The use of titanium hydride in blending and mechanical alloying of Ti-Al alloys

by I.A. Mwamba*† and L.H. Chown*†

Synopsis

Titanium sponge, which is almost pure titanium, is extremely ductile and not easily processed into titanium powder. One method of producing powder is the hydride-dehydride (HDH) process, where titanium sponge is hydrided to form brittle titanium hydride (TiH_2). Titanium hydride is easily milled to produce powder and is then dehydrided to form Ti powder.

In this work, titanium hydride powder obtained from titanium sponge was used as a starting material for blending and mechanical alloying with elemental powders. Firstly, titanium hydride powder was blended with aluminium elemental powder to produce a homogenized powder, which was then compacted and sintered to produce powder metallurgy compacts. Secondly, titanium hydride powder was mechanically alloyed with aluminium elemental powder and then compacted. The mechanically alloyed powder was characterized in terms of particle size distribution, morphology and microstructure. In both blending and mechanical alloying, the green compacts were characterized by assessing the green density, while the sintered compacts were characterized by their sintered density, microstructure, and hardness. The two processes have resulted in the formation of $TiAl_3$ intermetallic compound.

It was established that by simple mixing and homogenizing, titanium hydride can be used as a starting material to produce powder metallurgy components in which porosity is a benefit rather than a problem, much akin to metallic foams.

From the products obtained in the TiH_2–Al system, it appears that titanium hydride can be used as a precursor in mechanical alloying. However, the possible formation of complex hydrides may introduce detrimental properties, and needs to be further investigated. For the production of non-porous components, it would be advisable to dehydrogenate the TiH_2 powder before milling i.e. producing titanium powder by the hydride-dehydride (HDH) method.

Keywords

Mechanical alloying, titanium hydride, titanium aluminide and blending

Introduction

Titanium hydride (TiH_2) is a chemical compound of titanium and hydrogen, which is brittle and, in powder form, highly reactive when exposed to heat or strong oxidizers[1]. Owing to its high reactivity, titanium hydride powder has found application in pyrotechnics, initiator squibs and igniters[2].

Metallurgical and chemical uses of titanium hydride include: a source of pure hydrogen for foaming metals, deoxidizing agent for the absorption of carbon in powder metallurgy and the production of titanium alloys and semi-finished sintered articles[3]. In structural applications, hydrogen in titanium alloys is known for its detrimental effects, as it can lead to structure embrittlement by the formation of TiH_2, potentially resulting in catastrophic failure[4–5]. However, research on titanium hydride has established that hydrogen also has positive effects in titanium alloys[6]. This finding has led to the development of the thermohydrogen processing technique (THPT), where hydrogen is used as a temporary alloying element to enhance the processability and fabricability of titanium products in processes such as sintering, compaction, machining, and hot working[7]. In powder metallurgy, THPT is one of the methods available for microstructure modification with enhancement of mechanical properties.

TiH_2 can exist in two allotropic forms, depending on the temperature and pressure: tetragonal and cubic, with the tetragonal form being the room temperature phase. Phase transformation from tetragonal to cubic has been observed with increasing temperature, corresponding to the decomposition of the titanium hydride, which recombines with increasing pressure[8]. A study of the decomposition behaviour of titanium hydride powders has shown that the onset of titanium hydride decomposition occurs at ~450°C and is complete at 700°C[9]. The decomposition onset

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* *Advanced Materials Division, Mintek*

† *DST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand..*

This paper was first presented at the, Light Metals Conference, 27–29 October 2010, Misty Hills, Muldersdrift.

Table I

Chemical composition of the titanium powder produced by HDH process

Compound/element	Elemental composition, % (ppm)							
	TiH_2 /Ti	Mg	Fe	H	C	N	O	Cl
TiH_2	Balance	-	-	3.50	-	-	-	-
Dehydrogenated Ti powder	Balance	0.06	0.44	(112)	0.99	(7.05)	(110)	(<50)

corresponds to the melting point of TiH_2[10]. Heat treatment of the hydride resulted in an increase in the decomposition temperatures.

