Phase transformations in a heterogeneous Ti-xNb-7Zr-0.8O alloy prepared by a field-assisted sintering technique

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Abstract

Biomedical metastable alloy Ti-xNb-7Zr-0.8O with a compositional gradient of Nb was prepared from elemental powders by a field-assisted sintering technique (FAST). The aim was to investigate phase transformations over a wide range of compositions, facilitating the designing of biomedical Ti alloys. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) investigations revealed that Nb-rich regions retained the β phase, surrounded by transition region consisting of the β and ω phases, while Nb-lean regions consisted of the α and β phases. The Nb concentration, above which formation of the ω phase occurs during cooling instead of the α phase, was determined to be 22 wt%, an important parameter for the low-modulus alloy design. The paper validates the viability of using FAST to prepare heterogeneous Ti alloys permitting to study microstructure over a wide range of compositions. This technique could also be readily used as a high-throughput method for designing other alloy systems.

The experimental results were supplemented by calculation of Gibbs energy curves and schematic phase diagrams, which allowed to explain a competition between α and ω formation depending on alloy composition. Such semi-empirical approach can serve as a useful tool for general alloy design, in particular for biomedical Ti alloys.

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1. Introduction

Metastable bcc β-Ti alloys have been considered as perspective candidates for load bearing implants manufacturing for more than two decades [1–7]. Several multicomponent alloys have been proposed,
however precise composition and microstructural tailoring is difficult, because of many degrees of freedom and a number of specific requirements.

It is generally accepted that for the long-term exposure in the human body environment, harmful alloying elements, such as Al or V should be avoided in the implant design and only biocompatible elements should be used. This requirement is the first guideline for the selection of β-stabilizing elements: Nb, Zr and Ta can be used without limits and Mo and Fe to a limited extent [4,8,9]. In designing alloys which are competitive to those currently in use, there is an effort to achieve not only superior material properties, but also to achieve reduced costs. This includes investigation of novel fabrication methods reducing buy-to-fly ratio, such as additive manufacturing, as well as reducing the content of the expensive elements, such as Ta.

Another critical requirement for the alloy design is achieving the lowest possible elastic modulus to avoid so-called stress shielding effect. Stress shielding results from the different elasticity modulus of a bone and the metallic implant and it may lead to a need for a revision surgery and therefore most of the research efforts has been focused on minimizing elastic modulus of the alloy. While conventionally used stainless steel has the modulus of approximately 200 GPa and the common α + β Ti alloys exhibit a modulus in the range of 100–110 GPa, β-Ti alloys may exhibit moduli as low as 50–90 GPa, depending on the composition, which is much closer to the elastic modulus of bone (approximately 30 GPa [3]). Another important requirement for the practical use of the alloy is a sufficient yield strength, which is often contradictory to the low modulus requirement.

Ti-Nb-Zr-Ta system has been shown more than two decades ago to have some of the desired properties – namely good biocompatibility and low modulus [1,10]. More recently, it was found that addition of oxygen in concentrations up to 0.7 wt% leads to significant strengthening while maintaining low elastic modulus and good ductility in Ti–35Nb–7Zr–6Ta alloy [2,5,11]. Achieved elastic modulus and ductility depend not only on the oxygen content, but on the particular composition, as the mechanical properties are a result of a complex interplay of multiple elements involved [12,13].

Ti-Nb-Ta-Zr-O system falls to the group of metastable β-Ti alloys, which retain their body-centered cubic structure when quenched from the β phase field to the room temperature. Hexagonal ω phase is a metastable phase, which can be formed either athermally during the quench of an alloy with lower amount of β stabilizing elements (athermal thermal, , or) by ageing of the quenched alloy (athermal thermal, ) [14,15]. However, the presence of the ω phase typically leads to an increase in the elastic modulus [6,16] and decrease in ductility [17,18], so its presence is generally avoided. When the amount of β stabilizing elements is reduced even more, martensitic α′ (orthorhombic) or α (hcp) phases are formed during quench [14]. These phases decompose into equilibrium α and β phases during subsequent ageing [19].

