Solution Heat Treatment of Ti-Nb alloys using a molten salt shield

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Abstract

Ti-Nb alloys have attracted growing attention for biomedical implant application due its low elastic modulus. Nb is a β-stabilizer in Ti alloys and retains its high biocompatibility. Thermal treatment plays a key role for optimization of mechanical properties and microstructure of Ti-Nb alloys. However, high oxygen affinity of Ti alloys requires the use of a protective atmosphere during their processing at high temperatures. In this context, we propose the use of molten salt as novel atmosphere protection during solution heat treatment of Ti-Nb alloys avoiding elaborated encapsulation. For that, Ti-Nb parts were solution treated in molten KCl followed by water quenching. Microstructure and phase transformation were evaluated by SEM, EDS, X-Ray Diffraction, Elastic Modulus and Vickers microhardness measurements. No evidence of oxidation of Ti-Nb parts was found, which suggested that molten salt was an effective measure to protect Ti alloys from oxidation. After treatment, a martensitic microstructure was achieved. A martensitic structure enables to decrease elastic modulus to ca. 35 GPa, which can avoid stress shield in the case of bone implant application.

Keywords:
Ti-Nb alloys, solution heat treatment, phase transformation, metal and alloys, biomaterials

Introduction

Ti-Nb alloys have attracted growing attention for aerospace and biomedical implant applications due their combination of mechanical properties and corrosion resistance. Nb is a β-stabilizer in Ti alloys and it contributes to lower the elastic modulus in binary alloys [1, 2]. Nb is a non-toxic element and it makes the oxide layer on Ti alloys-based implants more stoichiometric and corrosion resistant avoiding inflammation [1, 3, 4, **5**]. By adjusting Nb content, both (α+β) and β-type alloys can be manufactured. (α+β)-type alloys have good combination of density, mechanical properties and strength at higher temperatures, while β-type have a higher strength and lower resistance to temperature.
Powder metallurgical (PM) technologies are attractive to process less ductile metals as titanium alloys which are challenging to produce with traditional mechanical forming techniques [6]. PM technologies such as metal injection molding [2, 7, 8, **9**] and tape casting [10] have been applied for fabrication of (α+β) and β-type Ti-Nb based alloys starting from elemental powder mixtures.

In spite of the advantages of PM technologies for production of Ti alloys, sintering of Ti alloys is a critical step due to titanium´s high oxygen affinity. In general, a high vacuum furnace is required to minimize oxygen uptake. Recently, new sintering technologies have been adapted to Ti-Nb alloys such as microwave sintering [11] and spark plasma sintering (SPS) [12, 13].

However, these approaches require SPS device or a microwave generator, which are also expensive and not widely available. To overcome this issue, Dash et al. [14] proposed the sintering of titanium, using molten salt as a protective atmosphere. The molten salt avoided the contact of the sample with oxygen without the need of a vacuum furnace.

Heat treatment plays a key role in optimization of microstructure and mechanical properties of Ti-Nb alloys. In the case of producing PM parts starting from elemental powder mixtures, heat treatment can improve microstructure homogenization and mechanical properties.

Most common heat treatments applied in ($\alpha + \beta$) Ti alloys are solution treatment, quenching and ageing. A typical heat treatment to increase mechanical strength and hardness of ($\alpha + \beta$) Ti alloys ααconsist of solution above β-transus temperature followed by quenching and a cycle of ageing.

Solution treatment just followed by water quenching can be applied to decrease elastic modulus and the stress shield effect [15], which is desired in the case of bone implant application. For demonstration, Suesawadwanid et al. [13] reported that water quenching of Ti5Nb and Ti15Nb alloys induced α'' phase formation reducing their elastic modulus.

High temperatures (> 850 ºC) are required for solution treatment of Ti-Nb alloys. At these temperatures titanium spontaneously forms an oxide layer in contact with air atmosphere.

To avoid oxidation during solution treatment and quenching, titanium alloys are normally encapsulated in quartz capsules, under vacuum or an inert gas [15]. The encapsulation step is time consuming and increases the processing costs.

In this study, we applied a molten salt as protective shield during solution heat treatment of Ti-Nb alloys, using a similar approach as reported by Dash et al. [14] for Ti sintering. To the best our knowledge this is the first time that a molten salt shield was applied to avoid oxidation of oxygen affine alloys like Ti-Nb alloys during heat treatment. Therefore, the main novelty of our approach is to do the heat treatment of Ti alloys in conventional tube or chamber furnaces without need of elaborated encapsulation in evacuated quartz capsules.

