Fabrication and characterization of Ti-Nb-HA alloy by mechanical alloying and spark plasma sintering for hard tissue replacements

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Abstract. In the present research work, a β-type Ti-35Nb-10HA alloy was successfully fabricated by mechanical alloying of titanium (Ti), niobium (Nb), and hydroxyapatite (HA) powders followed by consolidation using Spark Plasma Sintering technique. The effect of HA on the microstructure and mechanical properties were studied. The microstructure, surface topography, and element composition of the Ti-Nb-HA alloy was investigated using optical microscope, field-emission scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The micro-hardness of the specimens was measured on a Vickers hardness tester. The microstructure examination of the compact revealed that the alloy distinctly shows the primary grain boundaries along with secondary grain boundary. It was observed that complex reactions between HA and alloy elements occurred during the sintering process of Ti-35Nb-10HA alloy and biocompatible phases [Ca₃(PO₄)₂, CaTiO₃, Nb₅P₃, CaO, Ti₅P, Nb₄O₅, and TiO₂] were generated in the compact, which is beneficial to form apatite and improved the bioactivity of the alloy for osseointegration. The fabricated Ti-35Nb-15HA alloy exhibits maximum micro-hardness (~786 HV), which is very high value as compared to the alloys reported in literature. Based on these above observations, it is expected that the as-fabricated Ti-35Nb-10HA alloy is suggested for dental and orthopaedic applications.

1. Introduction
To meet the requirements of joint replacement challenges, the development of various implants material has been witnessed and the need of biomaterials is increasing rapidly [1]. Biomaterial artificial or natural material is used to fabricate the artificial organ or implants to restore the functionality of diseased or dysfunctional natural organ [2]. The biomaterials are categorized as metallic, ceramics and polymers [3]. The common metallic biomaterials are stainless steels (SUS-316L), cobalt-chromium (Co-Cr), titanium (Ti) and its alloys [4]. Among these, Ti and its alloys have recently gained increasing attention for application in the biomedical field owing to their superior biocompatibility and excellent mechanical properties [5]. There are some serious weaknesses of the Ti alloys: (1) the elastic modulus of Ti alloys (CP-Ti and Ti-6Al-4V) are much high (110 GPa) as compared to bone (10–45 GPa). This distinct mechanical mismatch of elastic modulus between the implant, the surrounding bone and its tissues will cause stress shielding, which start bone resorption.
and implant start loosening and results in implantation failure [8]. (6-7); (2) the presence of Al and V restricts the applicability of Ti-6Al-4V because during abrasion, it releases ions and creates cytotoxicity which results in allergic reactions. As a result of this, the implant must be removed from the body by using a secondary surgical intervention and additional surgery causes an increase in costs to the health care system, as well as emotional stress to the patient [8]. In order to overcome above said drawbacks, the researcher developed biocompatible V and Al-free β-phase Ti alloy such as Ti-Nb, Ti-Zr, Ti-Nb-Zr, Ti-Nb-Ta-Mo, Ti-Nb-Ta-Sn and Ti-Nb-Ta-Zr (TNTZ) alloys [2,4,5, 9-12]. Recently developed β-Ti alloys have lower elastic modulus of 55 GPa (comparable with that of bone i.e., ~20 GPa), higher strength, lower density, better corrosion resistance abilities, and superior biocompatibility than commercially pure Ti and Ti-6Al-4V alloys [13-17]. The β-type Ti-33Nb-7Ta-5Zr alloy has been widely used for the fabrication of biomedical implant, due to its unique combination of mechanical properties especially low elastic modulus (55 GPa), non-toxic, excellent biocompatibility and superior electrochemical properties [18-19]. The Nb β-stabilizer reduces the elastic modulus and decreases stress shielding difference between bone and implant, and promotes load sharing [20-22]. The Zr element provide a high level of blood compatibility and the Nb and Ta elements provides a passive oxide film consisting of dense rutile structure on the alloy surface enhanced corrosion properties and bioactivity [23-26]. However, despite their excellent mechanical properties, Ti and its alloys do not effectively meet the requirements of osseointegration that involves efficient binding to surrounding tissues and bone [27]. Thus, to maximize their bioactivity, the surface of Ti-based implants has been modified by depositing a layer of bioactive substance hydroxyapatite (HaP) through mechanical, physical, chemical, or biochemical treatments, which increases the fabrication cost of the implants [2,12,28]. For this reason and in order to avoid secondary treatment, a better fabrication technology for the production of nanoporous bio-compatible structure, low modulus β-type Ti alloys comprising non-toxic and non-allergic elements are urgent needed for the next generation of implants.