Several approaches have been proposed to optimize the composition based on a phenomenological description of the electronic structure – a simple calculation of e/a (valence electrons per atom) ratio [20] and Bo-Md diagram [21,22]. While these results have proven to be extremely useful in general alloy design, the fine tuning must be always done experimentally using real alloys. In the Ti-Nb-Ta-Zr-O alloying system, O is conventionally considered as an α-stabilizing element (with respect to the β transus temperature), however it is also ‘β-stabilizing’ with respect to the martensitic α′ → α′ transformation, interstitially blocking the active slip system required for the transformation [23,24]. The effect of oxygen on the ω phase formation is still not fully resolved. However, it was suggested by Niimoto [25] that oxygen content can suppress the formation of , during quenching [24,26,27] and also promote the formation of , during ageing [25]. Finally, we have shown recently that Ta can be omitted without compromising the mechanical properties [28]. 0.7 wt% of oxygen was in this case acting as a β-stabilizer with respect to β → α′ transformation, compensating the effect of missing Ta. Due to these reasons, our study focuses on the Ti-Nb-Zr-O system.

As argued in the previous paragraphs, development of complex biomedical alloys necessarily involves optimization of the composition for many constituents simultaneously. The properties are at first assessed from the microstructural point of view. Conventional preparation is mostly done by arc-melting and subsequent homogenization. The whole process must be realized in order to obtain one composition of interest. Tailoring the composition is therefore a time- and resource-demanding process. This drawback can be overcome by a preparation of samples possessing gradients in composition, which can be subsequently investigated as a whole and data for the whole compositional range can be obtained. This can be done either at the macroscopic level (e.g. by diffusion between sections of different composition in the sample), by additive manufacturing methods, such as LENS™ [29], which can vary the composition along the build direction, or at the powder level, by creating a diffusion profile between elemental powder particles, which is the scope of this study.

We try to make use of the fact that during sintering of Ti alloys from blended elemental powders (BEPM), Nb, as the element with the slowest interdiffusion and the highest melting point, may not be fully homogenized during sintering. Sintering of Ti alloys from BEPM has already been explored by several authors [30–32], and we chose field-assisted sintering technique (FAST, also called spark plasma sintering, SPS) for the consolidation as it is a fast method with well adjustable parameters [33].

The aim of this study is to investigate a possibility of using FAST to prepare such a heterogeneous alloy and to study the phase transformations during cooling in the wide range of composition.

2. Experimental methods

The experimental material was prepared using blended-elemental powder metallurgy (BEPM), with TiO₂ powder being used as a controllable source of oxygen. Prior to sintering, the powders were mechanically blended. The basic properties of the powders utilized are summarized in the Table 1. All handling was performed in air.

The sintering was done in the SPS 10–4 furnace (Thermal Technology LLC, USA), using a graphite die and foil, the produced samples were 15 mm in diameter and approximately 7 mm in height. The whole process is performed in vacuum of the order of 1 Pa.

The sintering program started with 200 K/min heating to a temperature 50 K below the desired sintering temperature and continued with the reduced rate of 50 K/min to the sintering temperature to limit the degree of overshooting. Then, a piston pressure of 80 MPa was applied and isothermal sintering was performed for 3 sets of conditions: 1300 °C for 15 min and 30 min and 1400 °C for 15 min. The isothermal part was followed by an exponential cooling with a cooling rate of approximately 200 K/min at 800 °C and approximately 100 K/ min at 600 °C; the cooling rate is comparable to air cooling. The actual course is shown in the Fig. 1.

The content of O, N, and H was measured by carrier gas hot extraction method (CGHE) using Leco ONH836 analyzer. The method is based on the high temperature melting of the specimen and a subsequent analysis of the evolved gaseous reaction products [34]. Wavelength Dispersive Spectroscopy (WDS) analysis was performed using a JEOL JXA-8530F microanalyzer. SEM and Energy Dispersive Spectroscopy (EDS) were performed using Thermo Scientific Apreo and Zeiss Auriga Compact. The preparation of a lamella for TEM investigations by FIB was performed in a dual-beam Zeiss Auriga Compact. The JEOL 2200FS TEM was used for the TEM experiments. All observations were done in the central region of the sample to avoid carbon contamination present near the sample surface.
3. Results

All samples were successfully sintered under the specified conditions. Low-magnification SEM micrographs are shown in the Fig. 2. Three distinctive regions of specimens can be identified: first, white undissolved Nb particles; second, surrounding grey β regions; and third, dark regions further from the Nb particles consisting of both the α and β phases (shown at higher magnification below). This microstructure is a direct consequence of a slowly diffusing Nb. Nb atoms from Nb particles diffused into the Ti particles – surrounding β regions were enriched by Nb sufficiently to maintain their bcc crystal structure, while in the less enriched regions a two-phase microstructure formed during cooling. The amount of undissolved Nb decreases with the increased sintering temperature and time as a direct consequence of the enhanced diffusion at higher temperatures.

