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Mechanical Properties Optimization via Microstructural Control of a Metastable  $\beta\mbox{-type Ti-Nb}$  based Gum Metal

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#### UNIVERSITY OF CALIFORNIA SAN DIEGO

## Mechanical Properties Optimization via Microstructural Control of a Metastable $\beta$ -

## type Ti-Nb based Gum Metal

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of

Philosophy

In

Materials Science and Engineering

by

Sumin Shin

Committee in charge: Professor Kenneth S. Vecchio, Chair Professor John Kosmatka Professor Jian Luo Professor Chia-Ming Uang Professor Kesong Yang

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University of California Sand Diego

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B.S. in Materials science and engineering, Pukyong National University, Busan, Korea

2007 M.S. in Materials science and engineering, Hanyang University, Seoul, Korea

2007-2010 Researcher, Korea Institute of Industrial Technology, Korea

2014-2019 Teaching Assistant, Department of Mechanical Engineering, University of California

San Diego, USA

2019 Ph.D. in Materials science and engineering, University of California San Diego, USA

#### PUBLICATIONS

"Extraordinary strength-ductility synergy in a heterogeneous structured β-Ti alloy through microstructural optimization" Material Research Letter, vol. 7, pp467-473, August 2019

"Effect of twinned-structure on deformation behavior and correlated mechanical properties in a metastable β-Ti alloy" Journal of Alloys and Compound (Accepted), August 2019

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"Multifunctional Non-Equiatomic High Entropy Alloys with Superelastic, High Damping, and Excellent Cryogenic Properties" Advanced Engineering Materials, vol. 18, pp 941-949, May 2018.

"Enhancement of <001> recrystallization texture in non-equiatomic Fe-Ni-Co-Al-based high entropy alloys by combination of annealing and Cr addition" Journal of Alloys and Compounds, vol. 768, pp 277-286, July 2018.

"Observations on {332}<113> twinning-induced softening in Ti-Nb Gum metal" Materials Science & Engineering A, vol. 724, pp 189-198, March 2018.

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#### FIELDS OF STUDY

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Studies in Materials Science and Engineering Professors Kenneth S. Vecchio

## ABSTRACT OF THE DISSERTATION

## Mechanical Properties Optimization via Microstructural Control of a Metastable β-type Ti-Nb based Gum Metal

by

Sumin Shin

Doctor of Philosophy in Materials Science and Engineering

University of California San Diego, 2019

Professor Kenneth S. Vecchio, Chair

Metastable  $\beta$  titanium alloys are essential materials for biomaterials and aerospace applications. It is well known that their properties can be manipulated by tailoring the  $\beta$  phase stability and/or microstructural design, which not only results in the activation of multiple deformation mechanisms but also leads to non-homogeneous plastic deformation. Aiming at an improved understanding of the deformation mechanisms associated with the  $\beta$  phase stability, especially the effects of elemental distributions on the deformation mechanisms, three groups of

Ti–23Nb–0.8Ta–2Zr–O (at%) alloys with varied  $\beta$  phase stability were produced, which correspond to the occurrence of stress induced  $\alpha$ " martensite transformation, mechanical twinning and slip dislocation, respectively. The  $\beta$ -phase stability dependence of deformation features can explain the possibility of manipulating the mechanical properties without the evident elastic properties.

In twin-dominated metal, the prevailed deformation mechanism is found to be modified into multiple twinning systems based on the dependence of crystallographic orientation. Twinned structure mainly composed of {332}<112> twin system is proposed to account for the Twin-Induced Plasticity (TWIP) effect. Thermomechanical-cycling processes are systemically applied to control a volume fraction of mechanical twins. The dissociation residual stress and passage of {332}<113><sub>β</sub> twin can render multiple mechanical twins form into the β-phase matrix and thus induce a softening effect for enhancing uniform ductility of Ti-Nb Gum metal, attributed to well-distributed twins throughout the entire microstructure based on the 'composite effect'.

Lastly, this paper reports on a heterogeneous-structured  $\beta$ -Ti alloy with an exceptional combination of high strength and ductility, resulting from optimized hierarchical features in a lamellar microstructure. The microstructure is achieved by controlling a fraction of coarse/fine domains, spatial grain-size distribution, and different types of grain boundaries. The large degree of microstructural heterogeneity leads to obvious mechanical incompatibility and strain partitioning during plastic deformation. These experimental results demonstrate that the microstructure design can be undertaken to open new possibilities to expand the material property window between the relatively low Young's modulus related to chemical composition optimization and better formability linked to improved ductility and enhanced strain hardening.

