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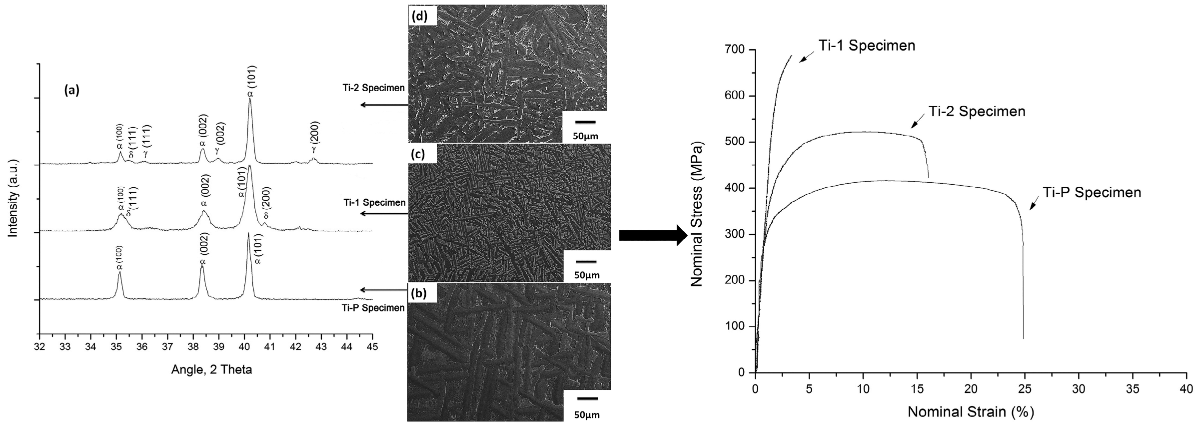
(a)
Intensity (a.u.)
Angle, 2 Theta
Ti-2 Specimen
Ti-1 Specimen
Ti-P Specimen
(d)
(c)
(b)
50µm
Nominal Stress (MPa)
Nominal Strain (%)
Ti-1 Specimen
Ti-2 Specimen
Ti-P Specimen

Preparation of Strong and Ductile Pure Titanium via Two-Step Rapid Sintering of TiH_2 Powder

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Abstract

The present work demonstrates the feasibility of preparing bulk-Ti, with high strength and good ductility, via spark plasma sintering of TiH_2 powders. The microstructure and mechanical properties of bulk titanium prepared under two different processing conditions, i.e. (i) Simultaneous dehydrogenation and sintering under one-step spark plasma sintering (SPS), and (ii) dehydrogenation in vacuum followed by Spark Plasma Sintering i.e. two-step SPS , are presented and discussed. The one-step sintering process, i.e. process (i), resulted in Ti specimens with very high tensile strength, but poor ductility. On the other hand, two-step sintering process, i.e. process (ii), resulted in bulk Ti with high strength and high ductility.

Keywords

Titanium hydride, Pure-Ti, Spark Plasma Sintering

1. Introduction

Titanium alloys have exceptional potential for expanded usage in various industries. However, initial high cost of Ti and the complex fabrication and subsequent machining process often limit their applications. However, powder metallurgy (P/M) processing has emerged as an efficient method with a possibility to produce titanium alloys with wide range of compositions, controlled properties, and near net shape characteristics. Particularly, P/M processing approach based on elemental powders are of particular interest due to relatively lower processing cost as well as its higher maneuverability with respect to materials, microstructural, and product designing [1, 2]. However, the usage of pure-Ti powder poses several problems, such as high affinity toward oxygen, nitrogen, and carbon, sticking with vials and balls during blending and milling, and higher cost associated with preparing high-purity Ti powders. These factors lead to lack of compositional/microstructural control together with less than expected cost advantages [3, 4]. In comparison to pure-Ti powder, use of titanium hydride powder has several advantages, including lower initial price, less impurity contents, and relative ease of handling during mechanical mixing/milling without encountering the problem of sticking due to its inherent brittleness, leading to higher powder yield, smaller particle size, and better compositional control. The fine-sized titanium hydride powder can be utilized to obtain sintered products with high density, fine grained microstructure, and relatively higher strength at a relatively lower sintering temperature [5, 6].