No residual porosity associated with the sintering process itself was found because the sintering temperature proximity to the melting point of both Ti (1670 °C, [15]) and an ideally homogeneous alloy (approximately 1750 °C, ThermoCalc). The only porosity in the material is the porosity originally present inside the large as-received Nb particles.

After the sintering, the content of the light elements present within the material was checked. The samples sintered at 1300 °C /15 min and 1400 °C /15 min were tested with the assumption that the remaining

| Table 1 | Elemental powder characteristics. |
|---------|----------------------------------|
|         | Melting point (°C) | Supplier | Purity | Oxygen content (wt%) | Size & morphology |
| Ti (Grade 2) | 1670 °C | TLS Technik | 99.8% | 0.18 ± 0.01 | spherical, 20–80 μm |
| Nb | 2477 °C | Alfa Aesar | 99.7% | 0.24 ± 0.04 | irregular, 20–500 μm |
| Zr (Grade 702) | 1855 °C | TLS Technik | (Zr + Hf) > 99.2% | 0.17 ± 0.01 | spherical, 20–80 μm |
| TiO₂ (anatase) | 1825 °C | Sigma Aldrich | 99.9% | – | agglomerated, <1 μm |

Fig. 1. Temperature course during the heating and cooling stage of the sintering program for the sample sintered at 1400 °C for 15 min; isothermal part is shown in a reduced length. The cooling rate is also plotted for the cooling stage. The pyrometer readings below 600 °C are not reliable and thus not displayed. Cooling conditions are fully reproducible for all samples.

Fig. 2. Low magnification SEM BSE micrographs showing the heterogeneity of the sintered specimen. White areas are undissolved Nb particles.
1300 °C /30 min condition lies within the measured range. Two small specimens for CGHE measurement were prepared from the central part of each sample, far from any possible carbon contamination originating from the graphite die. The results are presented in the Table 2. The difference between the two samples is not statistically significant.

The detailed investigations presented in the following text were performed on the sample sintered at 1300 °C for 30 min.

A closer look on the \( \alpha + \beta \) region of the sample reveals three different types of \( \alpha \) precipitates: the grain boundary alpha (\( \alpha_{GB} \)), which nucleates at GBs and grows along GBs, lamellar alpha heterogeneously nucleating at GBs or at \( \alpha_{GB} \) growing into the grain interior (\( \alpha_{htg} \)) and lamellar alpha nucleating intragranularly within the grains (\( \alpha_{int} \)), cf. Fig. 3 and Fig. 4a. EDS analysis shows segregation of Ti and Nb into alpha and beta, respectively.

A closer look at the region of transition between \( \beta \) and \( \alpha + \beta \) microstructures (Nb rich and Nb lean, respectively) can reveal early stages of the alpha precipitation, as shown in the Fig. 4b. It can be seen that at a given temperature, \( \alpha_{GB} \) can precipitate at areas with higher Nb content than \( \alpha_{int} \) in the grain interior. This can be attributed to the role of GBs as preferential nucleation sites, lowering the energy barrier for precipitation, possibly further enhanced by the oxygen, which is known to segregate at GBs [12,24]. The lamellar \( \alpha_{htg} \) in the vicinity of the GBs nucleates from the \( \alpha_{GB} \) and its growth is controlled by temperature. The long, parallel \( \alpha \) colony-type lamellae in the Fig. 4a appear in areas with lower Nb content and therefore nucleated at higher temperatures. Due to the increased temperature and diffusion, these lamellae grew to bigger sizes. On the other hand, short and thin lamellae seen in the Fig. 4b appear in areas with higher Nb concentration suggesting that they formed during cooling at lower temperatures, and due to the reduced diffusion could not grow significantly.