There are various new fabrication technologies such as laser beam machining, ion beam machining, hot isostatic pressing (HIP) and hot sintering, has been developed and used for the production of nanoporous bio-compatible structure of β-type Ti alloys [29-30]. These techniques produce nano-porous structure, but there long sintering time, temperature weaken the mechanical and electrochemical properties, which failed the implant at cyclic load condition and long term performances. Recently, the nano-porous β-type Ti alloys was successfully fabricated by a Spark Plasma Sintering (SPS) technique using powder metallurgy route consisting of mechanical alloying powders [31]. As a novel powder sintering process with distinct characteristics compared with conventional sintering techniques, the spark plasma sintering (SPS) technique enables alloys with good properties to be fabricated in a shorter holding time and a high pressure at rapid heating and cooling rates (>100 °C/min) and relatively lower sintering temperature [32]. Sharma et. al. fabricated nano-porous β-type Ti-Nb alloy by spark plasma sintering process using powder metallurgical route for mechanical alloying of Ti and Nb powders. The Ti-Nb alloy exhibited low elastic modulus and high hardness (530 HV) at 1525 K of sintering temperature [33]. Zhang et. al. fabricated interconnected nanoporous Ti-HA biocomposite by spark plasma sintering process. It was reported that the SPS-prepared nanoporous Ti-HA biocomposite possessed not only low elastic modulus (8-15 GPa) but also exhibited high compressive strength (86-388 MPa) and also good bioactivity [34]. Hussein et. al. fabricated nano-grained Ti-Nb-Zr alloy using mechanical alloying and subsequent spark plasma sintering technique. The developed nano-structured alloy exhibited better microstructure and much high surface hardness (660 HV) as compared to the same alloy with other techniques [35]. Han et. al. fabricated Ti-Zr-Ni quasicrystalline alloys by spark plasma sintering technique and studied their mechanical properties such as micro-hardness, young’s modulus, tensile, and compressive strength. It has been reported that the maximum micro-hardness, compression strength, the elastic deformation and Young modulus of the alloy was 7.03 GPa, (662 ± 50) MPa, 2.7 ± 0.1%, and (30 ± 3) GPa, respectively. The synthesized alloy also exhibited excellent wear resistance properties [36]. He et. al. synthesized nanoporous β-type Ti-13Nb-13Zr-HA alloy by spark plasma sintering process using powder metallurgical route for
mechanical alloying of powder (Ti, Nb, Zr, and HA) and the effect of HA content on microstructure, mechanical and corrosion properties has been studied [37]. Patra et. al. fabricated nano-Y$_2$O$_3$ dispersed W-Ni-Mo and W-Ni-Ti-Nb alloy using by spark plasma sintering process using powder metallurgical route for mechanical alloying of powder [38], Zou et. al. synthesised and fabricated successfully Ti-35Nb-7Ta-5Zr alloy using mechanical alloying and spark plasma sintering technique. A nano-/ultrafine grained alloys with high strength and high hardness compared to same alloys with other technique were prepared [39-40].

Till date no research study has been reported on the fabrication of Ti-35Nb-10HA alloy by combining powder metallurgical route for mechanical alloying of powders and spark plasma sintering technique. So, in the present research work the investigation on the fabrication of porous Ti-Nb-HA alloy by spark plasma sintering process using powder metallurgical route are urgent needed for the next generation of implants. A comprehensive and critical investigation of the microstructure, morphology, phase composition, mechanical properties like micro-hardness and elastic modulus of the as-prepared alloys were conducted to evaluate the efficacy of SPS technique as a porous implant fabrication for preparing materials for biomedical applications.

2. Materials and Method

2.1. Alloy design and Mechanical Alloying

The composition of the Ti-Nb-HA alloy was designed and selected by combining the d-electron alloy design method with the molybdenum equivalence (Moeq) and electron to atom ratio approaches. The Elemental powders of Ti (Purity 99.9%, 25µm), Nb (Purity 99.9%, 25µm), and HA (Purity 99.9%, 0.5 µm) were used as alloying materials. The powders were mixed in an atomic weight percentage of 35% Nb, 10% HA, and rest is Ti. Figure 1 shows the shape and size of powder particles before mechanical alloying. The powder mixture was weighed and loaded in tungsten carbide vial with tungsten carbide balls to give a call to powder weight ratio of 10:1. The powder mixture was mechanically alloyed in a high energy planetary ball mill (Fritsch, Pulverisette 7) at rotational speed of 300 rpm for 8 hrs.

