



# Production of titanium metal powder by the HDH process

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## Synopsis

Laboratory-scale tests were conducted at Mintek for the production of titanium powder from particulate Kroll sponge by the hydrogenation-dehydrogenation (HDH) process. The aim of this work was to produce titanium powder for powder metallurgical consolidations. The work involved the production of titanium powder at optimized conditions, which included hydrogenation in a horizontal tube furnace at 600°C for 2 hours, milling using planetary and roller mills, and dehydrogenation in a vacuumed retort fitted in a muffle furnace running at 700°C for 36 hours. The titanium powder produced in this project matched the elemental specifications of commercially available titanium powder, except for high carbon content. Nevertheless, the powder has been tested further in mechanical alloying and has been found suitable for the production of powder metallurgical compacts.

## Keywords

Powder metallurgy, titanium components, HDH process, ball milling.

## Introduction

Mintek, specialists in mineral and metallurgical technology, are involved in various research and development work for advanced materials, including the extraction and alloying metallurgy of titanium metal. Titanium metal and allied alloys have been a subject of research globally due to their important role in current industrial applications and the projected increase in their demand in the near future. The extraction, transformation and machining of titanium metal is quite challenging from the perspective of purity (contamination), safety hazards and costs. Mintek has extensive experience in handling reactive metals, including metal vapours and powders. This paper describes the experience gained in the production of titanium metal powder by the HDH process.

## Background

Titanium is a metallic transition element. It is the fourth most abundant structural metal. It falls in the category of light elements. Titanium can easily be alloyed with other widely used elements such as iron and aluminium.

Currently, most of the titanium is commercially produced as sponge by reducing titanium tetrachloride with magnesium in what is known as the Kroll process (named after William Kroll, who invented the process in 1946)<sup>1</sup>.

The major markets for titanium include commercial aerospace, defence, industrial, medical, domestic, and emerging applications. Near-net shape processes such as casting and powder metallurgy are the most common processes used to prepare titanium metal for these applications. Titanium ingot can also be used at a cost. Moreover, the ingot cannot be used directly due to its poor machining or fabrication properties. Casting operations are costly and result in relatively high yield losses. The sources of high cost in casting include the labour intensive induction melting electrode preparation, multiple melt sequence and intermediate and final conditioning. Hence alternative sponge preparation processes such as powder metallurgy are a subject of intensive investigations<sup>1</sup>.

In powder metallurgy, titanium metal powders are produced, further compacted and sintered to form useful products for various sectors<sup>1</sup>. There are two basic approaches used to produce titanium alloy powders; i.e., pre-alloyed and blended elemental methods. The former approach uses ready-mixed alloy components prior to subsequent alloying. This approach has a higher cost<sup>2,3</sup>.

However, the blended elemental approach uses pure titanium and other alloy components or a master alloy (e.g. 60:40 Al:V) to produce the useful Ti-6Al-4V alloy. This approach is relatively cheaper and results in competitive alloys. Moreover, this approach is open to the incorporation of reinforcing particles into the

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titanium powder prior to making the subsequent components<sup>2,3</sup>. The main sources of titanium powder for the blended elemental approach are the sponge product of the Kroll magnesium process and titanium scrap. Adversely, the surface of the titanium scrap is generally contaminated with grease, lubricating oil and/ or oxide film which may be transferred to the subsequent titanium powder. Hence additional processing stages are established to eliminate these sources of contamination, thereby increasing the cost of the process. The primary product purity is vital to subsequent alloy performance and the preservation of economic viability of the process is equally important; hence titanium powder for use in the blended elemental approach is mainly produced from titanium sponge<sup>1</sup>.

In general, there are a number of important characteristics that a titanium powder must have to facilitate powder metallurgical consolidation. Firstly, the powder needs to be relatively fine. This ensures a high packing density, thereby decreasing porosity. This also assists in developing strong bonds during sintering, thereby increasing strength. The finer the powder, the higher the final density and the stronger the component<sup>1,4</sup>. Secondly, the particles of the powder should be semi-spherical. Some angularity on particles can assist packing and sintering, but above a certain point angularity becomes counter-effective<sup>1</sup>. The particles may have only specific surface coatings or alterations as this may significantly affect the strength of the final components<sup>1,5</sup>. Finally, it is important that the particles are compositionally homogeneous because in the case of alloy powders, heterogeneity may compromise the benefit introduced by using an alloy<sup>1</sup>.