The minimum concentration of Nb to suppress the \( \beta \to \alpha \) transformation for a given cooling regime is important from both theoretical and technological points of view. EDS analysis was performed on the transition areas of all samples similar to the one illustrated in the Fig. 5, far from any GBs. In order to avoid inconsistency related to the deconvolution of overlapping Zr L and Nb L peaks resulting in quantification errors, we have also employed WDS with standards to check the composition of 1300 °C /30 min sample. The estimation of the Nb content sufficient to suppress alpha phase formation is influenced by two uncertainties. Firstly, the error of the WDS measurement itself, and secondly, the error of positioning of the incident area. The second uncertainty was estimated as 0.5 wt% (the difference between the top left and bottom right corners of the field of view in Fig. 5 is 3 wt%) and was appropriately combined with the first type of uncertainty and shown in Table 3. The oxygen content was not measured via WDS/EDS because the sensitivities of both methods are not sufficient. In addition, due to significantly higher diffusion coefficient, the oxygen content is assumed to be homogeneous after sintering and values obtained by the CGHE (Table 3) can be applied for the whole volume. It can be seen in Table 3 that the values obtained by EDS are slightly underestimated, which is caused by the overlapping Nb L and Zr L peaks.

Because the size of the \( \alpha \) lamellae at the transition region is at the limit of SEM resolution, we have prepared a lamella using FIB for TEM investigations. The SAD patterns and TEM micrographs are shown in Fig. 6.

| Table 2 | Carrier gas hot extraction analysis of two sintered samples. It is assumed that the 1300 °C /30 min sample lies within the range given by these two measurements. |
|---------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|         | O (wt%) | N (wt%) | H (wt%) |
| 1300 °C, 15 min | 0.826 ± 0.035 | 0.016 ± 0.001 | 0.015 ± 0.001 |
| 1400 °C, 15 min | 0.870 ± 0.024 | 0.015 ± 0.001 | 0.022 ± 0.001 |

Fig. 3. A detailed micrograph (a) and EDS maps (b)–(d) showing segregation of the Ti and Nb into \( \alpha \) and \( \beta \) phase, respectively. Zr distribution is much more homogeneous in comparison with Ti and Nb.
The BF micrograph shown in Fig. 6a is divided into two regions - \(\beta\) and \(\alpha + \beta\) regions. The boundary is fuzzy, and isolated \(\alpha\) clusters can be found in the \(\beta\) region. The most important result of the TEM investigations is the presence of \(\omega\) reflections visible in the SAD pattern (Fig. 6b, c). A corresponding DF image using \(\omega\) reflections is shown as Fig. 6d. Fine \(\omega\) particles of approximately 30 nm in size were formed in both \(\beta\) and \(\alpha + \beta\) regions.

The EDS line profiles were acquired from the three distinct regions marked in the Fig. 6d to estimate the extent of element segregation between \(\alpha\) and \(\beta\) phase. The results presented in the Fig. 8 show that the concentration of Nb within the \(\alpha\) precipitates is by approximately 10–20 wt% lower than that of the surrounding \(\beta\) matrix. The concentration of Zr within the \(\alpha\) lamellae is only slightly lower than in the \(\beta\) matrix, suggesting that Zr acts as a weak \(\beta\) stabilizer.

4. Discussion

Due to the moderate cooling rate of approximately 100 to 500 K/min, diffusion plays an important role in the phase transformations during cooling. Alloying elements segregate into the formed phases and stabilize them, even though the overall Nb gradient is unchanged. In the gradient sample, we try to capture the phase transformation pathways as a function of a local composition under a given cooling regime.

The cooling starts from temperatures above the \(\beta\)-transus, we observe \(\beta\) phase material with an inhomogeneous Nb concentration. During cooling, \(\alpha\) starts to nucleate in the less \(\beta\)-stabilized regions (i.e. with low Nb concentration), which are characterized by a higher local \(\beta\)-

![Fig. 4.](image)

(a) \(\alpha\) morphology at regions with different Nb content, showing the varying lath thickness. The orange rectangle is shown in detail as (b). The yellow line marks the position and width of an EDS line profile presented in (c). (b) \(\alpha\) nucleation at and in the vicinity of the GB. (c) EDS line concentration profile showing the Nb gradient. The line scan had a finite width to smooth the influence of abrupt concentration changes between \(\alpha\) and \(\beta\) on the right side of the Fig. 4a.

