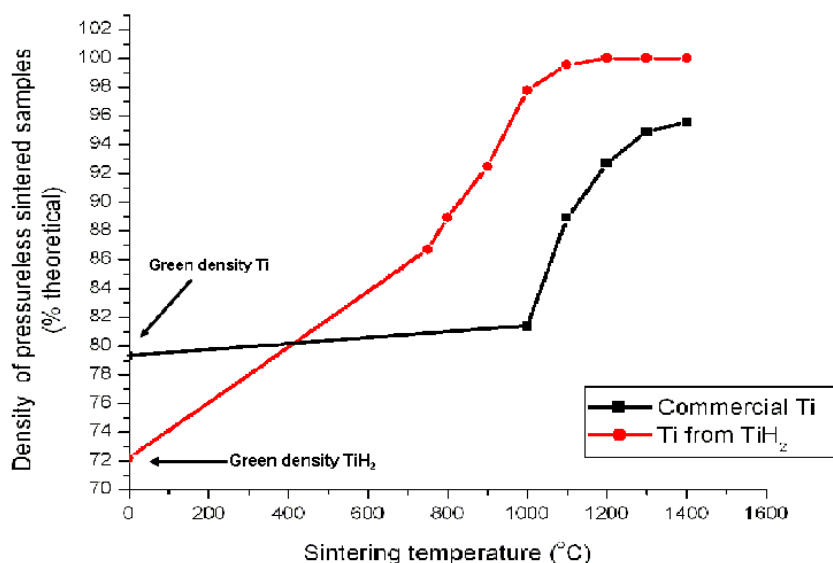


Figure 4: Relative density of pressureless sintered samples of commercially obtained Tipowder (44µm) and of Ti obtained from TiH₂ against sintering temperatures

The more rapid densification of TiH₂ compacts (as shown in figure 4) despite the observed lower green density relative to commercial Ti compacts could be attributed to lower grain size of TiH₂, as well as enhanced mobility of Ti atoms resulting from more vacant active sites created after hydrogen removal. Fragmentation of hydride particles during compaction as reported by Bhosle *et al.* (2003) and Robertson and Schaffer (2009) could probably make an additional contribution.

More so, the present study achieved a density of 3.91g/cm³ at 750°C for sintering time of 90min while Bhosle *et al.* (2003) that used nanoscale particles under vacuum recorded a density of 4.48 g/cm³ at the same temperature but in a sintering time of 120min. The difference in densities could probably be as result of nanoscale particles and longer sintering time used. At 1400°C, a higher and better sintered density of 4.54g/cm³ (100% relative density) was achieved with very insignificant porosity but no swelling compared to sintered relative density of 88.2% with swelling observed by Robertson and Schaffer (2009).

Figure 5 shows the X-ray diffraction patterns of starting TiH₂ based material and that of Ti obtained from TiH₂ at different temperatures of room temperature (RT), 680°C, 750°C, 1000°C, 1200°C, and 1400°C respectively. XRD analysis and weight change measurement indicate that within the temperature range considered, all compact samples heat treated below 715°C contained TiH₂ and TiH. On the other hand, samples heat treated at 715°C and above during 120min dwelling time were free of TiH₂ and TiH with XRD only showing the presence of Ti metal and a very insignificant single peak of Ni as impurity. All observed peaks of the heat treated samples can be matched with single phase α-Ti phase (00-044-1294, ICSD data base) as observed for material produced from the commercial Ti powder.

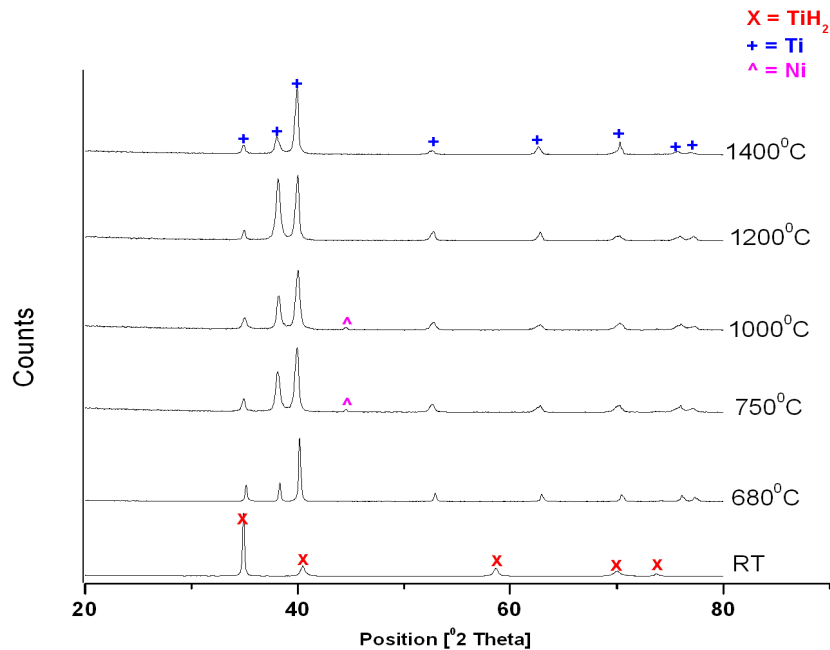


Figure 5: XRD patterns of dehydrogenated and pressureless sintered TiH_2 powder and compacts at various sintering temperatures.