ΧХ

# **Chapter 1**

# Introduction

## **1.1 General introduction**

Over the past 20 years, there has been growing interest in materials science and industrial fields for Ti alloy and its technology and applications. As a result, the manufacturing and production practices for the use of Ti alloys have matured more rapidly than other structural materials in the metallurgy history [1-3]. The major advantages for Ti alloys to be applied in various engineering fields are the relatively high specific strength and a superior corrosion resistance, and also very good biocompatibility in many case impact human safety and well-being [2]. There have been a large number of titanium alloys which are successfully developed by Ti ingot melting and processing into mill products, and secondary fabrication [3]. Specifically, improving the performance and reliability of Ti alloys is attributed to the focus on eliminating production defects and avoiding unexpected failures, which has been producing good results. However, it is still required for variations in materials performance including an appropriate degree of conservatism and production cost [4].

Titanium and its alloy can be grouped into three major categories with  $\alpha$ -alloys,  $\beta$ -alloys and  $\alpha$ + $\beta$  alloys, which is dependent on alloying elements. More importantly, their properties are based on microstructure and phase stability which, in turn, is thought to be strongly composition dependent [5]. Not only that titanium and Ti alloys are also extremely sensitive to impurities, especially oxygen and nitrogen, where form alloy the type of interstitial solid solutions or metallic phases with titanium. Particularly, with only hundredth fractions of a percent, they significantly affect the properties of Ti alloys [6-8]. The most numerous and traditional group are titanium

alloys which represent solid solutions. As a rule, they are structural alloys with a high ratio of strength and ductility, satisfactory fusion weldability, capability of hardening heat treatment, good thermal stability, and other properties required for modern structural materials. Figure 1.1 shows examples of the growth in the use of Ti alloys in widely differing applications, and with a range of engineering demands, that in many cases impact human safety and well-being [3]. Their excellent specific strength predominantly led to their introduction in aircraft gas turbines as early as 1952 when they were used for compressor blades and discs in the famous Pratt and Whitney J57 engine [9]. However, the use of Ti alloys for structural members in aircraft has been more slowly due to their high cost relative to aluminum alloys. In fact, more than half of the world's production of titanium and related alloys is firstly used for non-aerospace application i.e. chemical engineering and architecture purpose in many environments, which is mainly attributed on its outstanding corrosion resistance [3]. Although Ti alloys are usually more expensive than other materials they replace, their adoption is based on expected cost savings over the planned lifetimes of the particular equipment or machines. Conclusively, in arears such as for automotive components, aerospace, bio materials, military hardware, and sports equipment, their unique mechanical, physical and chemical properties are usually the main attraction.

## 1.2 Classification of titanium alloys

Titanium has a number of features that distinguish it from the other light metals; the interaction of titanium with other alloying elements is influenced on the temperature of the allotropic transformation of titanium. The elements alloyed with titanium dominantly determine to a considerable degree the diversity of properties of Ti alloys [1]. Given that titanium is a transition metal with an incomplete shell in its electronic structure, most substitional elements having a size factor within ~20% can make it to form solid solution.

Although various classes of phase diagram have been applied with different elements, the titanium-rich sections of pseudo-binary systems enables them to be classified into three simply types, particularly dependent on  $\alpha$  or  $\beta$ -phase stability alloying addition. Alloving elements in titanium dissolve in those phases, in which they increase forces of atom-atom interaction and enhance their relative stability. Figure 1.2 presents typical elements dependent phase stabilities in titanium [3]. With respect to titanium, alloying elements are divided into elements stabilizing the  $\alpha$ -phase and those stabilizing the  $\beta$ -phase in titanium (Figure 1.2 a and b). It should be noted that elements having little effect on the temperature of allotropic transformation in titanium (tin, zirconium) are singled out into a group of neutral strengtheners. Elements that dissolve preferentially in the  $\alpha$ -phase expand this field thereby raising the  $\alpha/\beta$ transus (ex: aluminum increases the elastic constants of solid  $\alpha$ -solution). On the other hands, molybdenum and vanadium, which stabilize the  $\beta$ -phase, decrease the elastic constants of  $\alpha$ solution, thus increasing these characteristics for  $\beta$ -solution by a formation of an immiscibility gap, as shown in Figure 1.2c. Elements of this type have an effect on the structure and properties of alloys, which differs from that of typical  $\alpha$ - or  $\beta$ -stabilizing elements, while the  $\beta$  stabilizers Cr, Fe, Cu, Ni and Si form intermetallic compounds through a eutectoid reaction (Figure 2d) [3].