![Fig. 5.](image)

Transition region between \(\beta\) and \(\alpha + \beta\) regions with a rectangle showing the approximate positioning and size of the WDS and EDS area scans.

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Table 3

| Sample         | Method       | Ti (wt%)     | Nb (wt%)    | Zr (wt%)    |
|----------------|--------------|--------------|-------------|-------------|
| 1300 °C, 15 min| EDS, standardless | 71.9 ± 0.8  | 18.6 ± 0.4  | 8.8 ± 1.1   |
|                |              | (± 0.7)      | (± 0.7)     | (± 0.7)     |
| 1300 °C, 30 min| EDS, standardless | 72.9 ± 1.4  | 20.6 ± 0.9  | 5.8 ± 0.5   |
|                |              | (± 1.1)      | (± 0.6)     | (± 0.6)     |
| 1400 °C, 15 min| EDS, standardless | 71.7 ± 0.7  | 20.0 ± 0.1  | 7.5 ± 0.7   |
|                |              | (± 0.6)      | (± 0.6)     | (± 0.6)     |
| 1300 °C, 30 min| WDS, standard | 68.7 ± 1.0  | 22.2 ± 0.6  | 8.0 ± 0.3   |
|                |              | (± 0.8)      | (± 0.8)     | (± 0.8)     |
Fig. 6. (a) An overview BF micrograph of the lamella showing the transition between $\alpha + \beta$ and $\beta$ regions. (Image gamma correction was adjusted to partially compensate for the non-uniform lamella thickness.) (b-c) SAD pattern of [110] $\beta$ zone axis with $\omega$ reflections visible between the $\beta$ spots from the $\beta$ (b) and $\alpha + \beta$ (c) regions. (d) An overview DF micrograph of the lamella using $\omega$ reflection showing high density of $\omega$ particles in both $\beta$ and $\alpha + \beta$ regions. Square areas A and B are shown in detail in the Fig. 7, lines 1–3 mark positions of the EDS line scans presented in Fig. 8. The lamella was prepared from the sample sintered at 1300 °C for 30 min.
transus temperature, which depends on the local composition. The precipitation of α starts in the regions where this local β-transus is higher than the temperature at that moment. Decreasing the concentration of Nb has effectively the same effect on phase transformations as decreasing the temperature and vice versa.

A driving force for homogeneous nucleation is relatively low just below β-transus, so α phase is created only at grain boundaries (α_{GB}) which serve as preferential sites for a heterogeneous nucleation. This layer of α_{GB} then serves as another nucleation site for α lamellae growing into the grain interior (Fig. 3a). The length of the lamellae is limited by surrounding lamellae, while the thickness is mainly controlled by diffusion [35], which is in turn controlled by the temperature. Since the kinetics is fast just below the β-transus, these colonies of parallel α laths can be up to 20 μm long (cf. Fig. 4a). Intragranular nucleation of α_{int} becomes possible in the grain interior when the undercooling becomes sufficiently large – i.e. at lower temperatures. Conversely, the kinetics at these temperatures is slower and therefore these α lamellae are significantly smaller (cf. Fig. 4b). This mechanism also applies to the regions with higher content of Nb, but at correspondingly lower temperatures, which implies higher undercooling but slower kinetics of the process. These precipitates can form also in the grain interior, but cannot grow as fast as the precipitates in the Nb lean areas and become smaller and more numerous (Fig. 4b).

In order to support the experimental evidence by theoretical thermodynamic considerations, we have calculated Gibbs free energy curves for α and β using ThermoCalc software for temperatures between 0 and 600 °C. Fig. 9 shows Gibbs energy of α phase (solid curves) and β phase (dashed curves) for Ti-xNb-7Zr-0.8O alloys for different temperatures. Unfortunately, it was not possible to reliably calculate the Gibbs energy also for the α phase due to the lack of thermodynamical data for a given alloy composition.

