Synthesis of Ternary Ti-25Nb-11Sn Alloy by Powder Metallurgy Route Using Titanium Hydride Powder

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In the present work, Ti-25Nb-11Sn (mass%) alloys were successfully prepared by an advanced powder metallurgy method. The alloys were synthesized by mechanical milling of powder mixture, consisting of titanium hydride (TiH2), elemental niobium (Nb) and elemental tin (Sn) powders, followed by their consolidation via Spark Plasma Sintering (SPS) method. The use of brittle TiH2 powder, instead of ductile elemental Ti powder, resulted in ~100% powder yield of mechanically milled (MMed) powder even after long time mechanical milling. The resulting MMed powders consisted of homogeneously distributed nano-sized titanium/niobium hydride powder particles together with a few micron-sized pure Nb particles. The mechanical milling also led to the lowering of dehydrogenation temperature of the hydride particles. Sintering of short time mechanically milled powder (72 ks) resulted in the fine-grained heterogeneous microstructure consisting of β phase and orthorhombic martensitic α’ phase. On the other hand, sintering of long time mechanically milled powder (180 ks) resulted in the evolution of β-phase and α’-phase. The specimen containing α+β phase exhibited higher average hardness as compared to the average hardness of specimen containing α’+β phase.

Keywords: titanium hydride, mechanical alloying, spark plasma sintering, beta titanium-niobium-tin alloys

1. Introduction

Among structural biomaterials, titanium and titanium alloys exhibit the most suitable characteristics for structural medical implants in the human body, due to the combination of its outstanding properties such as excellent biocompatibility, good corrosion resistance, and high specific strength. In particular, it has been reported that the currently used titanium alloys, such as Ti-6Al-4V, are composed of cytotoxic elements like V and Al, which may cause severe problems in the human body1,2. Besides the issue of allergic elements, another issue with the existing titanium based biomaterials is that their modulus of elasticity is significantly higher (>100 GPa) than that of human bone (<30 GPa), leading to stress-shielding that can potentially cause bone resorption and eventual loosening of implanted device. Therefore, it is desirable to use low Young’s modulus titanium alloys which are free from potential allergic or carcinogenic elements. Recently, beta titanium (β-Ti) alloys, containing niobium (Nb) and tin (Sn), have been found to possess very low Young’s modulus (~36 GPa), which is comparable to the Young’s modulus of human bone (~30 GPa). Furthermore, Nb and Sn are favorable non-allergic and non-carcinogenic alloying elements. Therefore, Ti-Nb-Sn alloys are considered as a very promising biomaterials for long-term structural implant applications in the human body.

In spite of all the excellent properties, use of titanium-based alloys is very limited due to the high initial cost, complex fabrication, and subsequent machining processes. Therefore, there is an urgent need for the development of a suitable fabrication strategy to prepare commercially viable and acceptable quality Ti-based products. A conventional powder metallurgy (P/M) based processing approach based on cold compaction of powders followed by pressure-less sintering, which is also called “blended elemental powder method (BEPM)”, is considered as most cost effective near-net shape process. Therefore, it could be a suitable method to achieve low cost near-net shape products. However, an initial high cost of high purity Ti powder and its high reactivity with the air, during fabrication process, in combination with the poor mechanical properties has restricted the BEPM approach to be exploited for commercial applications.

Over the past few years, the advance P/M process based on mechanical milling (MM) of elemental powders followed by their rapid sintering, such as spark plasma sintering, has been taken into account for synthesizing a wide variety of alloys with fine-grained microstructure and excellent mechanical properties. Furthermore, this approach is also capable of preparing complex alloy systems, wherein various alloying elements have a wide difference in their melting points; thus, difficult to prepare through conventional ingot metallurgy route. Therefore, it is envisaged that such an advanced P/M process can overcome those issues and, therefore, could be a promising approach of preparing a variety of titanium-based alloy systems. However, it has been reported that, during mechanical milling process, titanium powder has a very high tendency to agglomerate and cold weld with the vial walls and balls due to highly ductile nature of titanium powder, which may result in compositional change and/or low recovery of milled powder. Although, the issues of agglomeration and sticking of powder, during mechanical milling, can be controlled by using suitable Process Control Agents (PCA), such as stearic acid and ethanol, but it also leads to the introduction of contaminations such as formation of carbides, nitrides, and oxides in the MMed powders. Therefore, these issues need to be addressed to exploit powder metallurgy approach as a suitable processing route to prepare near-net shape components of titanium-based alloys.