#### **1.3 Solid β-Solution in titanium alloys**

As dicussed in Section 1.2, alloying of titanium is dominated by the ability of elements to stabilize either of the  $\alpha$ - or  $\beta$ -phases. This behavior, in turn, is related to the number of bonding electrons, i.e. the group number, of the element concerned. Alloying elements with electron/atom ratios of less than 4 stabilize the  $\alpha$ -phase, elements with a ratio of 4 are neutral, and elements with ratios greater than 4 are  $\beta$ -stabilizing. Compared with  $\alpha$ , the  $\beta$  phase is characterized by the following properties [10] :

- High ductility
- Lower resistance to plastic deformation (low Yield strength)
- Diffusion rates that are higher by at least two orders of magnitude
- Poor creep resistance
- Little anisotropy of physical and mechanical properties

A generalized titanium– $\beta$ -stabilizing element phase diagram, which includes  $\alpha$ -,  $\alpha$ + $\beta$ - and  $\beta$ -regions in solid-solutions (at low temperatures) is presented in Figure 1.3. This diagram indicates each one is normally composed of two curves plotted from a common origin, which represents the temperature for allotropic transformation. The lower curve can be limited the region of the existence of solid  $\alpha$ -solution, and the cross-section of this curve with the abscissa axis in point  $C_{\alpha}$  corresponds to the ultimate concentration of its solid solution at room temperature [2]. The upper curve determines the boundary between the  $\alpha+\beta$ - and  $\alpha$ -regions, and the point of its intersection with the abscissa axis  $C_{\beta}$  corresponds to the minimum required concentration of the  $\beta$ -stabilizing component to form solid  $\beta$ -solution stable within the entire temperature range. Note that this diagram is available both for binary alloys of titanium with a  $\beta$ -stabilizing element. At a certain temperature (for instance, T1), irrespective of the content of the  $\beta$ -stabilizing element in the alloy, its content in the  $\alpha$ - and  $\beta$ -phases is constant (C<sub>1 $\alpha$ </sub> and C<sub>1 $\beta$ </sub>, respectively). An increase in the content of the  $\beta$ -stabilizing element in the alloy with titanium at a given temperature in the  $\alpha$ + $\beta$ -region is accompanied by an increase in the amount of the  $\beta$ -phase, without a change of its chemical composition. Consequently,  $\beta$ -titanium alloys can be defined as those containing enough total alloying elements that enable the  $\beta$  phase to be retained in either a metastable or stable condition after cooling to room temperature during heat treatment, seen in Figure 1.4 [9, 11]. This implies that the amount of the elements is sufficient to passing through the martensite

start line (M<sub>s</sub>). Alloy compositions that place them between the critical minimum level ( $\beta_c$ ) of these stability elements (i.e. where the M<sub>s</sub> line intersects the room temperature axis) and the similar intersection point of the  $\beta$ -transus line ( $\beta_s$ ), are commonly referred to as metastable  $\beta$ -titanium alloys since they will precipitate a second phase (usually  $\alpha$  or  $\alpha''$ ) upon ageing.

Metastable  $\beta$  titanium alloys can be defined those alloys in which precipitation of  $\alpha$  phase is fully suppressed by containing sufficient elements as the  $\beta$ -phase stabilizer. Although  $\beta$  phase is nearly 100% retained after  $\beta$ -field solution and fully cooling, the phase in metastable  $\beta$  titanium alloys is still unstable at room temperature. As a result, secondary phases such as  $\alpha$  phase, hexagonal/trigonal  $\omega$  phase and orthorhombic  $\alpha$ " martensite may precipitate during cold deformation or heat treatments carried on above room temperature. The secondary phases play important roles in affecting deformation behaviors and mechanical properties and have attracted the most research interests. It has been revealed that very high strengths (well above 1 GPa) can be achieved by In addition to the secondary phases [3, 12]

#### 1.4 Phase stability in titanium alloys

The metastable structural state in titanium alloys can be induced during post treatments associated with heating and cooling. Metastable structures formed have a significant effect on the physical and mechanical properties and this is to be taken into account when processing titanium alloys. Structural transformations occurring during the sharp cooling of titanium alloys with various contents of  $\beta$ -stabilizing elements can be followed using a generalized "titanium– $\beta$ -stabilizing element" phase diagram, as described in Figure 1.5.