Various techniques are used for the consolidation of powders [7-10]. Particularly, spark plasma sintering technique has several advantages over the conventional hot pressing, including higher heating/cooling rates and a greater applied mechanical load. Hence, SPS technique offers a possibility to achieve dehydrogenation and consolidation of titanium-hydride powder in a comparatively shorter period of time, together with high density products with controlled microstructure and properties [11]. However, a very small amount of information is available in the literature on the TiH_2 based powder metallurgy technology and mechanical properties of bulk-Ti alloys prepared using titanium hydride powders [12-16, table-2]. Therefore, it would be interesting to carry out a feasibility study about the microstructure and mechanical properties of bulk-Ti prepared via SPS of TiH_2 powder, to realize the full potential of elemental powder based P/M approach using titanium hydride powders. Hence, the present study is an initiative to evaluate the feasibility of fabricating high purity bulk-Ti via spark plasma sintering using titanium hydride powder as starting material. The microstructure and mechanical properties of the fabricated Ti compacts, thus prepared, are presented and discussed.

2. Materials and Methods

TiH_2 powder (45μm pass, ~99 % pure, supplied by “Kojundo Chemical Laboratory Co. Ltd.” Japan) and pure-Ti (45μm pass, 99.98% pure, Gas-atomized low oxygen titanium powder, supplied by “Osaka Titanium Technologies Co. Ltd”, Japan) were used as starting materials.. The sintering was carried out using graphite die and punch under high vacuum atmosphere (~10^{-3} Pa) in DR.SINTER Spark Plasma Sintering machine (“Sumitomo Coal Mining Co. Ltd.”, Japan). The powders were consolidated using two different approaches: (i) One-Step SPS process: the pressure and temperature were increased simultaneously from zero pressure to 50 MPa and room temperature to 1200 °C, respectively. The holding time at 1200 °C was 1 h. Subsequently, the furnace was cooled to room temperature. High purity Ti powder was also sintered under similar conditions. (ii) Two-Step SPS process: The first step involved dehydrogenation at 800 °C for 0.5 h without any applied external pressure for maximum dehydrogenation. In the second step, temperature and pressure were increased, simultaneously, from 800 °C to 1200 °C and zero pressure to 50MPa, respectively. Subsequently, the powder mass was held at 1200 °C for 0.5 h followed by furnace cooling up to room temperature. After sintering, disc-shaped compacts with dimensions 15 mm (diameter) x 5mm (height) were obtained. Henceforth, in the subsequent discussion, the specimens prepared by one-step sintering of TiH_2, two-step sintering of TiH_2, and one-step sintering of pure Ti powders will be referred as Ti-1, Ti-2, and Ti-P specimens, respectively. Tensile tests were carried out at an initial strain rate of $5.6x10^{-4}$ using specimens with gauge size 3mmx1mmx1mm. Average Vickers micro-hardness was obtained at a load of 980.7 mN (Hv0.1) and dwell time 10 sec. Moreover, dehydrogenation temperature of TiH_2 was analyzed by TG/DTA (Thermo gravimetric and differential thermal analysis) and at a constant heating rate of 20 $Kmin^{-1}$ under argon atmosphere.

3. Results and discussion

3.1. Initial Powders

The results of XRD analysis of the initial powders are shown in Fig. 1(a). For pure Ti and TiH_2 powders, hexagonal close-packed (hcp) and cubic phases were identified, respectively. The XRD pattern of the titanium hydride powder was similar to the standard data corresponding to the hydride powder containing 95.96 mass% titanium and 4.04 mass% hydrogen. Fig.1 (b) and 1(c) shows DTA and TGA plots, respectively, obtained from as received TiH_2 powder. The presence of two overlapping endothermic events clearly suggests that the decomposition process occurs in two stages. The DTA plot shows one small peak (indicated by T_1) at 469 °C due to low enthalpy change followed by second large peak (indicated by T_2) at 536 °C due to comparatively larger enthalpy change. Thermo-gravimetric analysis confirms that dehydrogenation starts above approximately 440 °C and completes at approximately 700 °C (Fig.1c). A first hand estimation from TG analysis shows that approximately 3.53 mass% hydrogen was lost, which is slightly lower than the theoretical hydrogen content, i.e. 4.04 mass%, in the initial hydride powder. Similar findings have also been reported by other researchers [17, 18].