Recently, researches underline the advantages of titanium hydride powder to be used as a precursor for titanium. In particular, use of extremely brittle TiH2 powder, instead of highly ductile pure titanium powder, can overcome the sticking/
agglomeration issues without adding any process control agents, and, therefore, can also control the contamination related issues, during mechanical milling/alloying process. As a result, a uniform distribution of elemental powders with almost complete recovery can be ensured even after a long time mechanical milling. It has also been reported that temporary hydrogen alloying can have a beneficial effects on the microstructure, i.e. it refines the microstructure\(^\text{11}\). Moreover, ultra-fine grained Ti alloys are reported to exhibit superior properties, viz. higher wear resistance and increased cell adhesion, compared to the coarse grained counterparts, owing to its high surface energy at the grain boundaries\(^\text{12}\). With the aim of maintaining ultra-fine grained microstructure after compaction of MMed powders, a suitable rapid sintering process had to be used. Therefore, a pressure assisted sintering, such as “Spark Plasma Sintering (SPS)” process under high vacuum, can be a suitable approach, which also ensures compaction of MMed powders with very high density and without introducing any appreciable contamination\(^\text{13,14}\).

In the present study, an attempt has been made to fabricate fine-grained beta Ti-25Nb-11Sn alloys via a new powder metallurgy approach. In principle, the proposed P/M route is based on mechanical milling of powder mixture, containing titanium hydride, niobium and tin, followed by their sintering via spark plasma sintering method. The effects of mechanical milling time on the dehydrogenation temperature of hydride powder have been evaluated by thermal analysis. Moreover, microstructure and mechanical properties of the sintered Ti-25Nb-11Sn alloy compacts have been evaluated, and the results related to this aspect are presented and discussed.

2. Experimental Procedures

Titanium hydride powder (with the purity of 99.9% and mean particle size of 25 µm) and elemental metal powders of Nb (with the purity of 99.9% and mean particle size of 20 µm) and Sn (with the purity of 99.5% and mean particle size of 20 µm) were weighed (in argon atmosphere) to achieve an initial nominal composition of Ti-25Nb-11Sn (mass%) powder mixture. The particle size distribution analysis was performed by laser diffraction particle size analyzer (SHIMADZU, SALD-2300). The SEM micrographs of the as received initial powders (IP) are presented in Fig. 1. The Initial powder particles exhibit the irregular shaped morphology having both coarse and fine-sized particles. An X-ray diffraction (XRD) analysis (Fig. 2) of the initial powders revealed that TiH\(_2\) and Nb, both the powders, had cubic crystal structure whereas Sn had tetragonal crystal structure.

Ti-25Nb-11Sn powder mixture was mechanically milled under argon atmosphere at room temperature, using planetary ball mill with stainless steel balls and vials, operating at a speed of 200 rpm. The ball to powder weight ratio was kept 5:1. The powder mixture was mechanically milled for a total time period of 72 ks and 180 ks, separately. The mechanically milled powders were sintered via Spark Plasma Sintering (SPS) under high vacuum conditions using graphite die and punch. In order to prepare high density compacts with negligible porosity, temperature and compression pressure were programmed to rise simultaneously, until stabilized to the maximum operational temperature and compression pressure, and hold it at the same conditions for 1.8 ks. Disc shape compacts with diameter of 15 mm and thickness of 5 mm were prepared. The specimen prepared by the sintering of 72 ks MMed powder is further referred as ”specimen-A” and the specimen prepared by the sintering of 180 ks MMed powder will be further referred as ”specimen-B”.