Experimental

Gas atomized Ti powders (D_{10} = 23.8 µm, D_{50} = 40.6 µm, D_{90} = 58.2 µm) and acicular Nb powders (D_{10} = 9.6 µm, D_{50} = 17.8 µm, D_{90} = 33.3 µm) manufactured by TLS Technik and H.C. Starck GmbH, respectively, were used as starting powders.

Ti-10Nb and Ti-17Nb samples of 11 mm diameter and 6 mm height were produced by powder compaction at 100 MPa. Sintering was performed at 1300 °C for 180 min at low oxygen partial pressure (< 10^{-3} Pa) in a vacuum furnace.

Prior the solution heat treatment, samples were encapsulated with KCl salt (T_m = 770°C) and compacted at 120 MPa. Afterwards the samples were placed in a porcelain crucible, which was filled to the edge with salt particles and closed. The crucible was placed in a conventional chamber furnace in air atmosphere and heat up to 1000 ºC for 60 minutes for the complete homogenization. Afterwards the furnace temperature was reduced to 800ºC and the samples were water quenched. During water quenching the crucibles were broken and the salt was dissolved in the water bath. For comparison, a Ti-Nb part was treated at same condition without the molten salt shield. A summary of experimental condition is shown in Table 1.

Microstructural characterization was performed in the cross section of polished samples by using scanning electron microscopy (JSM6360, Jeol Technology). Energy Dispersive Spectroscopy (EDS) analysis was performed using a Quantax 75 (Bruker Nano GmbH). The X-Ray diffraction analyses were performed on the surface and cross section of Ti-Nb parts using Brag-Brentano geometry (θ-2θ) (Dengi D-Max 2000 X-Ray Diffractometer, Rigaku). A Vickers Microhardness was measured in HMV Shimadzu Microhardness tester applying a load of 1.916 N for 15 s following to ASTM E92-82/2003. Elastic modulus was measured by ultrasound methods.

Table 1. Experimental conditions and Microhardness values.

Sample nomenclature	Compo-sition	Sintering Tempe-rature (ºC)	Heat Treatment		Micro-hardness (HV)	Elastic Modulus (GPa)
			Solution Treatment	Quen-ching		
Ti10Nb as sintered	10 wt.% Nb / 90 wt.% Ti	1300	-	-	300 ± 58	79 ± 8
Ti10Nb_SST-Q	10 wt.% Nb/ 90 wt.% Ti	1300	1000 ºC with molten salt shield	Water	230 ± 39	36 ± 6
Ti17Nb as sintered	17 wt.% Nb/ 83 wt.% Ti	1300	-	-	386 ± 57	72 ± 7
Ti17Nb_SST-Q	17 wt.% Nb/ 83 wt.% Ti	1300	1000 ºC with molten salt shield	Water	235 ± 22	35 ± 5
Ti17Nb_AST-Q	17 wt.% Nb / 83 wt.% Ti	1300	1000 ºC without molten salt shield	water	-	-

Results and Discussion

Solution heat treatment in air atmosphere was performed on sintered Ti-Nb parts with and without a molten salt shield. As expected, samples treated without a molten salt shield showed a strong oxidation evidenced by a formation of white oxidation layer on the surface. Contrarily, samples treated using molten salt shield have a metallic appearance and no white oxidation layer was observed on the surface (Figure 1). XRD analyses confirmed that there was an oxide layer composed by rutile TiO_2 on the surface of the sample solution treated without a molten salt shield, while any peak related to oxide phase was observed in XRD pattern of the surface of the samples treated in molten salt shield (Figure 1). Furthermore, no residual salt was observed in XRD and EDS analysis. These results indicate that molten salt shield is an effective measure to avoid oxidation.