3.2. Microstructural Characteristics of the Sintered Bulk -Ti Specimens

In Fig.2 (a), the XRD profiles of Ti-1 and Ti-2 specimens are compared with the Ti-P specimen. The diffraction patterns of Ti-P specimen consist of hcp α-phase only. However, Ti-1 specimens indicated the presence of δ-phase (tetragonal hydrides) along with α-phase. Interestingly, the XRD profile of Ti-2 specimen exhibit the presence of primarily α-phase with minor amounts of δ and γ-phases. In the Ti-H system, following hydride phases are known to exist; (i) δ-phase (51.22-66.67 at% hydrogen) with f.c.c.

structure of CaF_2 type in which hydrogen atoms occupy tetrahedral sites randomly and (ii) the γ hydrides (1-2.9 at% hydrogen) with f.c.t. structure and having c/a ~ 1.09 [19]. These results indicate that a significant quantity of hydrogen is retained in the Ti-1 specimen. In the Ti-2 specimen, the presence of γ-phase indicates the retention of relatively lower amounts of hydrogen as compared to that of Ti-1 specimen. Therefore, it is apparent that the two-step process is more effective in achieving sintered compacts with significantly small amounts of retained hydrogen. In titanium, for hydrogen concentrations lower than 20 at%, in addition to the strong diffraction peaks from α phase, the weak diffraction peaks i.e. {111} {002} and {200} from the γ-phase and very weak diffraction peaks i.e. {111} from δ-phase was also reported by Nakamura et al. [19].

In addition to the above results, the relative amounts of hydrogen in the pure titanium compacts, prepared from titanium hydride powders, was also estimated by calculating lattice parameters using the XRD profiles (shown in Table-1). It can be observed that the c/a ratio of α-phase in Ti-1 specimen is larger than that calculated for Ti-2 specimen. In general, increasing the hydrogen concentration leads to an increase in c/a ratio and to a negligible increase in the specific lattice volume [20, 21]. The calculated lattice parameters for δ and γ-phases were found in good agreement with the results presented by A. San-Martin et al. [20].

The Ti-P specimen exhibited lath-type microstructure with basket-weave type morphology, having lath-width ~20µm and lath-length in the range of 50 to 200 µm (Fig.2b). Generally, in Ti alloys, such microstructure is developed due to slow cooling from β-region. The α-phase begins to form below the beta transus, which is about 882 °C. The α-phase forms in laths, with a crystallographic relationship, i.e. most close-packed plane of α-phase parallel to a special plane in the β-phase, to the β-phase, in which it forms. Slow cooling from beta phase leads to the nucleation of alpha nuclei, which grows faster along the common plane and grows very slowly perpendicular to this plane [22]. As a result, such laths are developed. Fig.2c shows the microstructure of Ti-1 specimen, which is also lath-type; however, it contains comparatively finer laths (lath width <5µm). The finer lath size can be attributed to the finer grain size due to a possibly higher hydrogen concentration in the specimen [22]. The α-Ti (H) phase (darker in Fig.2c) + δ-TiH_x (needle shaped, brighter in Fig.2c) can be observed. This observation is further correlated with the XRD results, as shown in Fig. 2a, in which only α and δ phases can be observed. The similar results about the phase transformation during dehydrogenation of TiH_2 were observed by P. Sun et al. [23]. It can be observe that the microstructure of Ti-2 specimen was also lath type with lath-width ~ 15μm (Fig.2d), and its appearance is more or less similar to the microstructure obtained from Ti-P specimen (Fig.2b). These microstructural characteristics further substantiate the findings that the two-step sintering process is more efficient for dehydrogenation as compared to one-step sintering.