The brittleness of titanium hydride is an advantage in the mechanical breaking down of this compound to produce powder. This opens doors for powder metallurgy as a cost-effective method for processing titanium alloys into useful components. It has also been shown that finished titanium parts can be manufactured at a cost nine times lower than the conventional route by using a technique based on TiH_2 powder[11]. Powder metallurgy parts have also been successfully produced by powder injection moulding of titanium from TiH_2 powders[12].

In this work, titanium hydride powder obtained from titanium sponge was used as starting material in blending and mechanical alloying (MA) with aluminium elemental powder. The blended and mechanically alloyed powders were compacted and sintered. The sintered compacts were characterized to assess the extent of alloying.

Experimental procedure

Titanium hydride (TiH_2) powder production

The powder used for blending and mechanical alloying was obtained from the milling of hydrogenated titanium sponge. Titanium sponge produced by the Kroll process was hydrogenated to form titanium hydride TiH_2. The hydrogenated titanium sponge pieces were milled to less than 80 μm in a Retsch Mill Machine PM100.

Mixing of TiH_2 with elemental powders

The titanium hydride powder was mixed with specified amounts of elemental powders of aluminium, 99.7% purity and mean size 57 μm to reach the targeted composition. Table I gives the chemical composition of the titanium powder produced by HDH process at Mintek and Table II gives the proportions used in mixing TiH_2 powder and other elemental powders. The mixed powders were homogenized in air in a planetary mixer for 15 minutes. The three powders were only blended without any milling or grinding media in the mill to induce alloying. Alloying was expected to take place during sintering. As is shown in the table, the weights given for TIH_2 take into account the presence of hydrogen:

- ➤ Mix 1—95 g Ti powder and 5 g Al, thus 95 g of Ti is contained in 99 g of TiH_2
- ➤ Mix 2—40 g Ti powder and 60 g Al, thus 95 g of Ti is contained in 99 g of TiH_2
- ➤ Mix 3—10 gTi powder and 95 g Al, thus 10 g of Ti is contained in 10.5 g of TiH_2

Mechanical alloying

The TiH_2 powder was milled with aluminium elemental powder for 32 hours; the target material was $TiAl_3$. Stainless steel balls were used as grinding media in argon atmosphere and a ball-to-powder (BPR) ratio equal to 10. Table III summarizes the mixing proportions for mechanical alloying. The mixing proportion corresponded to the atomic ratio of 3 aluminium for 1 titanium.

Powder characterization

Properties characterized were: apparent density, particle size, size distribution, shape and chemical composition. The apparent densities of the different mixes were determined using the Arnold apparent density meter.

The size and size distribution of powder particles was determined by laser diffraction using a Malvern Mastersizer® 2000 in the size range of 0.02–2000 μm with water as dispersant. The particle shape was determined by scanning electron microscopy (SEM) on the FEI Nova NanoSEM®. XRD analysis was performed using the Siemens Diffraktometr D5000. The chemical composition of the powders was determined using a combination of X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

Powder compaction and sintering

Mechanically alloyed (MA) and blended TiH_2-Al powders were consolidated into cylindrical shapes using a uniaxial compaction press at a pressure of 100 MPa. Following the

Table II

Mixing proportions of TiH_2 with aluminium elemental powder for blending

Mix 1(g) 95Ti-5Al		Mix 2(g) 40Ti-60Al		Mix 3(g) 10Ti-90Al	
Al TiH_2	5 99	Al TiH_2	60 41.7	Al TiH_2	90 10.5

Table III

Mixing proportion for mechanical alloying

Milling system	Mix materials for $TiAl_3$ preparation (g)	
	TiH_2 powder	Aluminium elemental powder
TiH_2-Al	19.4	31.4

results of thermal analysis from previous work (unpublished), the sintering was done in argon atmosphere at 630°C for 1 hour for the 90Al-10Ti and 40Ti-60Al compacts, at 450°C for 1 hour for the compacts from the MA TiH_2-Al powders and at 1150°C for 95Ti-5Al compacts.