Figure 6 shows the SEM micrographs of the pressureless sintered samples produced from TiH_2 at different sintering temperatures. The SEM micrographs show clearly the evolution of porosity and the grain growth that took place at 750, 900, 1000, 1200 and 1400°C respectively. All the EDS analysis of the sintered samples confirmed the presence of only Ti without any observed foreign constituent, thus indicating that there were less than the detection limit impurities in the samples produced. Figure 6f shows the etched microstructure of Ti produced from TiH_2 powder with basket weave structure and an average grain size of 20 μm .

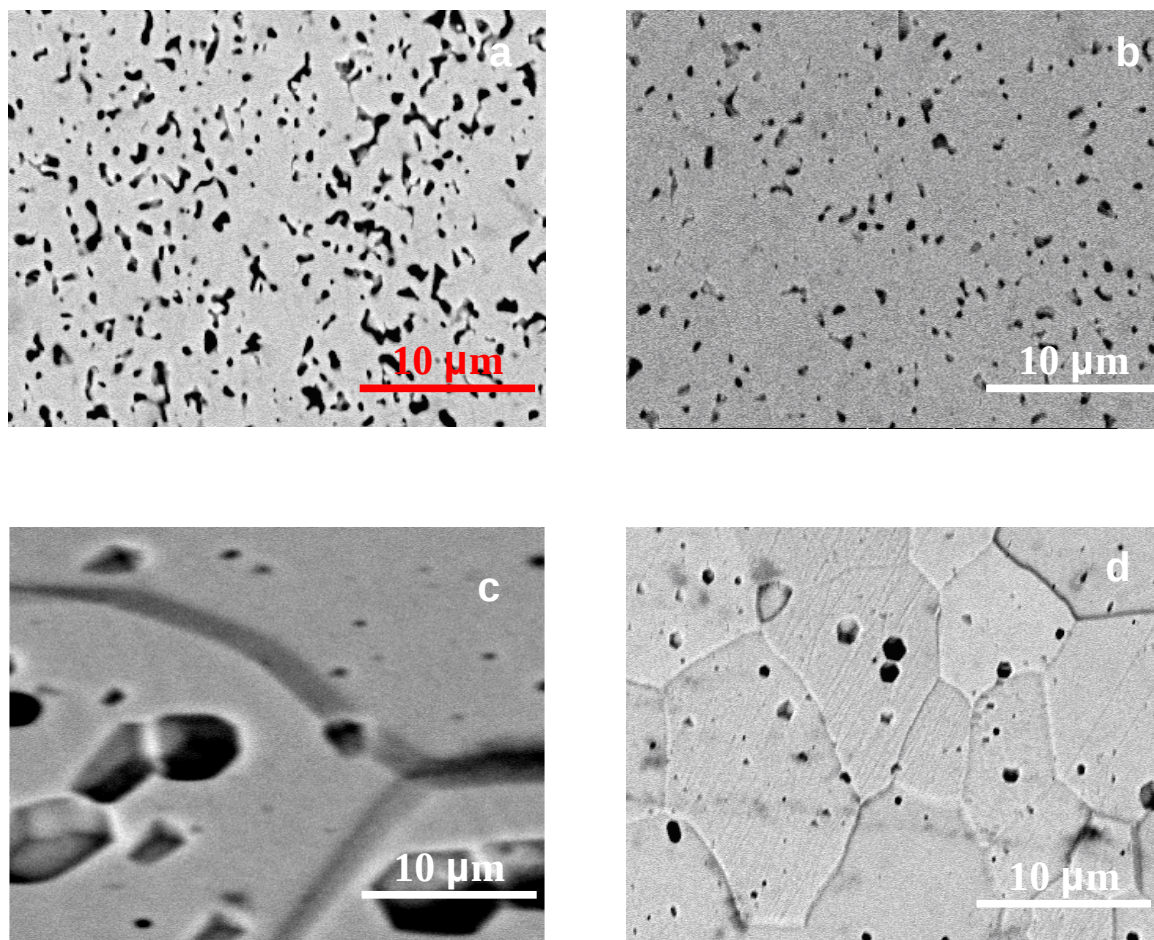


Figure 6: SEM micrographs of the sintered TiH_2 (a) at 750°C, (b) at 900°C, (c) at 1000°C and (d) at 1200°C

Figure 6(continuation): SEM micrographs of the sintered TiH_2 (e) at 1400°C (f) light micrograph of etched sintered Ti obtained from TiH_2 at 1400°C; sintered commercial Ti (g) at 1200°C and (h) at 1400°C.