### Basis of the current work

The processes used to prepare pure titanium powder for the blended elemental approach include chemical reduction (reduction of  $\text{TiO}_2$  by Mg), gas atomization, mechanical alloying, plasma-rotating electrode (PREP) and hydrogenation—dehydrogenation (HDH). Among these processes, gas atomization, PREP and HDH are the most common<sup>1</sup>. The powder produced by gas atomization is spherical in shape and has a particle size distribution (PSD) range of 50 to 300  $\mu\text{m}$  which is globally competitive<sup>1</sup>. However, the process set-up is relatively complicated. On the other hand, the powder produced by the PREP process is spherical and has a PSD range of 100 to 300  $\mu\text{m}$ . This powder has good flowing and packing properties and is thus ideal for high quality near net shapes<sup>1</sup>. However, it is relatively expensive.

The current project followed the HDH process. The main objective of this work was to produce titanium powder for powder metallurgical consolidation to make titanium components by blended elemental approach. With titanium,

as with other group IV elements, it is possible to introduce large quantities of hydrogen at elevated temperatures. Hydrogen reacts with titanium to form titanium hydride ( $\text{TiH}_2$ ) which is brittle and can be milled easily.  $\text{TiH}_2$  may contain a hydrogen content of 3.5% to 4.5% by weight<sup>1,7,8,9</sup>.

For milling the brittle  $\text{TiH}_2$ , among the options such as ball milling, jet milling and wet milling, the dry ball milling with an argon gas blanket was found to be the most appropriate. It is simple and efficient to operate a mill in this configuration, allowing for easy variation in test conditions and resulting in great flexibility in powder products. In addition, ball mills tend to produce a milled product with a large variation in particle size.

After sizing  $\text{TiH}_2$ , the interstitial hydrogen is subsequently removed using a vacuum heat treatment (vacuum is used to eliminate the reaction of titanium with oxygen and nitrogen) to produce titanium metal powder<sup>1,9</sup>. When compared to other powder production methods, the HDH process can introduce higher levels of contaminants and makes the final powder less suitable for use in critical aerospace applications<sup>1</sup>. However, the ease with which the process set-up is made makes it particularly well suited for preparing powders for the current work. In addition, milling of sponge via the HDH process gives much more flexibility in manipulating the PSD of the powder, an important consideration in the subsequent powder metallurgical consolidation<sup>1,7,8,9</sup>. In order to benchmark the Ti powder to be produced, a survey of various commercially available Ti powder was conducted; the typical chemical composition of commercial titanium powder is given in

Table I<sup>1</sup>.

Both titanium hydride and titanium metal in fine powder form are highly explosive. It is important to avoid any condition that tends to suspend particles in the air. Precautions should also be taken to prevent the build-up of static electricity or the creation of sparks. It is mandatory to introduce an inert atmosphere of argon where dust clouds are likely to form. Nitrogen cannot be used because it reacts with titanium to form titanium nitride<sup>11</sup>. A hazard and operability (HAZOP) study was also conducted to identify and evaluate other potential personal and environmental risks associated with the envisaged experimental equipment layout. The results of this study showed that milled  $\text{TiH}_2$  and titanium metal should be handled in an argon-filled glove box, whenever possible, to respond to the safety risks associated with fine powder of titanium hydride and titanium metal. The content of oxygen in the glove box should be maintained below 5% to eliminate the potential hazards.

### Experimental approach

This section gives a summary of the experimental equipment and work procedures.

Table I

#### Typical chemical composition of commercial titanium powders (mass %)

	Fe	H	C	N	O	Applications
Titanium powder	0.20–0.50	0.01	0.08	0.03–0.05	0.18–0.40	Industrial applications

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### Materials and samples

Titanium sponge produced by the Kroll process was supplied by Insimbi Alloy Suppliers Ltd. (Pty). The Kroll sponge was in a particulate form with a top size of less than 3 mm. The sample was subjected to chemical analysis to assess the content of the minor elements—results are summarized in Table II. Mg, Cr, Fe, Co, and Ni in various titanium samples were determined by a ‘Spectro citros vision’ model of inductively coupled plasma optical emission spectrometer (ICP-OES). For the determination of carbon, a combustion LECO technique in CS-200 determinator model was employed. Nitrogen and oxygen were determined by an ELTRA ON900 O-N determinator. The chlorides were determined by an ultraviolet spectrophotometer (UV)—a DR Lange CADAS 50 s model. Hydrogen content in TiH<sub>2</sub> and dehydrogenated powder was determined, at Bruker, by a G8 GALILEO analyser.