![Figure 1. SEM micrograph of raw powders showing morphology: (a) Titanium; (b) Niobium; (c) Hydroxyapatite](image)

2.2. Consolidation of powders using Spark Plasma Sintering

The alloyed mixture of powders was first pre-heated at 500 ºC for 2 h in an argon atmosphere (1 l/min) to evaporate the moisture and that consolidated via spark plasma sintering (SPS) method in a graphite
die at different sintering temperatures 950, 1100, 1250 °C with heating rate of 100 K/min (holding time 10 min) under vacuum conditions and the uniaxial pressure was maintained at 50 MPa [37-39]. A circular compact with diameter 20 mm and thickness 5 mm was fabricated. Figure 2 shows the photograph of high energy planetary ball mill, spark plasma sintering (SPS) machine (Dr. Sinter SPS-625, Fuji Electronic Industrial Co. Ltd., Japan), blended sample of powder in graphite die, red hot sample under vacuum condition during the process, and as-consolidated sample.

2.3. Characterization and Mechanical property Analysis

After consolidation of the alloy, the microstructure and morphology was investigated by optical microscope and field emission scanning electron microscopy (FE-SEM; JEOL 7600F), respectively. Before examination of microstructure, the specimens from sintered compact was prepared by adequate polishing methods [29,31]. After polishing the sample was etched with Kroll’s reagent, containing of 10 ml HF, 5 ml HNO₃, and 85 ml H₂O for 20s. The elemental and phase composition the compact was evaluated by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD; X’pert-PRO) using CuKα radiation at 45 kV, 40 mA at incident angle 2θ. The elastic modulus and hardness are the base property of the biomaterial is of interest for load bearing application. Nano-indentation is the only technique for determining both elastic modulus and nano-hardness of the material in a single experiment. Nano-indentation test was performed on Hyistron TI-950 indentation system using berkovich indenter. The hardness and elastic modulus of the composite were determined using Oliver-Pharr method.

![Figure 2. Photograph of equipments used in Sintering: (a) high energy planetary ball mill; (b) spark plasma sintering (SPS) machine; (c) blended sample of powders in graphite die; (d) red hot sample under vacuum condition; (e) as-consolidated sample.](image-url)
3. Results and Analysis

3.1. Microstructure of sintered Ti-Nb-HA alloy

Figure 3 shows the microstructure of the polished surface of sintered Ti-Nb-HA alloy at different sintering temperature. The microstructure examination raveled that the primary grain boundaries are clearly identified along with secondary grain structure. There are distinct gray and white areas along with dendritic structure was clearly seen from the micrographs. The gray area is Ti element enriched areas and white one is Nb element enriched areas. Apart from the presence of base metal elements, some residues (possible oxides) were also identified on the surface, except few micro-sized craters-like defects are observed randomly on the surface as dark black dots which are common observation in the SPS-treated surface. This is attributed due to the release or grain pullout of HA like bioceramics particles from the matrix during polishing and mechanical grinding [37]. In the previous research, it was reported that some perishing phases (TCP, CaTiO3 and Ti₅P₃) possessed poor bonding in the matrix and pull out due to brittle failure during grinding and mechanical polishing action [30]. It has also reported that large amounts of gases are released due to chemical reaction between the alloying elements and HA powders that leads to the creation of porosity and foamy-like shapes in the structure [15].

Figure 3. Microstructure of the Ti-Nb-HA alloy sintered at (a) 950 °C, (b) 1100 °C, and (c) 1250 °C

The sintered Ti-Nb-HA alloy exhibited different structure at different sintering temperature. The sintered Ti-Nb-HA alloy exhibited porous structure at low sintering temperature (950 °C). As the sintering temperature increases, the contact between the powder mixtures increased and pores/gap between powder particles decreased, indicating the densification of powder sintered alloy. The higher temperature, Nb a stabilizer helps in transformation of α-phases into transform β-phase. As a result,
the intensity of β-Nb phase gradually increases with the increase in sintering temperature. At sintering temperature of 1250 °C, a fully dense β-phase Ti-Nb-HA alloy was obtained. The increase in densification results in enhances the hardness and elastic modulus.