Conclusion

Titanium hydride powder was completely dehydrogenated and converted to Ti in argon controlled atmosphere at 680°C with a heating rate of 2°C/min after 120min. Titanium produced from the TiH_2 compact was pressureless sintered in an alumina tube furnace under argon controlled atmosphere and the densification results show a better performance compared to commercially obtained titanium that was sintered using the same technique and conditions. This results further show that Ti produced from TiH_2 possesses a better sintering behaviour than the commercial titanium powders. The reduction of the sintering temperature in comparison to the commercial powder was more than 200°C.

References

Abdallah, M. M. (1996). Corrosion of titanium and zinc alloy in Dead Sea water, anti-corrosion methods. *Journal of Mater.* 43 (1), 17–22.

- Adams, J., Duz, V. & Moxson, V. (2008). Powder metallurgy processes for producing titanium alloy products from hydrogenated titanium powder, proceedings. TMS2008: *Journal of Materials Processing and Properties*, 1, 363-367.
- Bhosle, V., Baruraj, E. G., Miranova, M. & Salama, K. (2003). Dehydrogenation of Nanocrystalline TiH_2 and consequent consolidation to form Dense Ti. *Journal of Metallurgical and Materials Transactions A*, 34A, 2793-2799.
- Grosgogeat, B., Reclaru, L., Lissac, M. & Dalard, F. (1999). Measurement and evaluation of galvanic corrosion between titanium/Ti-6Al-4V implants and Dental alloys by electrochemical techniques and auger spectrometry. *Journal of Biomaterials* 20, 933-941.
- Han, Z., Zhao, H., Chen, X.F. & Lin, H. C. (2000). Corrosion behaviour of Ti-6Al-4V alloy welded by scanning electron beam. *Journal of Mater. Sci. Eng. A277*, 38-45.
- Ivasishin, O.M., Savvakina, D.G., Bielov, I.S., Moxson, V.S., Duz, V.A., Davies, R. & Lavender, C. (2005). Microstructure and properties of titanium alloys synthesized from hydrogenated titanium powders. *Journal of Materials Science and Technology*, 4, 51-158.
- Ivasishin, O. M., Savvakina, D. G., Moxson, V. S., Duz, V. A. & Lavender, C. (2007). Proc. Cong. on 'Ti-2007 science and technology', Kyoto, Japan, 2007, *The Japan Institute of Metals*, 757-760.
- Jackson, M. & Dring, K. (2006). A review of advances in processing and metallurgy of titanium alloys. *Journal of Material Science and Technology*, 22(8), 881-887.
- Larsson, C., Thomsen, P., Aronsson, B., Rodahl, M., Lausmaa, J. & Kasemo, B. (1996). Bone response to surface-modified titanium implants: studies on the early tissue response to machined and electropolished implants with different oxide thicknesses. *Journal of Biomaterials*, 17, 605-10.
- Leyens, C. & Peters, M. (2003). Titanium and Titanium alloys: Fundamentals and Applications. Germany: WILEY-VCH Verlag GmbH and Co KGaA, ISBN 3-527-30530-5, pp. 34-43.
- Odwani, A. A., Tabatabaei, M. A. & Nabi, A. A. (1998). Performance of high chromium stainless steels and titanium alloys in Arabian Gulf seawater desalination. *Journal of Electrochem. Soc.* 120, 78-81.
- Panigrahi, B. B. (2007). Sintering behaviour of Ti-2Ni and Ti-5Ni elemental powders. *Journal of Material Letters* 6, pp. 152-155.
- Panigrahi, B.B., Godkhindi, M.M., Dasa, K., Mukunda, P.G. & Ramakrishnan, P. (2005). Sintering kinetics of micrometric titanium powder. *Journal of Materials Science and Engineering A* 396, pp. 255-262.

- Robertson, I. M. & Schaffer, G. B. (2009). *Comparison of sintering of titanium and titanium hydride powders*. Institute of Materials, Minerals and Mining, published by Maney, pp. 1-9.
- Saito, T. (2004). The automotive application of discontinuously reinforced TiB-Ti composite. *JOM*, pp33.
- Sandim, H. R. Z, Morante, B. V. & Suzuki, P. A. (2005). Kinetics of thermal decomposition of titanium hydride powder using in-situ high-temperature X-ray diffraction (HTXRD). *Journal of Materials Research*, 8(3), 293-297.
- Schmidt, H., Konetschny, C. & Fink, U. (1998). Electrochemical behaviour of ion implanted Ti-6Al-4V in ringer's solution. *Journal of Mater Science Technology*, 14, 592-598.
- Seagle, S. R. (1996). The state of the USA titanium industry in 1995. *Journal of Mater Science Engineering*, A213, pp. 1-7.
- Yamada, M. (1996). An overview on the development of titanium alloys for non- aerospace application in Japan. *Journal of Mater Science Engineering. A* 213, 8-15.
- Yu, S. Y., Brodrick, C. W., Ryan, M. P. & Scully, J. R. (1999). Effects of Nb and Zr alloying additions on the activation behaviour of Ti in hydrochloric acid, *Journal Electrochem. Soc.* 146 (12), 4429-4438.