3.3. Mechanical Properties

Figure 3 presents the mechanical properties and morphology of the fracture surfaces of titanium specimens. The average hardness of Ti-1 specimen is significantly higher as compared to that of the Ti-2 and Ti-P specimens (Fig.3a). The relatively higher average hardness values of Ti-1 compacts can be associated with the higher relative amounts of retained hydrides. The tensile engineering stress-strain curves of the various Ti samples are shown in Fig. 3(b). For comparison, the mechanical properties of the bulk Ti, under tensile loading, prepared from pure Ti and TiH_2 powders are also presented in Table-2. It can be observed that bulk-Ti prepared from TiH_2 powder resulted in higher yield strength (YS) and ultimate tensile strength (UTS) as compared to those of Ti specimen prepared by pure-Ti powder. Moreover, the YS and UTS of Ti-1 specimen are also higher to those of the Ti-2 specimen. However, the strain-to-failure is lowest for the Ti-1 specimens, and it shows almost brittle nature. On the other hand, the Ti-2 specimen demonstrates significant ductility, wherein the strain-to-failure is comparable to that of the Ti-P specimens. Briant et al. [24] have shown that increasing hydrogen content leads to increasing strength and decreasing ductility in Ti alloys due to enhanced susceptibility for hydrogen embrittlement. The fracture surfaces of Ti-P, Ti-1 and Ti-2 specimens are shown in Fig. 3c, 3d, and 3e, respectively. The Ti-P specimen exhibit micro-void-coalescence type ductile nature of fracture, as demonstrated by large dimpled morphology. However, Ti-1 specimens exhibit faceted morphology, indicating brittle nature of fracture. Interestingly, Ti-2 specimens consisted of comparatively small-sized dimples. The change in mechanical properties and fracture mode is consistent with the changes in the hydrogen contents in Ti-based materials, as demonstrated in other researches [25, 26]. Hence, it is apparent that the two-stage sintering process is extremely effective in providing bulk Ti with a combination of high strength and high ductility.

4. Conclusions

Titanium hydride powder was successfully utilized to prepare Ti compact with high strength and good ductility. One-step sintering resulted in high hardness, high strength, but low strain to failure under tensile loading, whereas two-step sintering resulted in moderate hardness, high strength, and comparatively higher strain-to-failure, i.e. ductility. The high hardness, high strength values, low ductility were attributed to the relatively higher hydrogen retention in the one-step sintered specimens. It was demonstrated that a novel two-stage spark plasma sintering strategy is extremely effective in delivering bulk titanium with high strength and high ductility.

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References

[1] M. Qian, Y.F. Yang, M. Yan and S.D. Luo; Key Engineering Materials Vol. 520 (2012) p. 24-29.

[2] Francis H. (Sam) Froes, Ma Qian; Titanium Powder Metallurgy, 2015, p. 601-608.

[3] M. Qian; Int. J. Powder Metall. 46 (2010) p. 29–44.

[4] Alireza Nouri, Peter D. Hodgson, Cuie Wen; Materials Science and Engineering C 31 (2011) p.921-928.

[5] C. F. Yolton, F.H. Froes; Method for Producing Powder Metallurgy Articles, (1980), US Patent 4,219,357.

[6] Bhupendra sharma, S. K. Vajpai, K. Ameyama; JALCOM 656 (2016) p.978-986; doi:10.1016/j.jallcom.2015.10.053.

[7] J. R. Groza, Antonios Zavaliangos, Materials Science and Engineering A287 (2000) p.171-177.

[8] R. Orru, R. Licheri, A.M. Locci, A. Cincotti,, G. Cao, Materials Science and Engineering R 63(2009) p.127-287.

[9] S. Grasso, Y. Sakka & G. Maizza, Science and Technology of Advanced Materials, 10 (2009), 053001 (24pp) DOI: 10.1088/1468-6996/10/5/053001.

[10] Z. A. Munir, D. V. Quach & M. Ohyanagi, Journal of American Ceramic Society, 2011, Vol. 94 [1] 1-19, DOI: 10.1111/j.1551-2916.2010.04210.x.