Note that a full description of thermodynamic equilibrium (phase composition and chemical composition of the phases) is not possible because Zr and O content is fixed (and position of the global minimum of Gibbs energy with respect to Zr and O content is therefore unknown). Instead, the intersections of α and β curves were marked in Fig. 9. These intersections clarify at which temperature the α phase starts to precipitate for a given alloy composition. For instance, for Nb content of 16 wt %, alpha starts to precipitate between 600 and 500 °C. Since the precipitation of the α phase for Nb content >22 wt% was not observed, it can be concluded that the α phase cannot precipitate at temperatures below 400 °C. Note again, that the competing process of α formation is not included in the Fig. 9.

To explain the phase transformation pathways including ω phase, we have drawn a schematic phase diagram (Fig. 10a) based on a binary Ti—Nb diagram [36] and a set of Gibbs energy curves for each phase for four temperatures (Fig. 10b–e). The evolution of Gibbs energies (especially positions of the intersections) should be qualitatively correct for the studied alloy. In the Fig. 10a, two phase diagrams are shown: stable α + β phase diagram (red) and metastable β + ω phase diagram (blue). ω_1 and ω_2 (also often denoted as ω_{lean} and ω_{rich}) are two metastable compositional variants of the bcc β phase. T_{ω_1}β curve connects the intersections of Gibbs energies for α and β phases for various temperatures (as shown in the Fig. 9). These intersections are not important in the determination of thermodynamic equilibrium (as the equilibrium is based on the common tangent construction), however, it is of particular importance for alpha phase precipitation in a metastable alloy. The martensite start (M_s) curve, drawn in many experimental phase diagrams, is always positioned left from this curve, e.g. [37]. T_{ω_1}β curve is a perfect analogy to the T_{ω_1}β curve; it connects the intersections of Gibbs energies for ω and β phases for various temperatures. Letters A, C, D and E denote intersections of Gibbs energies of α and β phases for the particular temperature. Similarly, B, D and F denote intersections of Gibbs energies of ω and β-phases for the particular temperature. Schematic position of Gibbs energies at these particular temperatures T_1–T_4 are shown in Figs. 10b–e.

Fig. 10b (temperature T_1) corresponds to a temperature above the ω solvus temperature and is directly comparable to the calculated curves in the Fig. 9. The Gibbs free energy of ω is high and only α phase may precipitate. Upon further cooling, the relative position of ω curve shifts down and intersects G_ω (Fig. 10c, temperature T_2). The coexistence of β and ω would be fundamentally possible, if α did not exist. However, the formation of α + β mixture is still more energetically favorable. At a certain temperature (denoted as T_3), which is illustrated in the Fig. 10d, all three curves intersect in a single point D, which is also an intersection of the two T_0 curves in the phase diagram Fig. 10a. For the temperature T_4 < T_1 (Fig. 10e), ω can be formed from β for concentrations x > x_D, which is observed by TEM in the Figs. 6 and 7.

It should be also noted that the precipitation of α is accompanied by a segregation of β stabilizing Nb, shifting the composition of the remaining β matrix to the right and stabilizing it. However, if β is not enriched with Nb sufficiently and has not yet reached the equilibrium with
appropriate content of α phase (due to slow segregation kinetics and a short time), ω phase may be formed in the metastable β phase. Particles of ω phase form between α lamellae upon further cooling in the same way as in the case of Nb richer composition, which is shown in the Fig. 7a.

The critical concentration of 22 wt% Nb (concentration x₀ in the Fig. 10) at the transition region corresponds, according to the Fig. 9, to the temperature of approximately 400 °C – i.e. the lowest at which α may precipitate. Below this temperature, isothermal ω forms in the β matrix with more than 22 wt% of Nb. Temperature range of 300–400 °C was already found favorable for ωiso formation in binary Ti–29Nb (wt%) alloy [38]. High content of oxygen was also shown to promote ωiso formation in Ti-29Nb-13Ta-4.6Zr-0.4O (wt%) alloy [25].

Despite Nb concentration of 22 wt%, no α” was found in the studied alloy. It is in an apparent contradiction with the quenched binary Ti–Nb alloy, in which α” forms for Nb concentrations up to 39 wt% [39]. However, the studied material contains β-stabilizing Zr [40] and a relatively high content of oxygen suppressing the martensitic transformation [22,41–44]. Furthermore, a relatively slow cooling rate allows conventional diffusion-assisted β → α and β → ωiso transformation.