The various phases of powders and compacts were analyzed by X-ray diffraction (XRD) analysis with a CuK\(_\alpha\) (\(\lambda = 0.15406 \text{ nm}\)) source at 40 kV voltage and 30 mA current. The microstructural characterization of the initial powders, MMed powders, and sintered compacts was carried out by Scanning Electron Microscope (SEM) equipped with Back Scattered Electron (BSE) detector. A basic compositional analysis was carried out by Energy Dispersive X-ray Spectroscopy (EDS) method. Mechanical properties of the sintered compacts were evaluated by Vickers micro hardness measurements. Average Vickers micro-hardness was estimated by indentation under load of 4.903N (HV0.5) and dwelling time of 15 s. An average of 20 indentations (randomly taken on the cross-section side of mirror polished specimens) was taken as the representative hardness value of the test specimens.

![Fig. 1](image) The morphology of as received (a) titanium hydride powder (b) pure Nb powder and (c) pure tin powder.

![Fig. 2](image) XRD pattern of initial powder mixture of titanium hydride, niobium and tin powders.
3. Results and Discussion

3.1 Yield, morphology, and structure of the mechanically milled powder

It is important to mention that the net weight of the as mixed powder (before mechanical milling) was 30 gram (i.e. 19.2 g TiH₂, 7.5 g Nb and 3.3 g Sn), and approximately ~30 g powder was recovered after mechanical milling for short time (72 ks) as well as after long time (180 ks), i.e. almost 100% powder was recovered. Therefore, it can be presumed that titanium hydride completely suppressed the sticking of powders during mechanical milling process.

The XRD pattern of initial powders’ mixture, as presented in Fig. 3, is compared with the XRD patterns of 72 ks and 180 ks MMed powders. The XRD pattern of the as-mixed powder comprised of peaks of respective initial powders (TiH₂, Nb and Sn) only, i.e. confirmed the absence of any significant oxidation or reaction between the initial powders during mixing stage. XRD pattern of mechanically milled powders (for 72 ks and 180 ks) are shown in Fig. 3. No visible contamination peaks (i.e. Oxides, Nitrides, carbides etc.) were found to be present in the XRD patterns of the milled powders. Together with the significant change in the peak intensity and peak width of the initial powders, interestingly, some new phases also evolved in the powder mechanically milled for 72 ks, as seen in the Fig. 3. An analysis of new peaks with the available XRD crystallographic database (JCPDS) indicated that these new peaks correspond to the niobium hydride (NbH). Such kind of hydrogenation behavior was also observed and discussed in other studies.15–17 Moreover, long time mechanical milling (180 ks powder) resulted in further peak broadening and reduction in the peak intensity of corresponding to titanium hydride phase, whereas XRD peak intensity increased for niobium hydride phase, as shown in Fig. 3. XRD peak broadening and intensity reduction can be attributed to the severe plastic deformation and fragmentation of powder particles during mechanical milling.18 It was observed that long time mechanical milling for 180 ks resulted in the disappearance of Nb and Sn peaks. There are two possible reasons for such disappearance of niobium and tin: (i) long time mechanical milling resulted in ultra-fine particles; therefore, the XRD peak intensity is extremely low and can’t be observed in the XRD pattern where-as peaks corresponds to the elemental niobium merged in the XRD peak of niobium hydride. (ii) Short time mechanical milling of the elemental powders (Nb and Sn) first produces the crystalline compound, which after prolonged mechanical milling, transforms to the amorphous state19. Therefore, it can’t be seen in the XRD analysis.

The detailed mechanism of particle size refinement by mechanical milling/mechanical alloying is presented by Gilman et al.20, Benjamin et al.21 and Koch et al.22. In those studies it is mentioned that in the early stages of milling process, the initial powder particles forms layered composites in which the powder particles may vary in size from few micrometer to hundred micrometers. With increase in milling time, fracturing and cold welding continues and leads to the comparatively (compared to the milling for short duration) smaller particle size with the composition of individual particles converging toward the overall composition of the starting powder mixture. Therefore, in the present study, 180 ks MMed powder displayed homogeneous powder mixture.