#### 1.4.1 Alloying elements

Increasing the solute content with sufficient quantities of beta phase stabilizing elements contributes to a progressive increase in the amount of metastable  $\beta$  phase that is retained on quenching from the  $\beta$  or  $\alpha$ + $\beta$  phase field. Many of these elements lower the beta transus temperature T<sub> $\beta$ </sub>, which is the lowest temperature that only the  $\beta$ -phase will retain, broden the  $\beta$ -phase field, narrow the hcp  $\alpha$ -phase field, or consists a combination of these three effects (Figure 1.4). The addition of beta-stabilizing elements exclusively influences the precipitation of the aforementioned martensitic phases and the metastable hcp  $\Box$ -phase when applied external stress or heating. On the one hand,  $\alpha$ '-martensite phase forms at lower concentrations of beta-stabilizing elements, whereas the orthorhombic  $\alpha$ "-martensite phase precipitates with the relatively high  $\beta$ -stabilizing elements [13, 14]. If the alloy contains a sufficient content of  $\beta$ -stabilizing elements to bring the *M*<sub>s</sub> temperature below room temperature then a fully metastable  $\beta$ -structure can be retained. The possible reactions (with the most important being underlined) and microstructures are summarized in Figure 1.6.

In Figure 1.5,  $\alpha$ -stabilizing elements, such as AI, Fe, and O, tend to increase T<sub>β</sub>, i.e., they raise the temperature at which the  $\alpha$ -phase is stable. Intentionally, the elements are often used for  $\beta$ -phase Ti alloys to promote  $\beta$ -phase stability because a volume fraction of the metastable  $\Box$ -phase or athemal  $\alpha$ " phases is restricted, which is affected on its kinetics of phase transformation during aging, consequently hinder its formation [15]. Furthermore, aluminum also acts to decrease the  $M_s$  temperatures [2] which is accompanied by suppression of the aforementioned martensitic phase transformations. Basically, the  $\Box$  or  $\alpha$ "- matrentic phases induce high strength and Young's modulus but very low ductility and fatigue and hence, this phases are desired with little volume fractions to avoid embrittles in Ti alloys [13, 16]. In addition, oxygen (O) and nitrogen (N) are considered to strong  $\alpha$ -stabilizing elements with high solid

solubility whereas carbon (C) is also an  $\alpha$  stabilizer but with lower solubility [3, 17, 18]. Although these interstitial elements obviously increase  $T_{\beta}$  in phase diagrams, they also act to suppress the precipitation of  $\alpha''$  or  $\Box$ -martensite phases, resulting in lower Young's modulus and high ductility in Ti alloys with a certain concertation [12, 15-18].

Next, neutral elements, such as zirconium (Zr) and tin (Sn), little affect  $T_{\beta}$  but known for  $\beta$ -stabilizing elements, based on the kinetics of isothermal  $\Box$ -phase transformation during aging. For example, the addition of Zr in binary Ti-Nb alloys contributes to not only decreasing the volume fraction of the  $\Box$ -phase, but also suppressed its nucleation through acting synergistically with Nb to stabilize the  $\beta$ -phase [15]. Additionally, it has also reported that the addition of Sn in binary Ti-V and Ti-Mo alloys limited the stability of the  $\Box$ -phase and reduced its volume fraction for a post hear treatment. Therefore, the neutral elements (Zr and Sn) can be used to decrease *Ms*, which is attributed to suppression of the martensitic transformation.