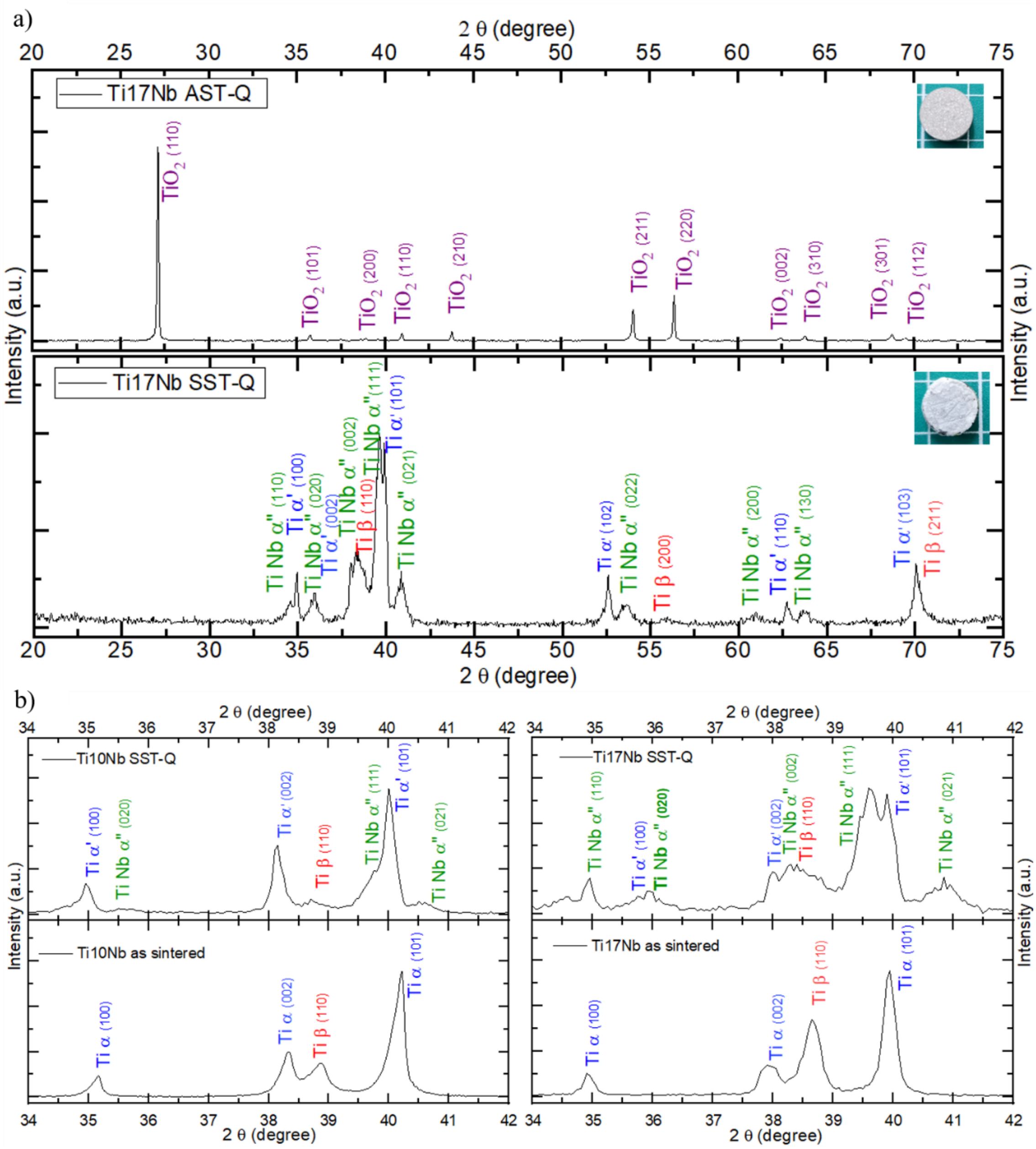

Figure 1.a) XRD patterns from the surface of Ti17Nb parts after solution treatment and quenching in air without molten salt shield (Ti17Nb_AST-Q) and with molten salt shield (Ti17Nb_SST-Q) and b) XRD patterns from the cross section of Ti10Nb and Ti17Nb parts as sintered and after molten salt shield solution treatment and quenching.

TiNb parts in the sintered state showed an (α + β) bimodal microstructure as indicated by the XRD (Figure 2) and the SEM analysis (Figure 3). β phase is rich in niobium as shown in the EDS maps (Figure 3 E and F). Ti17Nb parts showed a higher amount of β phase than Ti10Nb parts. Nb is β-phase stabilizer therefore increasing the amount of Nb is expected to increase the amount β phase, as already demonstrated in previous studies [2, 10]. The higher amount of Nb also promotes an increase of the microhardness (Table 1) which can be related to a possible presence of a very small precipitation of ω-phase (not detectable in XRD due to the detection limit of the XRD technique) as discussed by Fineki et al. [16]. Increasing Nb content from 10% to 17% increased the porosity from 4.8 to 8.3 vol %. This result is in accordance with the work of Zhao et al. [2].

Solution treatment followed by water quenching resulted in the formation of hexagonal α' and orthorhombic α" martensite (Figure 1). In agreement with the literature, the formation of martensitic phases led to the expected decrease of microhardness and elastic modulus values (Table 1) [8, 17].