This study showed the applicability of Field Assisted Sintering from blended elemental powders for the development and designing of biomedical Ti-based alloys. Possibilities of this approach are, however, much broader. It can be easily applied in a synthesis of other alloy systems [45], needing only an adjustment of the sintering parameters to reach the optimal diffusion rate. The approach can be adjusted for alloy systems containing elements with very dissimilar diffusion coefficients – multiple compartments containing powders of different compositions can be created inside the die, as investigated in [46]. While the suggested method is not suitable for macroscopic testing (e.g. full-scale mechanical tests, DSC/DTA), its strength lies in combination with experimental methods providing local information: electron
Fig. 9. Gibbs free energy curves of α and β phase from 0 to 600 °C calculated for the nominal alloy composition Ti-xNb-7Zr-0.8O by ThermoCalc. Concentrations at which the curves intersect are also displayed.

Fig. 10. (a) Schematic equilibrium and non-equilibrium phase diagrams of the system (adapted from binary Ti–Nb phase diagram [36]). The dashed/dash-dotted T0 curves mark the position of the intersections of the corresponding Gibbs free energy curves (α/β) and (β/ω). The curve T0α/β matches the marked intersections in the Fig. 9. (b)-(e) Gibbs free energy curves for individual phases corresponding to the sections of the phase diagram (a) at temperatures T1–T6.
microscopy techniques, micro/nanoindentation and other microscale experimental methods.

5. Conclusions

Field assisted sintering technique (FAST) was successfully used to produce Ti-Nb-Zr-O alloy with heterogeneous Nb concentration. Compositional gradient allowed microstructural investigation over different alloy composition within a single sample. Scanning electron microscopy investigation over gradient of Nb content allowed a detailed investigation of the phase transformation sequence in the studied alloying system. During cooling, α nucleation occurs first at grain boundaries, followed by intragranular nucleation inside the grains. The highest concentration of Nb at which α can precipitate during cooling was determined to be 22 wt% in the given alloying system. Calculation of Gibbs energy showed that α phase can precipitate only above approximately 400 °C. For higher concentrations of Nb, δ(α) becomes more energetically favorable and is formed during further cooling. The observed sequence of phase transformations for different alloy composition was described by a series of qualitative phase diagrams providing a unique insight to phase transitions in complex biomedical Ti-based alloys.

The described method may become viable for the design and development of biomedical Ti alloys. It could be easily transferred to other alloy systems. The applicability and versatility of the method for alloy design was clearly demonstrated.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M. Ninomi, Mechanical properties of biomedical titanium alloys, Mater. Sci. Eng. A 243 (1998) 231–236, https://doi.org/10.1016/S0921-5093(98)00808-X.
[2] I. Qazi, H.J. Rack, B. Marquardt, High-strength metastable beta-titanium alloys for biomedical applications, IOM. 56 (2004) 49–53, https://doi.org/10.1016/j.iomem.2003.12.201.
[3] M. Geetha, A.K. Singh, R. Asokan, A.K. Gogia, Ti based biomaterials, the ultimate choice for orthopaedic implants – a review, Prog. Mater. Sci. 54 (2009) 397–445, https://doi.org/10.1016/j.pmatsci.2008.06.004.
[4] L.-C. Zhang, L.-Y. Chen, A review on biomedical titanium alloys: recent Progress and Prospect, Adv. Eng. Mater. 21 (2015) 081015, https://doi.org/10.1002/adem.20150815.
[5] J. Štráský, M. Janeček, P. Harcuba, D. Preisler, M. Landa, 4-2 - biocompatible beta-Ti alloys with enhanced strength due to increased oxygen content, in: F.H. Froes, M.
A. Terayama, N. Fuyama, Y. Yamashita, I. Ishizaki, H. Kyogoku, Fabrication of Ti–Nb alloys by powder metallurgy process and their shape memory characteristics, J. Alloys Compd. 577 (2013) S408–S412, https://doi.org/10.1016/j.jallcom.2011.12.166.