[11] Z. A. Munir, U. Anselmi-Tamburini, M. Ohyanagi; J Mater Science 41 (2006) p.763-777; DOI: 10.1007/s10853-006-6555-2.

[12] H. Wang, M. Lefler, Z.Z. Fang, Ting Lei, S. Fang, J. Zhang, Q. Zhao, Key Engineering Materials Vol. 436 (2010) pp 157-163.

[13] M. Biasotto, R. Riceeri, N. Scuor, C. Schmid, M.A. Sandrucci, R.Dilenarda, P. Matteazzi, Journal of Applied Biomaterials & Biomechanics 2003;1;172-177.

[14] C. Machio, R. Machaka, H. K. Chikwanda, Materials and Design 90 (2016) 757-766.

[15] C.I. Pascu, O. Gingu, P. Rotaru, I. Vida-Smiti, A. Harbor, N. Lupu, J therm Anal Calorim (2013) 113:849-857.

[16] L. Bolzoni, E.M. Ruiz-Navas, E. Gordo, Materials and Design (2014) 226-232.

[17] V. Bhosle, E.G Baburaj, M. Miranova, K. Salama, Materials and Engineering A356 (2003) p.190-199.

[18] A.R. Kennedy, V. H. Lopez, Materials Science and Engineering A 357 (2003) p.258-263.

[19] H. Nakamura, M. Koiwa, H. Asano, H. Murata, F. Izumi; Scripta Metallurgica, Vol.20 (1986) p.213-216.

[20] A. San-Martin and F.D. Manchester; Bulletin of Alloy Phase Diagrams, Vol. 8 No. 1, 1987; p. 30-42.

[21] O.N. Senkov, M. Dubois & J.J. Jonas, Metallurgical and Materials Transactions A, Vol. 27A, 1996, 3963-3970.

[22] Titanium: A Technical guide, Matthew J. Donachie, Jr., p13-24, DOI: 10.1361/tatg2000p013.

[23] Pei Sun, Zhigang Zak Fang and Mark Koopman, Advanced Engineering Materials 2013, 15, No. 10, p.1007-1013; DOI: 10.1002/1dem.201300017.

[24] C. L. Briant, Z. F. Wang, N. Chollocoop; Corrosion Science 44 (2002) p.1875-1888.

[25] Ervin Tal-Gutelmacher and Dan Elizer, Materials Transaction, Vol.45, no.5 (2004) p.1594-1600.

[26] A.M. Alvarez, I.M. Robertson, H.K. Birnbaum; Acta Materialia 52 (2004) p.4161-4175.

Table-1: Calculated lattice parameters of Ti-1 and Ti-2 Specimens

	Ti-1 Specimen			Ti-2 Specimen		
Lattice parameters	a (Å)	c (Å)	c/a (Å)	a (Å)	c (Å)	c/a (Å)
α-phase	2.94977	4.6932	1.591	2.9471	4.6884	1.590
δ-phase	4.41	-	-	4.39	-	-
γ phase	-	-	-	4.235	4.623	1.091

Table-2: Comparison of mechanical properties of bulk-Ti prepared by TiH_2 powder

Initial Material	**Method Of Preparation**	**Sintering Temp. (K)**	**Vickers Hardness (Hv)**	**YS (MPa)**	**UTS (MPa)**	**Elongation (%)**	**Ref.**
TiH_2 Powder	Press & sinter	1200	N/A	N/A	N/A	N/A	10
Ti+TiH_2 Powder	Hot Isostatic Pressing	1020	50±2 HRB (Rockwell B)	265	310	N/A	11
TiH_2 Powder	Press & Sinter	(1)900 (2)1200 (3)1300	170-225 290-320 320-340	N/A	N/A	N/A	12
TiH_2 Powder	Spark Plasma Sintering	(1)1000 (2)1050 (3)1100	360-420	N/A	N/A	N/A	13
Pure-Ti Powder	P/M compact, Annealed	N/A	N/A	370	480	18	19
Pure-Ti Powder	**One-Step SPS**	**1200**	**180**	**280**	**365**	**24**	**Present Study**
TiH_2 Powder	**One-Step SPS**	**1200**	**267**	**575**	**690**	**3.5**	**Present Study**
TiH_2 Powder	**Two-step SPS**	**1200**	**243**	**360**	**530**	**16**	**Present Study**