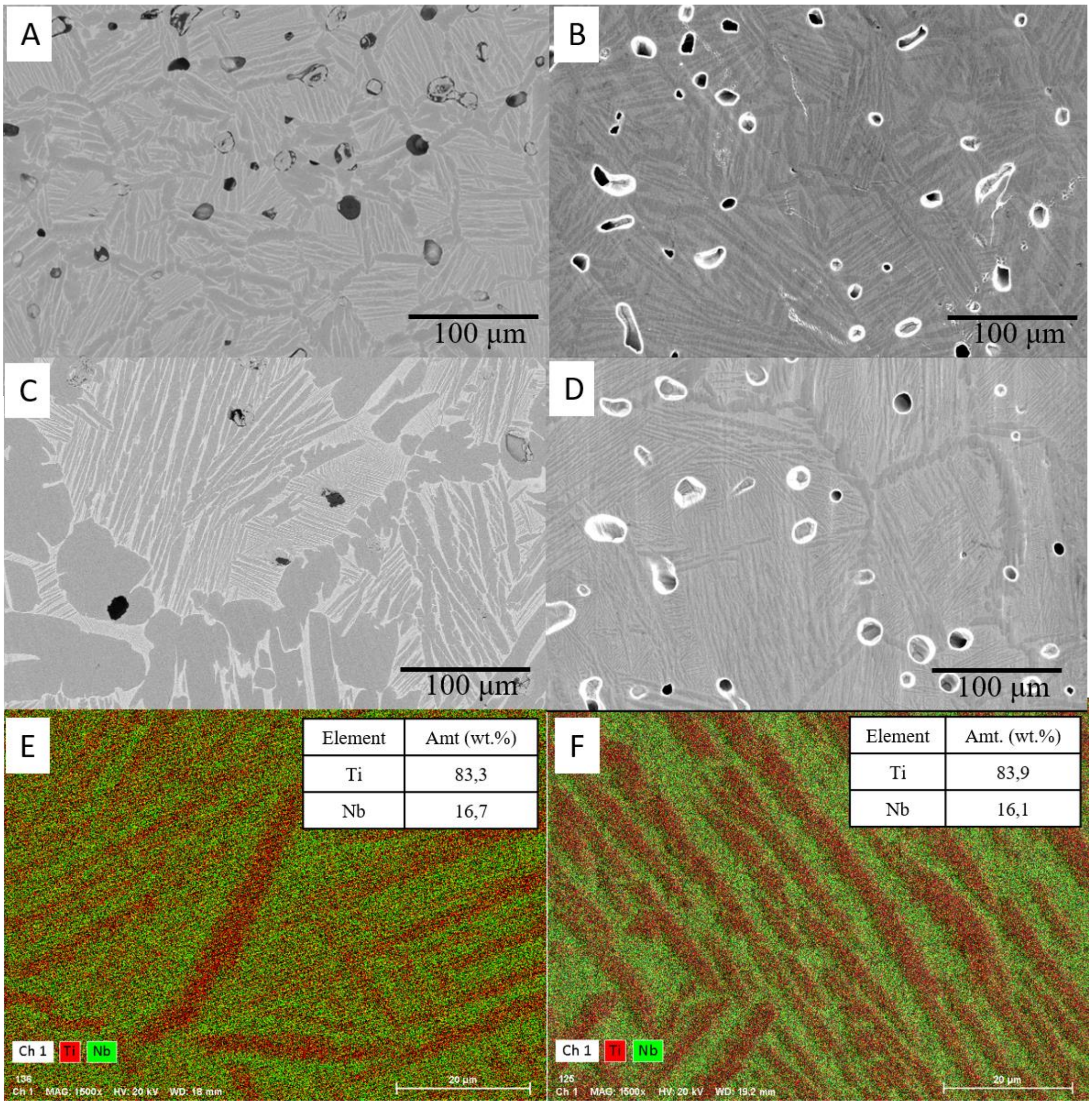

Figure 2. SEM images of Ti10Nb parts before (a) and after solution and quenching treatment(b). Ti17Nb parts before (c) and after solution treatment and quenching(d).
EDS compositional map of Ti17Nb parts before (c) and after solution treatment and quenching treatment (d).

Conclusions

Our results demonstrate that a molten salt shield is suitable to protect titanium alloys from oxidation during heat treatment. By applying a solution heat treatment using a molten salt shield followed by water quenching, orthorhombic and hexagonal martensite were formed in the TiNb alloys and as consequence the elastic modulus was reduced from ca. 72 GPa to 35 GPa in the

Ti17Nb. Martensitic Ti-Nb alloys are candidates for use as biomedical alloys, due their low elastic modulus, which can avoid stress shield effect. The present work demonstrated molten shield heat treatment is an attractive alternative for heat treatment of high oxygen affinity metal alloys on the lab scale which can effectively replace the more challenging encapsulation in evacuated quartz capsules. The method can be easily done in every lab using a simple tube or chamber furnace.

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