For a better understanding of the effect of mechanical milling process on the powder morphology, SEM and BSE analysis, as shown in Fig. 4, was carried out on the powders mechanically milled for a different time periods. A comparison of the powder morphology of 72 ks and 180 ks MMed powder mixtures (Fig. 4) with initial powders (Fig. 1) clearly shows that the mechanical milling led to the severe fragmentation of starting powders. Short time MMed powder (72 ks) can be distinguished by particle sizes of the nano-range (~500 nm) and few-micrometer size range. Through BSE analysis (Fig. 4(a)), it was revealed that the color composition of the coarse particles is brighter (i.e. heavy element) whereas for small particles it is relatively darker (i.e. comparatively lighter element). Therefore, it can be primarily assumed that the coarse particles are Nb rich particles.

In order to detect the elemental composition of mechanically milled powder, an EDS analysis as shown in Fig. 5, was carried out. EDS analysis of both the powders milled for 72 ks (Fig. 5(a)) and 180 ks (Fig. 5(b)) also indicated that the nano-sized particles were a mixture of Ti, Nb and Sn particles, whereas relatively coarser particles were only Nb-based particles. Possibly, such kind of variation in the size of pow-

![Fig. 3 XRD pattern of initial powder mixture and powders mechanically milled for 72 ks and 180 ks.](image)

![Fig. 4 Morphology of (a & b) 72 ks MMed powder and (c &d) 180 ks MMed powders (high magnification BSE micrograph of 72 ks MMed powder is shown in fig. 4(a)).](image)
under particles can be attributed to the brittle niobium hydride phase formed during mechanical milling, due to the mechanical-chemical reaction. It has been reported, elsewhere, that NbH is a very brittle phase, similar to the titanium hydride, and it can be pulverized into fine-sized particles during mechanical milling[23]. In case of long time mechanical milling, Nb surface continuously absorbs surrounding hydrogen, which comes from titanium hydride particles, and forms NbH and gets fragmented continuously due to its brittle nature, leading to the formation of nano-sized NbH particles. Hence, it can be observed that nano-sized particles of Nb are the result of NbH pulverization and relatively larger size particles are the result of Nb inner core. This phenomenon demonstrates that the TiH2-Nb-Sn powder mixture undergoes microstructural and phase changes owing to the combined effect of fragmentation of hydride particles and plastic deformation mechanism. The similar kind of active surface effect is reported by Sharma et al.[15] and Kazuto et al.[24]. Furthermore, the EDS analysis also demonstrated that there was no evidence of presence of any appreciable amount of oxygen or any other contaminant in both the MMed powder mixtures.

3.2 Thermal analysis

The phase transformation of initial powder mixture and mechanically milled powders was analyzed by differential thermal analysis (DTA) and results are presented in Fig. 6 (a), (b) and (c) respectively. The DTA plot of as mix powder (Fig. 6(a)), powder mechanically milled for 72 ks (Fig. 6(b)) and powder milled for 180 ks (Fig. 6(c)) shows three thermal events represented by peak P1, P2 and P3, respectively. All the thermal events, represented by P1, P2 and P3, are of endothermic in nature. The DTA plot of all the three powders, i.e. as-mixed power, 72 ks MMed powder and 180 ks MMed powder, showed small endothermic peak-P1 at approximately ~504 K, which is the melting point of Sn. Therefore, peak-P1 can be directly associated with the melting of Sn. The DTA plots show two consecutive thermal events represented by peak-P2 and P3 for all three powders. These peaks can be associated with the effect of endothermic nature of dehydrogenation process. These two consecutive peaks clearly indicated that the dehydrogenation occurred in two stages. In an study, Bhosle et al.[25] also demonstrated that dehydrogenation of TiH2 occurs in a two-step process as; TiH2 → TiHx → α-Ti, where 0.7 < x < 1.1.