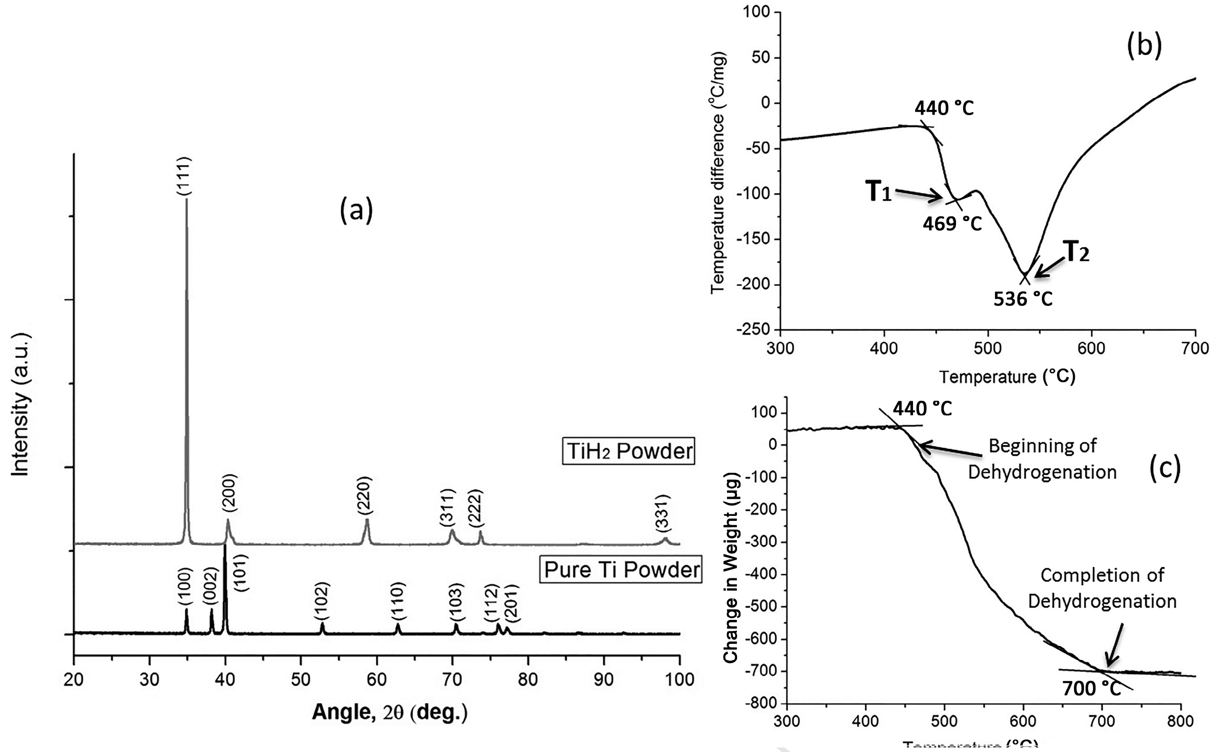
(N/A=data not reported)