The morphological and phase chemical compositions of various titanium samples were determined by Joel 840 scanning electron microscopy (SEM) and Siemens D500 X-ray powder diffraction (XRD) instruments, respectively. PSD analysis of the milled hydrogenated titanium sponge was done using a Malvern Mastersizer® 2000.

### Titanium metal powder production

The flow diagram of the HDH process for the production of

pure titanium powder is presented in Figure 1. As shown in the flow diagram, the HDH process is used to convert the titanium sponge to titanium powder.

### Hydrogenation process

Discrete masses of 15 g of the titanium sponge were weighed in respective sample boats and placed at the centre of a 25 mm diameter quartz tube reactor in a horizontal tube furnace. Two sample boats were processed in each run, making a total mass of 30 g per run. A high purity 75 mm alumina tube reactor was also used where an amount of 150 g of titanium sponge material was placed directly in the reactor. The inlet of the quartz or alumina tube was connected to a mass flow controller which was used to control the amount of gas (argon and hydrogen) passing through the reaction tube. The outlet of the reactor was connected to a heating organic oil (bubbler) to ensure that the system was sealed and that the small surplus hydrogen was not emitted directly to the atmosphere. The schematic drawing of the equipment set-up is shown in Figure 2.

The reactor tube was purged with argon during the initial heat up period prior to the hydrogen blow. At the end of the set hydrogenation period, the system was cooled down to room temperature in argon atmosphere. The hydrogenated sample was removed from the tube furnace and weighed and the mass recorded.

Table II  
Chemical composition of the ‘as received’ titanium sponge (Mass %)

	Mg	Cr	Fe	Co	Ni	C	N	O	Cl
Ti sponge	0.07	0.13	0.44	0.16	0.07	0.03	0.01	0.24	0.81

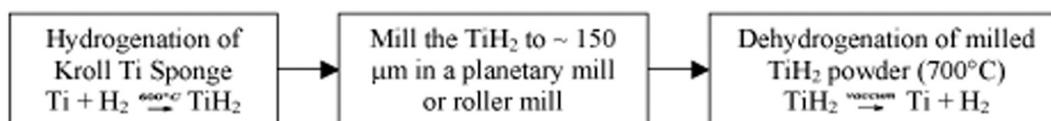


Figure 1—Flow diagram of HDH process for titanium powder production from sponge

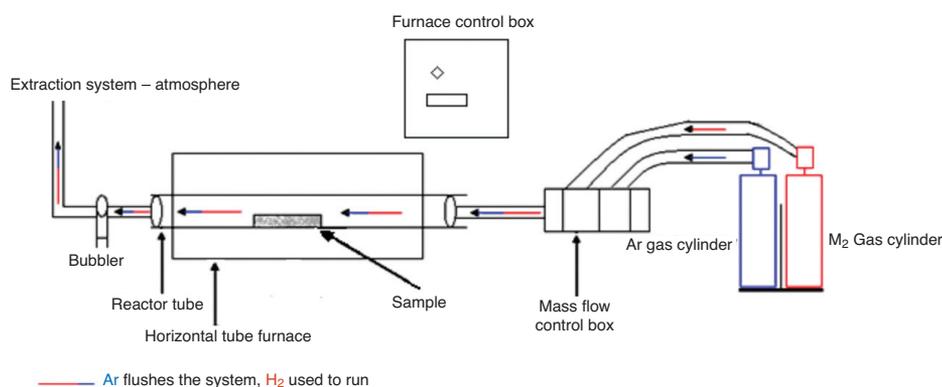


Figure 2—Schematic drawing of a horizontal tube furnace

## Production of titanium metal powder by the HDH process

During the optimization of the parameters of the hydrogenation process, the temperature was varied between 300°C and 800°C, and the reaction time was varied between 1 hour and 4 hours. The established optimum conditions for the hydrogenation of titanium sponge involve heating for 2 hours at a temperature of 600°C in a flow of about 1572 ml/min hydrogen through the sponge in a tube furnace.

### Milling of the hydrogenated material

The hydrogenated material was milled in order to get a fine powder of a particle size range of 100 µm to 1 µm. In the initial experiments, a RETSCH planetary mill (PM 100 model) filled with hardened 10 mm steel balls was used. The filling of TiH<sub>2</sub> into and subsequent sealing of a milling jar was conducted in an argon-filled glove box. The atmosphere in the glove box was maintained at an oxygen level of less than 5%.

The sealed milling jar was placed in a planetary mill as shown in Figure 3. The process involves milling a 50 g particulate TiH<sub>2</sub> in a mill operating at optimal speed and filled with 100 × 10 mm steel balls.