O. Guillot, J. Gonzalez-Julian, B. Dargatz, T. Kessel, G. Schierning, J. Räthel, M. Herrmann, Field-assisted sintering technology/spark plasma sintering: mechanisms, materials, and technology developments, Adv. Eng. Mater. 16 (2014) 830–840, https://doi.org/10.1002/adem.201300409.

R.A. Meyers, Encyclopedia of Analytical Chemistry, Wiley, 2006.

F.J. Gil, M.P. Ginebra, J.M. Manero, J.A. Planell, Formation of α-Widmanstätten structure: effects of grain size and cooling rate on the Widmanstätten morphologies and on the mechanical properties in Ti6Al4V alloy, J. Alloys Compd. 329 (2001) 142–152, https://doi.org/10.1016/S0925-8388(01)01571-7.

P.E.A. Turchi, Thermodynamic, Diffusion, and Physical Properties of Nb-Ti-U-Zr Alloys, Lawrence Livermore National Lab. (LLNL), Livermore, CA (United States), 2018 https://doi.org/10.2172/1439146.

G. Lindwall, P. Wang, U.R. Kattner, C.E. Campbell, The effect of oxygen on phase Equilibria in the Ti-V system: impacts on the AM processing of Ti alloys, Jom Warrendale Pa 1989 (70) (2018) 1692–1705, https://doi.org/10.1007/s11837-018-3008-8.

M. Bönisch, M. Calin, T. Waitz, A. Panigrahi, M. Zehetbauer, A. Gebert, W. Skrotzki, J. Eckert, Thermal stability and phase transformations of martensitic Ti-Nb alloys, Sci. Technol. Adv. Mater. 14 (2013), 055004, https://doi.org/10.1088/1468-6996/14/5/055004.

Q. Wang, C. Dong, P.K. Liaw, Structural stabilities of β-Ti alloys studied using a new Mo equivalent derived from [\|V/ (α + β)|] phase-boundary slopes, Metall. Mater. Trans. A. 46 (2015) 3440–3447, https://doi.org/10.1007/s11661-015-2923-3.

F.Q. Hou, S.J. Li, Y.L. Hao, R. Yang, Nonlinear elastic deformation behaviour of Ti-30Nb-12Zr alloys, Scr. Mater. 63 (2010) 54–57, https://doi.org/10.1016/j.scriptamat.2010.03.011.

T. Furuta, S. Kuramoto, J. Hwang, K. Nishino, T. Saito, M. Niinomi, Mechanical properties and phase stability of Ti-Nb-ta-Zr-O alloys, Mater. Trans. 48 (2007) 1124–1130, https://doi.org/10.2320/matertrans.48.1124.

E.G. Obbard, Y.L. Hao, R.J. Talling, S.J. Li, Y.W. Zhang, D. Dye, R. Yang, The effect of oxygen on α″ martensite and superelasticity in Ti-24Nb-4Zr-8Sn, Acta Mater. 59 (2011) 112–125, https://doi.org/10.1016/j.actamat.2010.09.015.

M. Tane, K. Hagihara, M. Ueda, T. Nakano, Y. Okuda, Elastic-modulus enhancement during room-temperature aging and its suppression in metastable Ti–Nb-based alloys with low body-centered cubic phase stability, Acta Mater. 102 (2016) 373–384, https://doi.org/10.1016/j.actamat.2015.09.030.

M. Tahara, T. Inamura, H.Y. Kim, S. Miyazaki, H. Hosoda, Role of oxygen atoms in α martensite of Ti-20at.% Nb alloy, Scr. Mater 112 (2016) 15–18, https://doi.org/10.1016/j.scriptamat.2015.08.033.

N.S. Weston, B. Thomas, M. Jackson, Processing metal powders via field assisted sintering technology (FAST): a critical review, Mater. Sci. Technol. 35 (2019) 1306–1328, https://doi.org/10.1080/02670836.2019.1620538.

J.J. Pope, E.L. Calvert, N.S. Weston, M. Jackson, FAST-DB: a novel solid-state approach for diffusion bonding dissimilar titanium alloy powders for next generation critical components, J. Mater. Process. Technol. 269 (2019) 200–207, https://doi.org/10.1016/j.jmatprotec.2019.02.011.