Compact characterization

The green compacts were characterized in terms of green density. For the sintered compacts, the sintered density, microstructure and hardness were characterized.

Results and discussion

Powder characterization

Mixed powder

The following mixed powders were assessed: 10Ti-90Al, 40Ti-60Al and 95Ti-5Al. The particle size and chemical analysis were not relevant for the mixed powders, since, for the starting materials, these properties were known. The only parameters needed were the physical characteristics and the amount of ingredients involved in the mixing.

Mechanically alloyed (MA) powder

Table IV lists the particle size distribution and the statistical parameters of the TiH_2 powders milled for 32 hours with aluminium. The results show that the powder particles were fine, with a d_{50} of 38 µm. Figure 1 shows the particle size distribution of the powder, and the shape of powder after 32 hours of milling is depicted in the SEM micrograph in Figure 2. This figure shows that the particles in the milled powder were irregular in shape, with agglomeration of the fine ones.

Where:

D [3,2,] µm	is the Sauter mean diameter, defined as the diameter of a sphere that has the same volume/surface area ratio as a particle of interest.
d_{50}, µm,	also known as median diameter or medium value of particle diameter, is a particle diameter or size value in case where a cumulative distribution percentage reaches 50%. 50 wt% of the particles are smaller than d_{50} and 50 wt% are larger than d_{50}.
d_{10}, µm	10 wt% of the particles are smaller than d_{10} and 90 wt% are larger than d_{50}.
d_{90}, µm	90 wt% of the smaller are larger than d_{90} and 10 wt% are larger than d_{90}.
SSA	is the specific surface area.

Figure 3 shows an XRD pattern of the TiH_2-Al powder which identifies the $TiAl_3$ peaks. This suggests that, after 32 hours of milling, Ti and Al have mechanically alloyed, resulting in the formation of the $TiAl_3$ phase. This was confirmed by EDS conducted on the powders (Table V). The EDS analysis was conducted on different particles and referred to as Analysis 1, 2, 3… Hydrogen from the starting TiH_2 was not observed in the final product.

Table V also shows that the final product was contaminated by iron, probably from the grinding media which were stainless steel balls. Synthesis of Ti_3Al and TiAl by mechanical alloying of TiH_2 and aluminium has been reported elsewhere[13]. It was shown that the use of titanium hydride instead of titanium in powder mixtures with aluminum results in a significant activation of diffusion processes, and leads to an accelerated production of single-phase titanium aluminides on heating. This is attributed to the small particle size of the charge, high density of defects (including those due to hydrogen-phase hardening) in the titanium and aluminum lattices and possible reduction of Al_2O_3 films by atomic hydrogen.

Table IV

Statistical parameters of particle size distribution for MA TiH_2-Al powder

Parameters	TiH_2-Al powder
D[3,2] µm	13.8
d_{10}, µm	5.0
d_{50}, µm	38.1
d_{90}, µm	170.5
SSA, m^2/g	0.284