For the optimization of the milling conditions, the milling time was varied between 5 and 30 minutes, and the mill rotation speed was varied between 300 and 500 rpm. The established optimum operating conditions of the planetary mill involve milling a 50 g particulate TiH<sub>2</sub> with 100 × 10 mm steel balls, running at 500 rpm for 10 minutes (reverse rotation switched on—stops after first 5 minutes for a minute and changes direction of rotation for the last 5 minutes). The optimum ball-to-powder ratio was 8.34.

A roller (tumbling) ball mill, designed and fabricated by Mintek, was also used to mill the TiH<sub>2</sub>. A photographic representation of the roller mill is shown in Figure 4 (a and b). In this experiment, the roller mill jar containing 540 × 10 mm and 60 × 20 mm hardened steel balls and filled with 500 g of TiH<sub>2</sub> was purged with argon for about 15 minutes to remove the traces of oxygen prior to the milling process. The mill was run at an optimal speed of 71 rpm (75% critical speed) at various time periods.

The established optimum conditions for this larger-scale milling involved milling 500 g of TiH<sub>2</sub>, with 540 × 10 mm and 60 × 20 mm hardened steel balls, running at 71 rpm (75% critical speed) for 10 minutes. The optimum ball-to-powder ratio was 8.49.



Figure 3—Sealed milling jar in a RETSCH planetary mill

### Dehydrogenation of the TiH<sub>2</sub> powders

The TiH<sub>2</sub> powders after milling with planetary and roller mills were dehydrogenated to get the respective final titanium powders. The milling jar of the planetary mill was removed and discharged in a sample container within the glove box purged with argon to ensure an environment oxygen level of below 5%. In this process, the jar was opened and the powder was cautiously (avoiding creating sparks) transferred into a labelled sample container using antistatic brushes. The sample was fed from the container into a retort outside the glove box (because the retort could not fit into the glove box). The retort was then sealed to ensure minimal exposure to atmospheric oxygen. The sealed retort connected to a vacuum pump system was placed in a muffle furnace.

In the case of the roller mill, the powder was directly transferred into the retort, as shown in Figure 5. The arrangement allows for milling of the material under a protective argon atmosphere, followed by transferring between the mill and the HDH retort while fully sealed in argon. As in the case of the planetary mill, the sealed retort was placed in a muffle furnace.

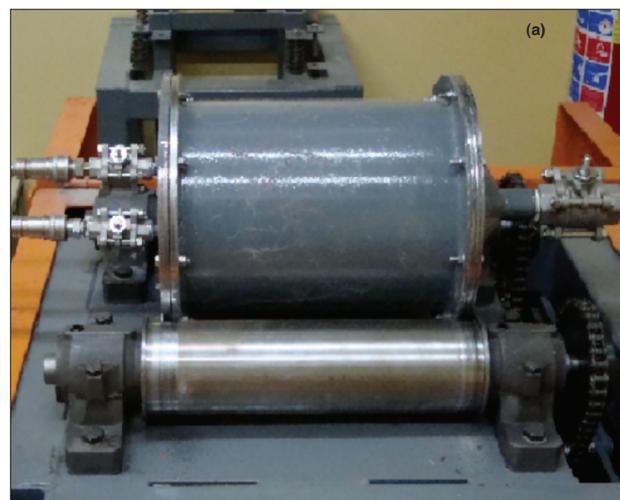


Figure 4—Photographic representation of Mintek's roller mill—(a) mill drum on the two driving rolls, (b) discharge frame

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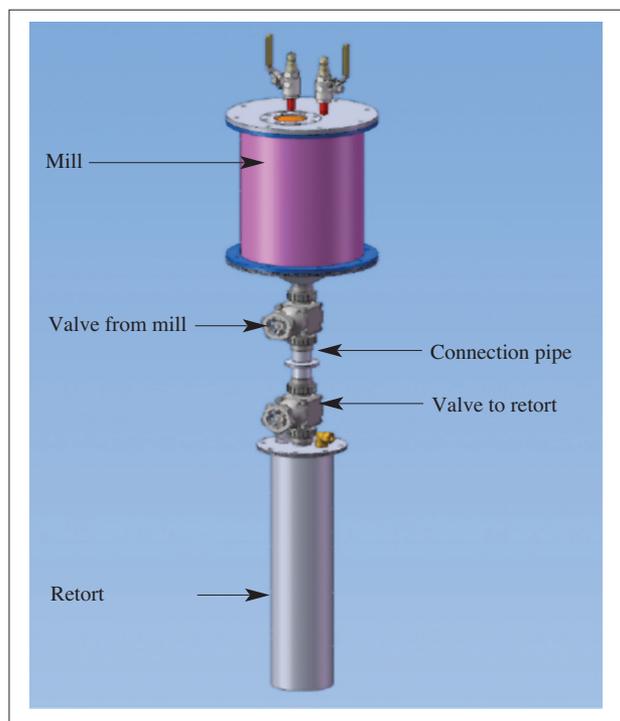