A considerable difference is noticeable between the dehydrogenation of as-mix powder (with particle size ~20–25 µm) and those mechanically milled for 72 ks and 180 ks (with particle size in nano to sub-micron size range). It can be observed that, as compared to the as-mix powder, the first dehydrogenation peak P2 for MMed powders are significantly shifting toward lower temperature side. This peak shifting indicates that, mechanical milling for extended time leads to the dehydrogenation of TiH2 to TiHx at relatively lower temperatures. A possible explanation for such peak shifting is the ease of decomposition of higher hydrogen containing titanium hydride phase (TiH2) due to (i) reduced particle size, (ii) increased surface area, and (iii) increase in defect concentration. A similar shifting was also observed for peak-P3, i.e. with increasing milling time, dehydrogenation from TiHx to Ti also occurs at a relatively lower temperature. Interestingly, the amount of hydrogen evolution during first stage significantly increased with increasing milling time whereas hydrogen evolution during second stage decreased with the increasing milling time. The results reported by Bhosle et al.[25] are in good agreement with the results shown in the present study. Similar to the dehydrogenation of titanium hydride powder, niobium hydride also can be dehydrogenated at approximately 653 K–763 K[26]. It is also shown above that the dehydrogenation temperature of a particular hydride depends on the powder particle size, i.e. can be changed with the particle size. In particular, the dehydrogenation temperature presented by Gabrial et al.[26], was for the NbH powder with particle size approximately 20 µm, whereas in the present study the particle size of niobium hydride, formed due to mechanical milling during mechanical milling, is almost in the nanometer size range. Therefore, it can be presumed that dehydrogenation of niobium hydride particles, present in the MMed powders (72 ks and 180 ks), would start and complete at lower temperatures due to relatively smaller particle sizes, as compared to those reported for the comparatively coarser particle size. It appears that the peaks corresponding to the dehydrogenation of NbH particles are superimposed on the peaks corresponding to titanium hydride phases. Nevertheless, it can be clearly observed that dehydrogenation of both titanium hydride and niobium hydride is almost completed well below 1000 K.

Furthermore, change in the powder weight during heating at a constant rate was analyzed by thermo-gravimetric analysis (shown in Fig. 6(d)). Weight changes occur due to the evo-
Table 1  Endothermic Peak positions (DTA plot) and dehydrogenation start and completion temperatures (TG plot) of As-mix and MMed powders.

<table>
<thead>
<tr>
<th>Powders</th>
<th>DTA Analysis (Temperature in Kelvin)</th>
<th>TG Analysis (Temperature in Kelvin)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Peak P1</td>
<td>Peak P2</td>
</tr>
<tr>
<td>As-Mix powder</td>
<td>504</td>
<td>745</td>
</tr>
<tr>
<td>MMed for 72 ks</td>
<td>504</td>
<td>650</td>
</tr>
<tr>
<td>MMed for 180 ks</td>
<td>504</td>
<td>620</td>
</tr>
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Fig. 7  XRD patterns of the Ti-25Nb-11Sn compacts prepared by sintering of 72 ks (specimen-A) and 180 ks (specimen-B) MMed powders.

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higher amounts of hydrogen evolved during sintering process. Therefore, uniform powder mixture combined with lower retained hydrogen content resulted in the hcp-α and bcc-β phase without formation of α’ martensitic phase. The calculated lattice parameters for β-phase is: \( a = 0.329793 \, \text{nm}, \) and for α-phase, it is: \( a = 0.2966 \, \text{nm}, \) and \( c = 0.469162 \, \text{nm}. \) These calculated lattice parameters are in good agreement with the results reported in other studies.