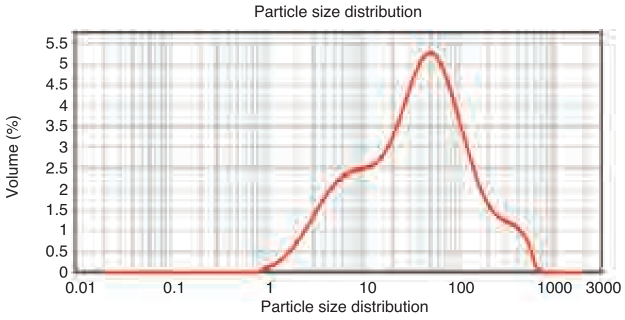


Figure 1—Particle size distribution for MA TiH_2-Al powder

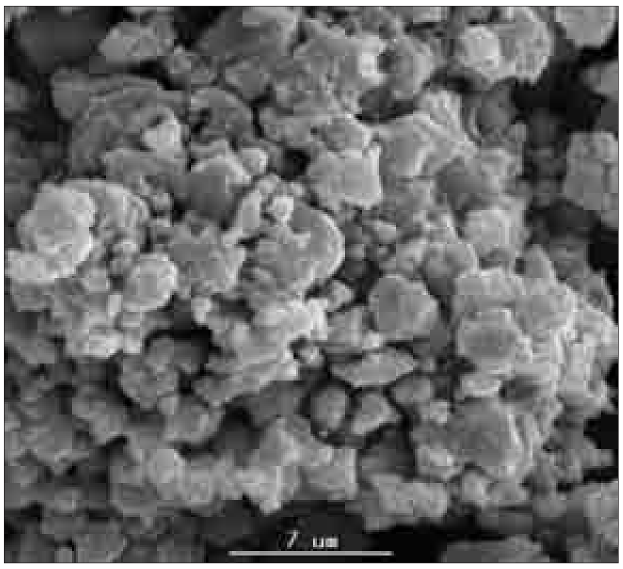


Figure 2—MA TiH_2-Al powder after 32 hours of milling

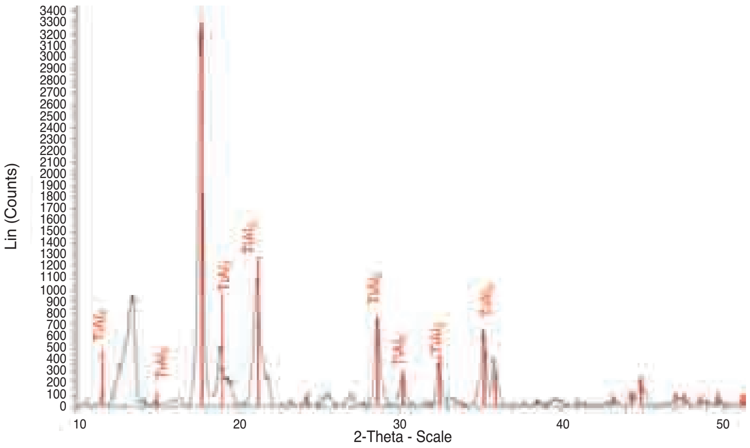


Figure 3—XRD pattern of the TiH_2—Al powder after 32 hours of milling

Table V

Typical chemistry of the particles in the MA TiH_2-Al powder

Sample	Analysis	Atomic % analysis		
		Al	Ti	Fe
TiH_2-Al	1	71	25	4
TiH_2-Al	2	71	25	4
TiH_2-Al	3	73	24	3
TiH_2-Al	4	72	25	3
TiH_2-Al	5	73	24	3

Figure 4—Typical green compact after uniaxial compaction

Powder response to compaction and sintering

The green and sintered densities and hardness of compacts from mixed powders 10Ti-90Al, 40Ti-60Al, 95Ti-5Al and the mechanically alloyed powders from the TiH_2-Al system milled for 32 hours were assessed. A typical green compact is shown in Figure 4. The apparent, green and sintered densities are reported in Table VI for the mixed powders and the mechanically alloyed powder. It was not possible to measure the sintered densities of compacts obtained from mixed powder due to the heavy distortion. Differential scanning calorimetry (DSC) should be done to ascertain an appropriate sintering temperature. From Table VI it can be seen that, while the apparent density was far less than the lightest material (aluminium in this instance), the green density was just slightly above the density of bulk aluminium (2.7 g/cm^3). The low densities observed in the green compacts in this work were probably due to the presence of pores, which contributed to lowering the density.