Figure 5—Graphic design of a manufactured roller mill closed system

For the optimization of the parameters for the dehydrogenation of  $TiH_2$ , the residence time at the set temperatures of the furnace was varied between 1 and 36 hours. The established optimum conditions for the dehydrogenation process involve heating the sample in a muffle furnace at  $700^\circ C$ , under vacuum (below 800 PA) for 36 hours.

At the end of the set dehydrogenation period the system was cooled down to room temperature while under vacuum. The pure titanium powder was then cautiously removed from the retort and weighed. It was then stored in the glove box. The respective sub samples of the planetary and roller mill powders were analysed by XRD and SEM to assess the quality of the final powders.

### Safety

When planetary milled  $TiH_2$  powder was transferred inside the glove box while the oxygen content was around 8%, sparks were observed and the material became gradually red. The small fire was covered with silica sand and was easily extinguished. Hence, it was decided that the treatment of fine  $TiH_2$  and pure titanium be conducted at oxygen levels below 5% whenever possible.

### Results and discussions

In the interests of brevity, only results of the optimum conditions are reported here.

#### Bulk chemical analysis

The results of chemical compositions of the titanium powder samples produced by the HDH process at Mintek are given in Table III. The hydrogen content of 3.50% in the hydrogenated titanium sponge was achieved; this indicates that the hydrogenation process was very effective as hydrogen content falls within the literature range.

As shown in Table III, the content of carbon in Mintek's titanium powder is higher than in commercially available powders (Table I). The source of carbon in the process is not known as its content in the starting sponge was lower than in commercial powders (Table II). However, the contents of other elements in this titanium powder meet the specifications.

Therefore, upon solving the carbon setback, the produced powder may find various applications, including in the manufacturing of linings and airplane parts.

#### Particle size distribution

The statistical analyses of the PSD of the planetary and roller milled titanium hydride are given in Table IV. The mean diameter of the titanium hydride powder,  $D$  [4,3], is 27.74 and 41.84  $\mu m$  for the planetary mill and roller mill, respectively. These statistical results show that the planetary mill produces a finer powder than the roller mill. The ball-to-powder ratio of the planetary mill is 8.34 which is slightly lower than that of the roller mill which is 8.49. There is a slight difference in the ball-to-powder ratios of the planetary and roller mills.

That the particle size of the planetary milled powder is relatively small may primarily be attributed to the higher energy intensity used by the planetary mill (milling of a relatively smaller sample at a relatively high speed using small size diameter steel balls). However, both planetary and roller mills proved effective in the size reduction of  $TiH_2$  for use in powder metallurgy.

Table IV

#### Summary of the statistical analysis of the PSD for the milled titanium hydride by planetary mill roller mills

	Planetary mill	Roller mill
$D_{10}, \mu m$	1.210	8.203
$D_{50}, \mu m$	8.809	30.80
$D_{90}, \mu m$	61.96	102.1

Table III

#### Chemical composition of the titanium powder produced by HDH process at Mintek

	Mg (%)	Fe (%)	H (%)	C (%)	N (ppm)	O (ppm)	Cl (ppm)
$TiH_2$	-	-	3.50	-	-	-	-
Ti powder	0.06	0.44	0.01	0.99	7.05	110	<50

Note: <50 ppm: the analyte concentration could not be accurately quantified as it is below its Limit of Detection (50 ppm)  
 '-': analysis was not conducted

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### Microstructural characterization

This section of the report gives a summary of XRD and SEM results of various titanium samples. The products of the current work are compared to the available commercial materials.

#### X-ray diffraction

The results of the phase composition of titanium hydride after milling are given in Figure 6. The diffractogram of the powder shows that the sample after milling consisted only of titanium hydride phase.