3.2. Surface morphology and elemental composition of sintered Ti-Nb-HA alloy

Fig. 4 (a) shows the SEM images of the polished surface morphology of sintered Ti-Nb-HA biocomposites at 950 °C. Similar to optical microstructural results, there are distinct gray and white areas seen from the SEM micrographs. According to the EDS results, the gray areas are Ti element enrichment areas and the white ones are Nb element enrichment areas.
From the EDS of chemical composition map analyses in Fig. 4(b), the Ti-Nb-HA sintered biocomposite consisted of O, Ca and P elements except the Ti and Nb elements. These results indicated that the desired biocomposite compositions was likely to successfully fabricated, and suggested that the chemical composition of biocomposite was prone to afford bioactivity to bone tissue [29]. In general the Ca/P atom ratio obtained from sintered (Ti-Nb-HA) biocomposites was 1.65, and this values were highly close to the stoichiometric Ca/P ratio of HA (1.67).

3.3. XRD pattern of sintered Ti-Nb-HA alloy

Figure 5 shows the XRD patterns of sintered Ti-Nb-HA bio-composite at different sintering temperature. The XRD pattern of sintered Ti-Nb-HA bio-composite revealed the presence of α’ phase (Ti) and β bcc phase (Nb) weak peaks partially overlapped on α’ peaks together with HA content. The Nb is a β-phase stabilizer which helps in transformation of phases at high temperature. The intensity of β-Nb phase gradually increases with the increase in sintering temperature, As the sintering temperature increases, the characteristics peaks of HA were appeared weak. The XRD pattern of sintered Ti-Nb-TA-Zr-HA composite at 1250 ºC revealed the presence of Ca$_3$(PO$_4$)$_2$, CaTiO$_3$, Nb$_8$P$_5$, CaO, TiP, Nb$_2$O$_5$, TiO$_2$, phases. This is due to the fact that the HA (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) is unstable at higher temperature and reacted with other elements which leads to the formation of new biocompatible phases in sintered composite. The formation of these phases is beneficial to form apatite thus improved the bioactivity of the alloy for osseointegration between alloy and natural bone tissues.

3.4. Mechanical Properties of sintered Ti-Nb-HA alloy

Hardness of the sintered Ti-Nb-HA alloys at various sintering temperature were measured. Fig. 6 shows the variation in the micro-hardness value of the Ti-Nb-HA with sintering temperature of 950°C, 1100 °C, and 1250°C. It can be clearly seen that the micro-hardness value of the compact increases significantly with increase in sintering temperature from 950°C to 1250°C; however, the average hardness value of increases marginally when sintering temperature increases from 950°C to 1100°C. This is because at lower sintering temperature the compact consists all four phases and alpha phase
have low hardness. Whereas, at higher sintering temperature only beta phase with minor amount of alpha phase. Therefore, the average value of sintered compact is high due to basically presence of beta phase.

![Image of microhardness graph](image)

**Figure 6.** Microhardness of the Ti-Nb-HA alloy sintered at 950, 100, and 1250 °C

4. Conclusions

From the present investigation on the mechanical alloying of powders (Ti, Nb, and HA) and consolidation of it by spark plasma sintering, following conclusion can be drawn:

1. A biocomposite (Ti-35Nb-10HA) was successfully fabricated by mechanical alloying of Ti, Nb, and HA powders followed by spark plasma sintering technique.
2. Microstructure examination reveled that the Ti-Nb-HA biocomposite distinctly shows the primary grain boundaries along with secondary grain boundary.
3. It was observed that complex reactions between HA and alloy elements occurred during the sintering process of Ti-35Nb-10HA biocomposite and biocompatible phases (Ca₃(PO₄)₂, Nb₈P₅, CaO, TiP, Nb₄O₅, and TiO₂) were generated in the compact, which is beneficial to form apatite and improved the bioactivity of the alloy for osseointegration.
4. The fabricated Ti-28Nb-7Ta-5Zr-10HA alloy exhibits maximum micro-hardness (~795 HV), which is very high value as compared to the alloys reported in literature.
5. Based on these above observations, it is expected that the as-fabricated β-type Ti alloy (Ti-35Nb-10HAp) is suggested for biomedical applications as a material for the production of dental and orthopaedic implants.

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