Microstructure of sintered compacts

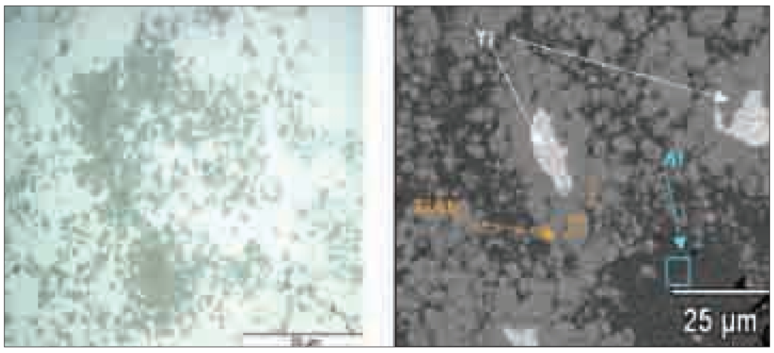
Compacts obtained from mixed powders

All compacts underwent exaggerated deformation during sintering, which is indicative of a very large amount of shrinkage due to hydrogen evolution, which takes place in the temperature range 450–700°C. It is believed that, in addition to the hydrogen evolution, the deformation observed was also due to the changes that took place in the aluminium powder at the sintering temperature (630°C). At this temperature, aluminium is in a semi-solid state

Table VI

Densities of mixed powders

Parameters	Mixed powders			MA powder
	10Ti-90Al	40Ti-60Al	95Ti-5Al	TiH_2-Al
App. density (g/cm^3)	1.3	1.3	1.3	1.39
Green density (g/cm^3)	2.7	2.9	2.8	2.15
Sintering temperature (°C)	630	630	1150	450
Sintered density (g/cm^3)	-	-	-	2.33



(a) Optical micrograph (b) SEM micrograph

Figure 5—Typical microstructure of alloy 10Ti-90Al

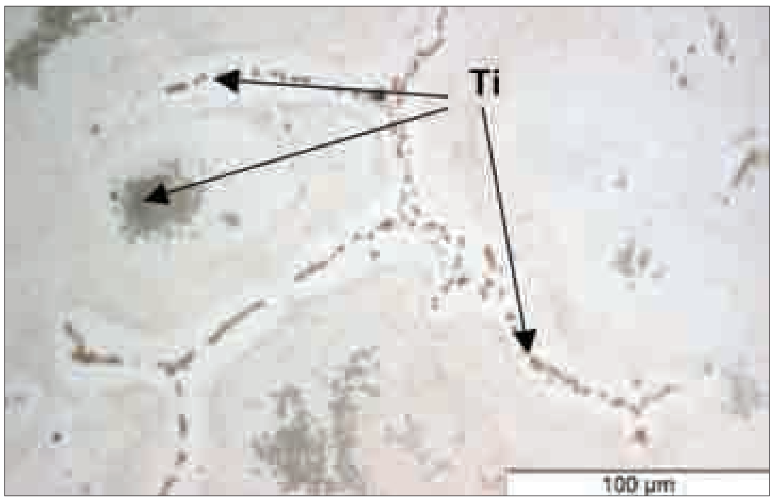


Figure 6—Optical micrograph of alloy 10Ti-90Al

corresponding to 60% solid fraction[14]. The extent of deformation was such that the compacts were discarded in the microstructure evaluation, and only alloy 10Ti-90Al was used to evaluate the change that took place in the compact microstructure during sintering. Figures 5(a)–(b) are optical and SEM micrographs of 10Ti-90Al, respectively. From these micrographs, it can be seen that after sintering, three phases were present in the compact: the aluminium matrix, and large, brownish phases appearing mostly in the centre of grains surrounded by agglomerated dark grey precipitates (Figure 5a). EDS analysis conducted on the samples showed that these phases were pure aluminum (dark phase), $TiAl^3$ (grey phase) and pure titanium (light phase) appearing mostly in the centre as shown in Figure 5(b).