The diffractograms of dehydrogenated titanium hydride powders milled by planetary and roller mills are given in Figure 7 (a and b). Fine titanium powder is highly reactive, and may easily react with oxygen and nitrogen in the atmosphere. The evidence of oxygenated and nitrogenized titanium in Figure 7 might be a consequence of this high reactivity of titanium. The chemical analysis results do not show any significant oxygen and nitrogen contents in the dehydrogenated powder. So it is believed that the oxygen contamination is not inherent to the process, but on the XRD

subsamples. Oxygen has a detrimental effect on the tensile ductility, fatigue strength, and stress corrosion in commercial pure titanium and various titanium alloys. Thus such contamination should be minimized.

#### Scanning electron microscopy

Figure 8 shows the scanning electron micrographs of commercially available and Mintek produced titanium hydride powders. There is a clear similarity in shape between these powders. The hydrogenated sponge particles show some angularity (which is needed in the metallurgical consolidation work), which indicates that it is more brittle. Flat cleavage facets are evident on the hydride particles from the two producers.

The SEM micrographs of the planetary and roller milled titanium hydride are shown in Figure 9. The micrographs show that both powders are angular in shape.

The angularity in the hydrogenated powders is transferred to the subsequent dehydrogenated powders, as shown in Figure 10. The planetary and roller milled powders are comparable to the commercial powder in terms of

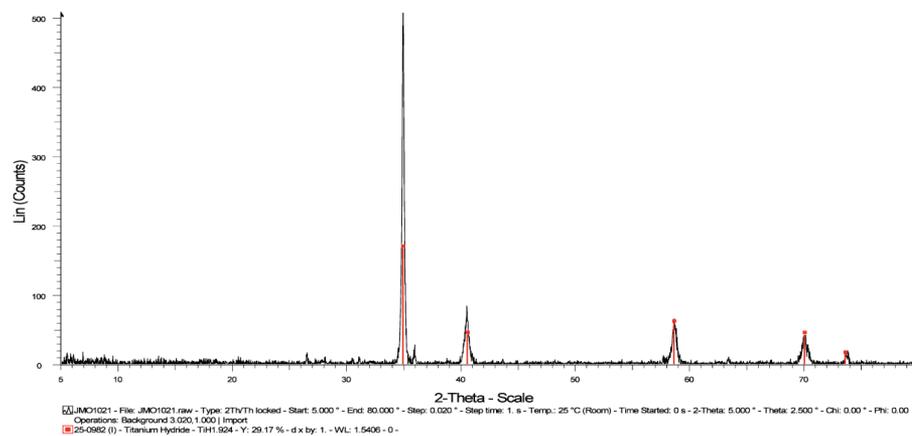


Figure 6—X-ray diffractogram of the milled hydrogenated titanium sponge

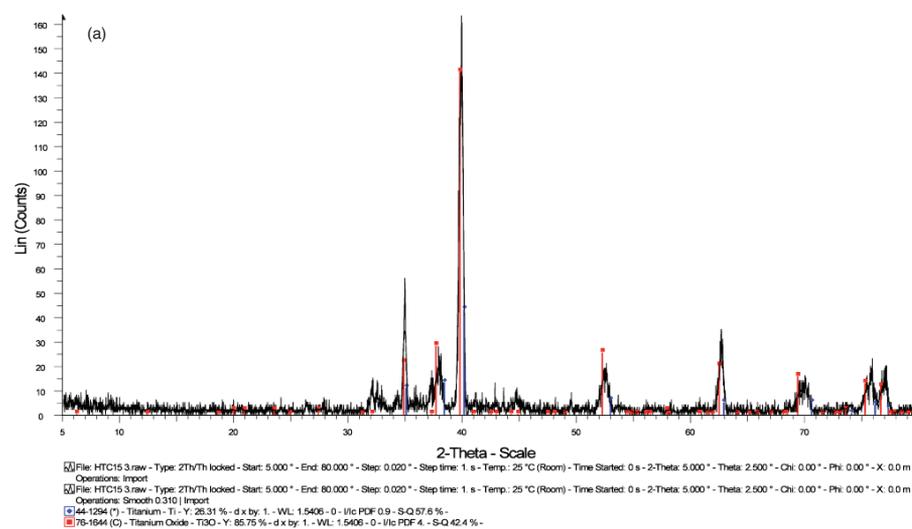


Figure 7—X-ray diffractograms of the, (a) planetary milled titanium powder and (b) roller milled titanium powder