In comparison to the lattice parameters of β-phase (\( a = 0.3324 \, \text{nm} \)) of specimen-A, lattice parameters of β-phase (\( a = 0.2966 \, \text{nm} \)) of specimen-B are smaller. Hao et al.\(^{27}\) has shown that an increasing amount of Nb increases the lattice parameter of β-phase. Therefore, it can be presumed that the β-phase in the specimen-A contains higher amounts of Nb as compared to the amount of Nb in the beta phase of specimen-B. The lattice parameter results are in good agreement with the XRD results shown above.

It should be noticed that the XRD peaks of β-phase is significantly broader and less intense, as compared to the β-phase of specimen-A. Therefore, it can be envisaged that the grain size of β-phase of specimen-B is significantly smaller as compared to the grain size of β-phase of specimen-A.

The typical SEM and BSE (backscattered electron) micrographs of the bulk Ti-25Nb-11Sn alloys, prepared by sintering of 72 ks MMed powder (Specimen-A) and 180 ks MMed powder (Specimen-B), are shown in Fig. 8. The Ti-25Nb-11Sn samples presented high densification, ~100% without appearance of any porosity. The microstructural analysis of specimen-A revealed that the beta phase is surrounded by the martensitic phase in the form of dense cluster of thin white needles. Moreover, very clear needle-like traces of martensitic phase can also be noticed inside the β-grains. The microstructure observed in the present study is very similar to the one reported by Eiji et al.\(^{31}\) and A. J. Prabha et al.\(^{32}\). Upon further milling to 180 ks, the microstructure of the sintered samples (Specimen-B) displayed a homogeneous distribution of the fine β-phase with α-phase. Moreover, no significant amount of martensitic phase was registered both in XRD pattern (as shown in Fig. 7) and microstructure analysis (Fig. 8(c) & 8(d)). Generally, in presence of hydrogen, the grain refine-
fraction of various phases and grain sizes. The higher hardness of specimen-B can be directly attributed to the either/both (i) effect of grain size or/and (ii) phase constituents. In general, with decreasing grain size hardness increases. On the other hand, Specimen-B consists of $\alpha + \beta$ phase, which has higher hardness as compared to the specimen-A which consists of $\beta + \alpha'$ phases. The reference results are consistent with the study performed by M. Ikeda et al. 34. It was demonstrated that Ti-Ta alloy with $\alpha + \beta$ phase has higher hardness as compared to that of Ti-Ta alloys with $\alpha'$ phase. Therefore, it can be presumed that the higher hardness of specimen-B is the combined effect of relatively smaller grain size and presence of $\alpha + \beta$ phases. The retention of hydrogen in the sintered material can also be related to the fact that complete dehydrogenation can only be achieved under conditions having high vacuum, no external pressure, and long heat treatment time. Therefore, it appears that dehydrogenation under pressure, during SPS, also had an impact on the retention of hydrogen in the sintered compacts. However, it must be pointed out that a long time heat-treatment can lead to an inefficient dehydrogenation, resulting in better mechanical properties.

4. Conclusions

Ternary Ti-25Nb-11Sn alloys were successfully synthesized from mechanical milling of titanium hydride, niobium and tin elemental powders, followed by their consolidation via spark plasma sintering technique. The use of brittle titanium hydride prevented the agglomeration, cold welding, and sticking of powders to the balls and vial’s walls during the planetary ball milling process. The mechanical milling for short time (72 ks) as well as long time (180 ks) resulted in a very high powder yield (~100%) after milling. The powder milled for short time consisted of bimodal particle size distribution, i.e. few micron-sized Nb and a mixture of nano-sized titanium hydride, niobium and tin particles, whereas long time milling (180 ks) resulted in a uniform distribution of fine sized niobium hydride and titanium hydride powder particles. Spark plasma sintering demonstrated the capability to prepare pore free high density compacts. The microstructure of bulk specimens prepared by sintering of 72 ks and 180 ks MMed powders exhibited $\beta + \alpha'$ and $\beta + \alpha$ phases, respectively. The hardness of the specimen prepared by long-time milled powder exhibit higher Vickers microhardness as compared to the microhardness of the specimen prepared by relatively short-time milled powder.

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