#### 1.4.2 β-phase stability in titanium alloys

As mentioned earlier, one important characteristics of metastable  $\beta$ -titanium alloys is the  $\beta$  phase stability, which is a function of its composition. It is a dominating factor in determining whether the martensitic transformation will occur as well as the amount of martensite formed in response to either a thermal driving force (e.g. quenching) or a stress driving force (e.g. deformation). For example, stress-induced martensite is significantly sensitive to the composition of  $\beta$ -phase that further relates closely to  $M_s$  temperature [18]. In addition, the deformation mechanism of these alloys is also dependent on the  $\beta$  phase stability [19-21]. In the stable  $\beta$  titanium alloys, slip-dominated deformation mechanism can be operative for plastic deformation, which is attributed to a local strain concentration, and resulting in limited ductility [19, 22]. Thus, the deformation mechanism in a stable  $\beta$  matrix is predominantly activated by slip

dislocations and eventually shear bands becomes the dominant mechanism during plastic deformation. With decreasing  $\beta$ -phase stability of titanium alloys, {112}<111> twinning, {332}<113> twinning system and stress-induced martensitic transformations ( $\beta \rightarrow \alpha''$  and  $\beta \rightarrow \omega$ ) would be favorable for the deformation mechanism, as shown in Figure 1.7. It has been found that the activation of multi deformation mechanisms can significantly improve the poor ductility associated with the slip-dominated deformation mechanism [19, 27, 24]. Therefore, tailoring the  $\beta$  phase stability or equivalently the deformation mechanisms has become an important approach of designing metastable  $\beta$  titanium alloys. This necessitates a accurately estimating of the  $\beta$ -phase stability, particularly attempts for designing more applicable metastable  $\beta$  titanium alloys.

#### Molybdenum equivalence (Mo<sub>eq</sub>)

Molybdenum equivalence ( $Mo_{eq}$ ) has been most widely used approach to evaluate and quantify  $\beta$ -phase stability in titanium alloys, which is represented as a linear sum of weight averages of alloying elements in weight percent (wt%). Molybdenum equivalence equation is given in Equation 1.1 [25]:

$$Mo_{eq} = 1.0(wt.\% Mo) + 0.67(wt.\% V) + 0.44(wt.\% W) + 0.28(wt.\% Nb) + 0.22(wt.\% Ta)$$
  
+ 2.9(wt.% Fe) + 1.6(wt.% Cr) + 1.25(wt.% Ni) + 1.70(wt.% Mn) + 1.70(wt.% Co)  
- 1.0(wt.% Al) (1.1)

In Eq. 1. 1, the constant is the ratio of concentration of molybdenum (Mo), which is required to preclude formation of the martensite phases. On the other hands, aluminum (Al) is excluded from the equation so that it tends to be an  $\alpha$ -stabilizing element, as discussed above. The effect of other  $\alpha$ -stabilizing elements and neutral element are incorporated into Eq. 1 through

the aluminum equivalency  $(Al_E)$  given by [25]:

$$AI_{E} = 1.0(wt.\% AI) + 0.17(wt.\% Zr) + 0.33(wt.\% Sn) + 10(wt.\% O)$$
(1.2)

It suggests that each element has a different effect on phase stability in Ti alloys. In general, a  $Mo_{eq}$  value of 10.0 is required to stabilize  $\beta$ -phase during quenching, and  $T_{\beta}$  tends to decrease with increasing  $Mo_{eq}$ . A high value of  $Mo_{eq}$  indicates a vigilantly stable phase in the alloy and is feature of multicomponent alloys. A list of  $Mo_{eq}$  values for many metastable b-phase Ti alloys is provided in Ref. 19.

#### *Martensite start (M<sub>s</sub>) temperature*

Neelakantan et al. [26, 27] proposed a linear dependence between the in-situ composition of the  $\beta$ -phase, expressed in weight percent (wt%) and atomic fraction (N), and the  $M_s$  temperature:

$$M_{\rm s} [wt\%] = 1156-150 Fe-107 Mn-96 Cr-67 Ni-49 Mo-41 Cu-37 V-17 Nb-7 Zr+15 Al$$
 (1.3)

 $M_{\rm S}$  [N] = 1156-17480Fe-12186Mn-11299Cr-8096Ni-9463Mo-5250Cu-4354V

Hence, the stability of  $\beta$  phase and *Ms* temperature can be estimated from the equation 1.1 and 1.3, respectively, based on in-situ  $\beta$  phase composition. More importantly, it is very useful to predict or design alloying composition, i.e. the more stable the  $\beta$ -phase, the lower the *Ms* temperature