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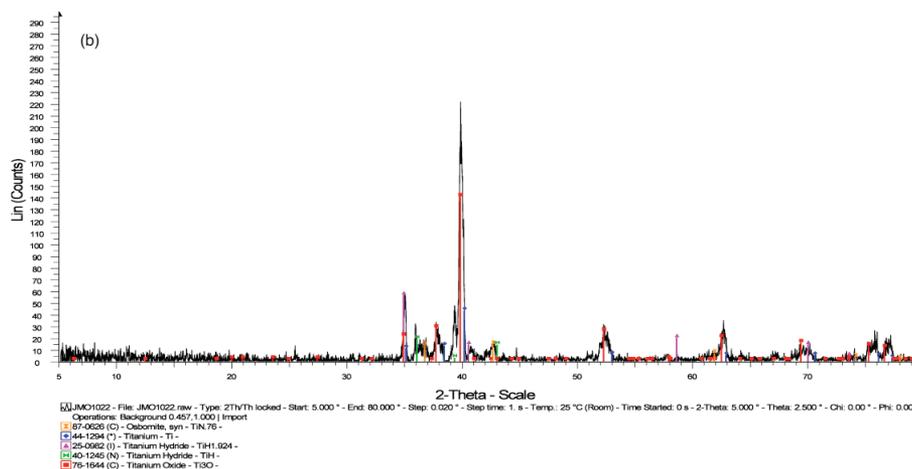


Figure 7 (continued)—X-ray diffractograms of the, (a) planetary milled titanium powder and (b) roller milled titanium powder

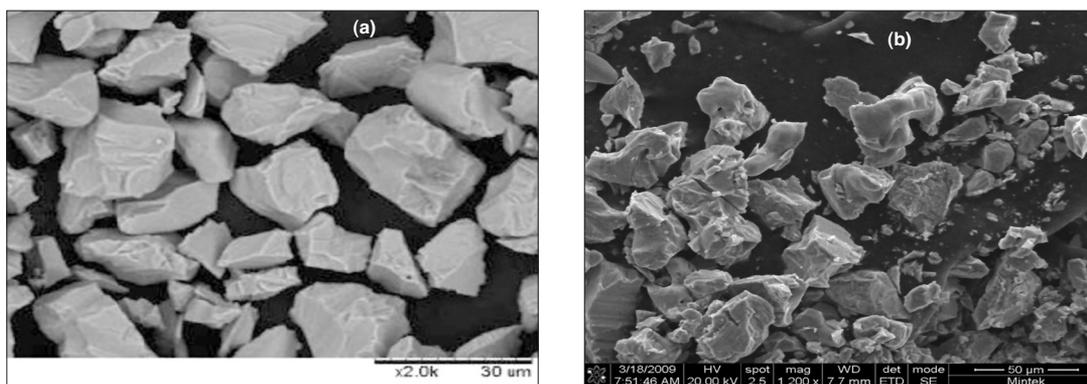


Figure 8—SEM micrograph of TiH<sub>2</sub> powder produced at (a) AG Materials Inc. [website: <http://www.agmaterials.com/products/titaniumhydride.html>], and (b) Mintek

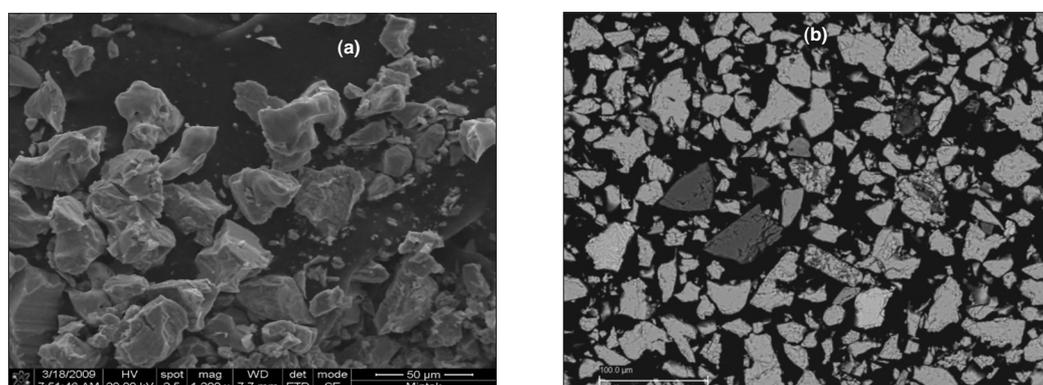


Figure 9—SEM micrographs of milled titanium hydride by (a) planetary mill, and (b) roller mill

angularity. However, the morphology of the particles of the planetary milled powder appears to be more irregular than the very angular shapes of the uncrushed titanium hydride. However, on closer inspection, it is evident that this is caused by the adhesion of very fine angular particles on the surfaces of larger particles, or by the agglomeration of fine particles. The adhesion of fine particles could be due to high vacuum and high temperature operations during dehydrogenation.