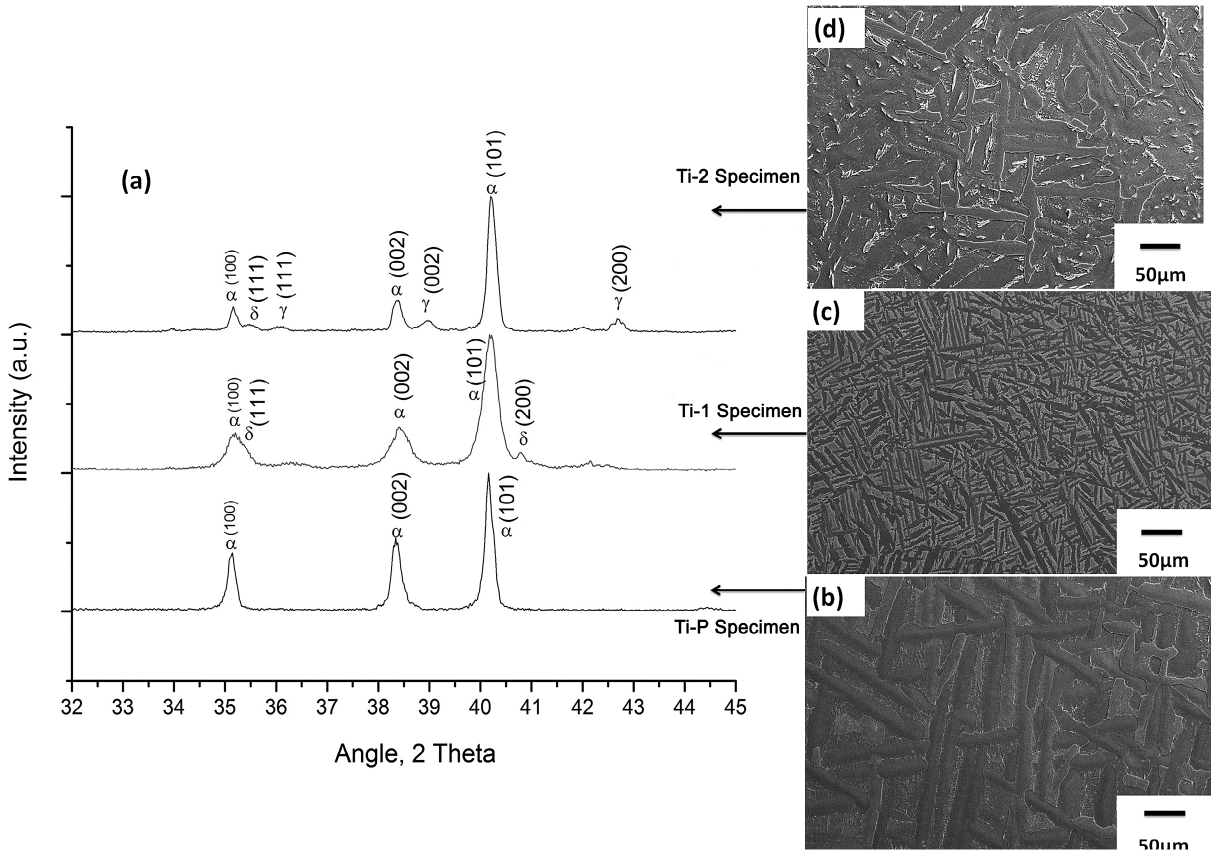
Figure Captions

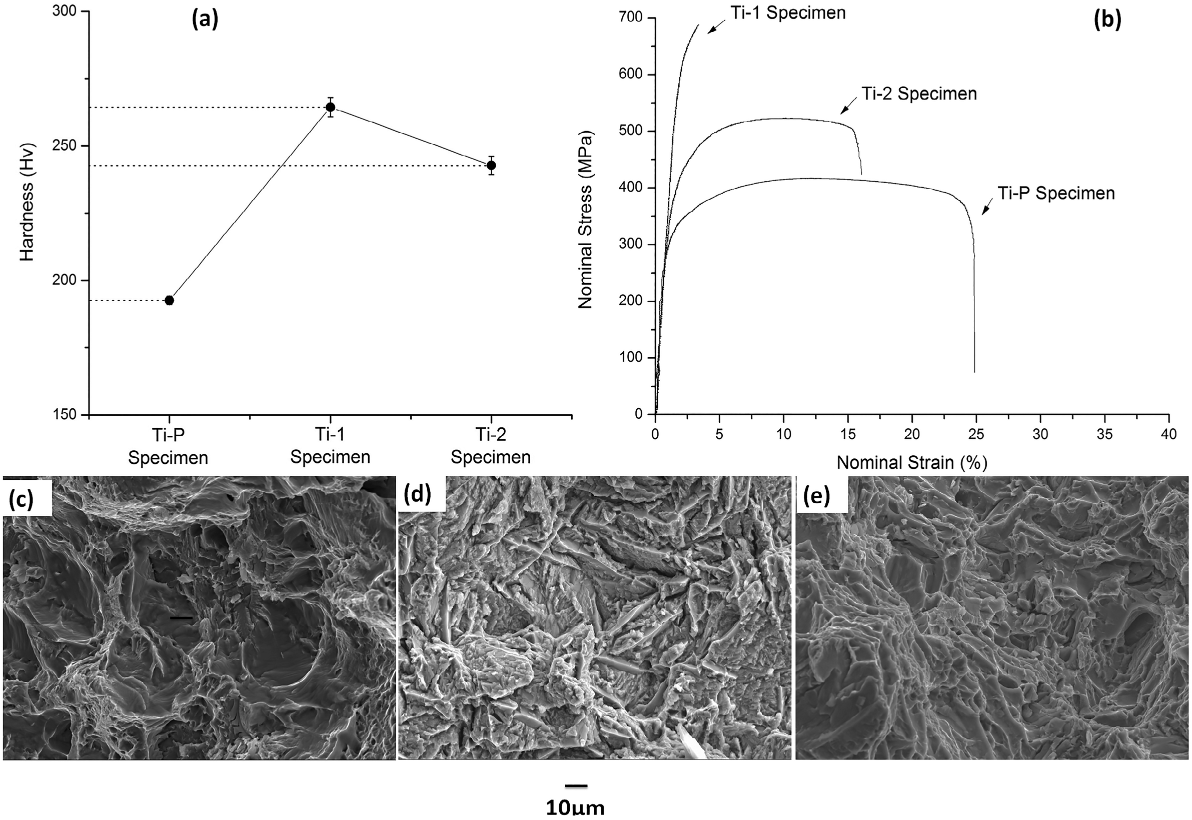
Fig.1. (a) XRD of as received Pure Ti and TiH_2 powders (b) differential thermal analysis (DTA) and (c) thermo-gravimetric analysis (TG) of initial titanium hydride powder

Fig.2. (a) XRD analysis and respective micrographs of (b) Ti-P, (c) Ti-1 & (d) Ti-2 specimens

Fig.3. (a) Hardness, (b) Stress-Strain curve and respective fracture surfaces of (c) Ti-P, (d) Ti-1 & (e) Ti-2 specimens


(a)
Intensity (a.u.)
TiH2 Powder
Pure Ti Powder
(111)
(200)
(220)
(311)
(222)
(331)
(100)
(002)
(101)
(102)
(110)
(103)
(112)
(201)
20
30
40
50
60
70
80
90
100
Angle, 2θ (deg.)
(b)
Temperature difference (°C/mg)
100
50
0
-50
-100
-150
-200
-250
440 °C
T1
469 °C
T2
536 °C
300
400
500
600
700
Temperature (°C)
(c)
Change in Weight (μg)
440 °C
Beginning of
Dehydrogenation
Completion of
Dehydrogenation
700 °C
100
0
-100
-200
-300
-400
-500
-600
-700
-800
300
400
500
600
700
800


(a)
Intensity (a.u.)
Angle, 2 Theta
α (100)
δ (111)
γ (111)
α (002)
γ (002)
α (101)
γ (200)
δ (200)
32 33 34 35 36 37 38 39 40 41 42 43 44 45
Ti-2 Specimen
Ti-1 Specimen
Ti-P Specimen
(d)
(c)
(b)
50μm
50μm


(a)
Hardness (Hv)
300
250
200
150
Ti-P Specimen
Ti-1 Specimen
Ti-2 Specimen
(b)
Ti-1 Specimen
Ti-2 Specimen
Ti-P Specimen
Nominal Stress (MPa)
700
600
500
400
300
200
100
0
Nominal Strain (%)
0
5
10
15
20
25
30
35
40
(c)
(d)
(e)
10µm

Highlights

- High density pure titanium compacts were prepared from titanium hydride powders.
- Two-step spark plasma sintering was extremely effective in dehydrogenation of TiH_2.
- The proposed method resulted in bulk-Ti with high strength and good ductility.