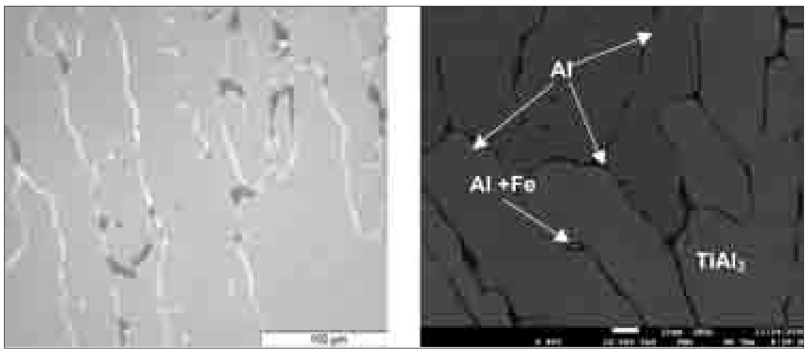
From this microstructure, it can be seen that the different phases had segregated and alloying was beginning to occur by diffusion. As is shown in the micrograph of Figure 5(b), in almost all cases pure titanium is in the centre of the precipitates and phase variation starts from the dark phase (pure aluminium), becoming grey where alloying is taking place to form $TiAl_3$ followed by the light phase (pure titanium), which is located in the centre where there has not yet been any contact between aluminum and titanium. As these transformations are solid-state transformations, it can be expected that a very long time will be needed to achieve full alloying at the chosen sintering temperature of 630°C. Titanium melts at 1665°C and is completely solid at 630°C, which suggests that the process was taking place by diffusion.

Figure 6 shows that pure titanium, which is seen at the centre of the grains, is also observed at grain boundaries as discontinuous lines of precipitates in the midst of a light phase.

Compacts obtained from MA TiH_2-Al powders

The microstructure of compacts pressed using the powder obtained from mechanical alloying for 32 hours in the TiH_2-Al system is shown in Figures 7(a) and 7(b). The optical micrograph in Figure 7(a) suggests that the sintered compact consists of elongated grains with insufficient bonding for a good sintering. Three phases can be identified in these micrographs: the grey matrix, a white phase along the grain boundaries and a dark phase in places at the grain boundaries.

The SEM micrograph (Figure 7(b)) shows that the white phase defines grain boundaries. Figure 8 also shows a darker grey phase appearing within the matrix, indicating that some alloying occurred during milling. The EDS results on the grains and grain boundary regions are summarized in Table VII. These results show that after milling for 32 hours,



9a.) Optical micrograph (b) SEM backscatter micrograph

Figure 7—Typical microstructure of the sintered compact obtained from MA powders

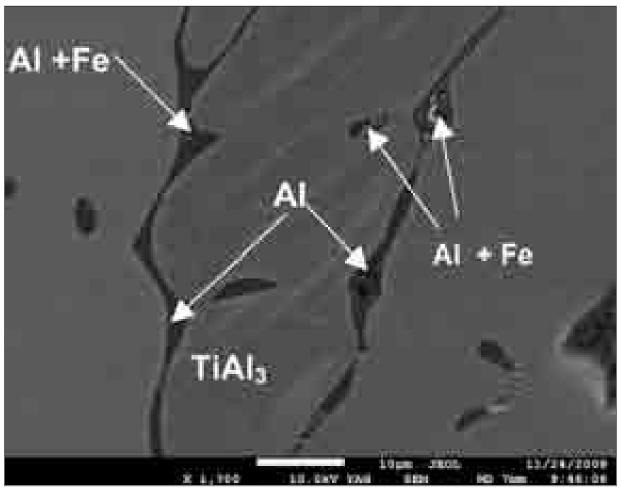


Figure 8—SEM backscatter micrograph of Alloy TiH_2-Al showing the dark grey $TiAl_3$ phase