### Comparison of planetary and roller mills

A comparison of the suitability of the two types of milling technology for the production of titanium powder for metallurgical consolidations was conducted. The planetary mill has shown great capability for the production of titanium powder for metallurgical consolidations. However, the direct milling costs largely depend on the capacity of the mill. The

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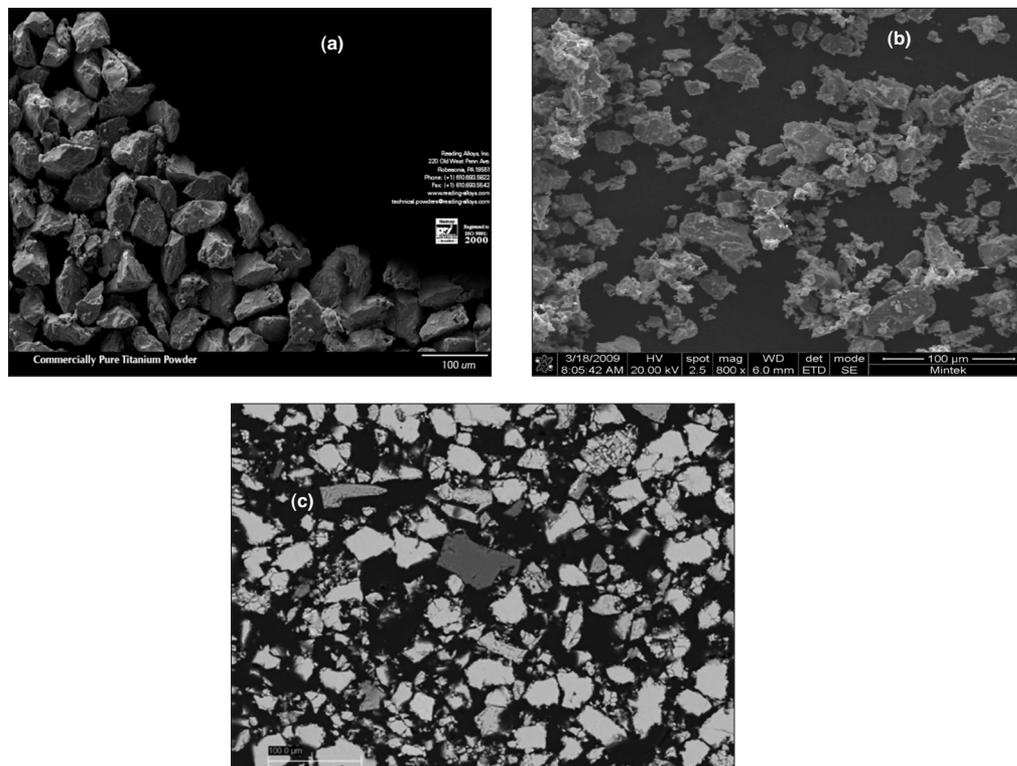


Figure 10—SEM micrograph of the, (a) commercial titanium powder, (b) planetary milled titanium powder and (c) roller milled titanium powder

planetary mill is a laboratory-scale piece of equipment. It would be relatively costly to increase the capacity of this mill. The energy consumption in this kind of milling is relatively high.

As opposed to the planetary mill, it is much easier to scale up the roller mill, thus reducing the running cost. At similar operational times, the unit milling cost of  $TiH_2$  by the planetary mill would be about six times that of the roller mill. One of the major contributors to the cost of the planetary mill is the high electrical power consumption.

### Conclusion

Laboratory-scale tests were conducted to produce titanium powder by HDH process. The hydrogenation and dehydrogenation stages of the process were optimized. Two ball milling technologies namely the planetary and roller mills were evaluated for the  $TiH_2$  particle size reduction to produce a suitable titanium powder. Both planetary and roller mills produced sufficiently fine titanium powder with mean diameters,  $D[4,3]$  of 27.74  $\mu m$  and 41.84  $\mu m$ , respectively. The powder particles were angular in shape and there was no evidence of detrimental coating. However, the planetary mill powder may only be produced at laboratory-scale at relatively high costs. Conversely, roller mill may easily be scaled up to produce a significant amount of powder.

The chemical analysis results showed that the elemental contents of the produced titanium powder matched the specifications of commercial titanium powder, except for the high carbon content. Nevertheless, the powder has been tested in mechanical alloying and has been found suitable for making powder metallurgical compacts.

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