Table VII

Typical composition intra- and intergranular in the sintered compacts

Elements	wt%		at. %	
	Intragranular	Intergranular	Intragranular	Intergranular
Al	63.31	98.10	75.39	99.0
Ti	36.69	0.90	24.60	0.5
Fe	-	1.00	-	0.5

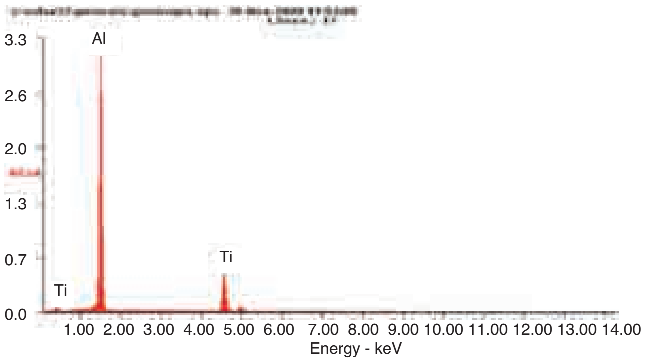


Figure 9—Typical EDS spectrum of compact grains in alloy TiH_2-Al

Table VIII

Micro- and macro-hardness of compacts

Evaluation parameter	Materials	
	10Ti -90Al	TiH_2-Al (MA)
Micro-hardness (HV0.5)	72	378
Macro-hardness (HV10)	49	105

the particles in the mechanically alloyed powder consist mainly of the $TiAl_3$ phase. The aluminium content of the intergranular region was more than 90 at.% Al, suggesting that aluminium was actually the binding metal. The process that explained the presence of aluminium at grain boundaries and in the pores was not investigated in this work. A typical EDS spectrum of such a particle is given in Figure 9.

Hardness of compacts

Table VIII gives the hardness of compacts obtained from mixed powder 10Ti-90Al and mechanically alloyed powder from the TiH_2-Al system. It can be seen that there was a large difference between the micro- and macro-hardness values for both alloys. In compacts obtained from mixed powders, the macro-hardness observed was the result of the global hardness of the aluminium solid solution matrix in which were embedded titanium and $TiAl_3$ particles while the micro-hardness was the average of different hardness measurements performed on different phases including aluminium, titanium and $TiAl_3$.

In compacts obtained from mechanically alloyed powders in the TiH_2-Al system, the macro-hardness measurement included the grains, pores and intergranular spaces filled with aluminium. Aluminium, which acted as binding material during sintering, possesses, in the pure state, a very low hardness (17HV10 or 167 MPa), which increases with alloying. This combination of phases of different hardness resulted in a hardness average lower than the micro-hardness average, which was measured on the compact grains completely made of $TiAl_3$. Micro-hardness is a localized characteristic defining the hardness of a particle or phase of the microstructure within the component. This meant that the higher the number of voids, the lower the macro-hardness. In this case, the evolution of hydrogen during sintering has left many voids which were filled with aluminium.

Conclusions and recommendations

The formation of $TiAl_3$ by blending and mechanical alloying of TiH_2 with aluminium elemental powder has shown that titanium hydride powder (TiH_2) can be used to produce by blending or mechanical alloying intermetallic compound in the Ti–Al system. During sintering there is better control of compact microstructure with powder from mechanical alloying than powder from blending.

TiH_2 powder as a precursor with aluminium produces sintered compacts with high porosity caused by hydrogen evolution. Depending on the application, this can be beneficial or detrimental. For structural components, where high strength is required, titanium hydride is not the correct precursor, but for applications where weight reduction is required, e.g. metallic foams, TiH_2 is appropriate. For other applications where there is a need to store hydrogen, mechanical alloying is ideal, as it introduces alloying elements into titanium hydride that can improve the hydrogen storage capacity.

Acknowledgements

The authors would like to thank Mintek and the DST-AMI for financial support and permission to publish the results.

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