1.4.3. Phase stability dependent deformation mechanism in metastable titanium alloys

#### DV-Xa cluster method (Bo-Md stability map)

In the DV-X $\alpha$  cluster method, two parameters, i.e. bond order (Bo) and metal d-orbital energy level (Md), are attempted to define the boundaries of the martensite and omega transformation in relation to the modulus of the  $\beta$  phase using experimental data from a wide variety of alloying systems. The former is the measurement of the bond strength between Ti and an alloying element. The latter is related to the electronegativity and the metallic radius of the alloying elements [28-30]. For a given alloy, the average values of bond order (Bo) and d-orbital energy level (Md) are given as follows [30, 31]:

$$\overline{Bo} = \sum_{i=1}^{n} x_i (Bo)_i \tag{1.5}$$

$$\overline{Md} = \sum_{i=1}^{n} x_i (Md)_i$$
(1.6)

Here,  $x_i$  is the atomic fraction of an alloying element and (Bo)  $_i$  and (Md)  $_i$  are the Bond order values and metal d-orbital energy level for element i, respectively. Furthermore, this phase stability map can be constructed using Bo and Md, as shown in Figure 1.8. The location of designed alloy is varied depending on its chemical compositions. In addition, the Bo-Md diagram provided correlation of the chemical stability of the  $\beta$ -phase with the occurrence of the dominant deformation mechanism using experimental data from a wide variety of alloying system [33], which is experimentally corresponding to the preferred activation of mechanically-induced twinning, stress-induced martensitic transformation and dislocation slip [28, 34]. The Bo-Md phase stability diagram is therefore a very useful tool for investigating how plastic deformation behavior is affected by alloy composition that corresponds the phase stability of  $\beta$ -Ti alloys.

#### Average electron-to-atom ratio and atomic radius difference

Recently, it has been pointed out that the Bo-Md diagram had errors to employ for some metastable titanium alloys to estimated phase stability regarding deformation mechanism. For example, it was found that the Ti–10V– 3Fe–3Al (wt.%) was located within the twinning region in Bo–Md diagram; however, in reality, the stress-induced martensitic  $\alpha$ " phase was found in the microstructure after cold deformation [35, 36]. As a result, Wang et al. [77] have proposed a semiempirical approach to estimate the effect of deformation behavior on  $\beta$ -phase stability in Ti alloys, where the average electron-to-atom ratio (e/a) and atomic radius difference ( $\Delta r$ ) are adopted, and thereby an e/a -  $\Delta r$  map was suggested, as illustrated in Figure 1.9. The main characteristics of the e/a -  $\Delta r$  map depicts that as follow:

- (1) The slip-dominant region has the relatively higher value of e/a than that of the twinning/stress-induced martensite (SIM) region, which are mainly activated under e/a < 4.2 and  $\Delta r > -2.5$ .
- (2) The critical values for e/a of the twinning/SIM region are seen a peak as Δr is close to 0, and then decline as the Δr increases.
- (3) Therefore, with increasing the  $\beta$  phase stability, it is proved that e/a and  $\Delta r$  also influence the deformation mechnism of  $\beta$ -phase titanium alloys through manipulating the difficulty of lattice shear.

# 1.5 Effect of Oxygen on mechanical/elastic properties in biocompatible β-titanium alloys

Due to an exceptional combination of unique elastic properties and excellent biocompatibility, metastable β-type Ti alloys (i.e. body-centered cubic) are very attractive to be utilized as structural biomaterials, covering implant, replacement for hard tissue and bone fixation

devices, and shape memory related applications as stents and even occluding structures to heal congenital heart defects [3, 39, 40]. In recent years significant theoretical and experimental developments have been achieved in optimizing alloy composition to meet the crucial demands for metallic biomaterial implants: extremely low Young's modulus (<50GPa) and significant large elastic strain (>2%) [41-43], which makes them more compatible with respect of to the natural elastic of bone. Biomedical materials are possibly failed by wear and corrosion, inflammation and mechanical degradation, and importantly necessary to overcome the stress shield effect that cause bone degradation and absorption [40, 41]. These factors, together with good stresscorrosion resistance, high mechanical properties and acceptable tissue tolerance has led to their application for prosthetic devices. More recently, concerns about possible long-term cytotoxic effects of elements such as vanadium, nickel and aluminum has drawn interesting in the investigation of alternative alloys. One example are the  $\beta$ -titanium alloy Ti-15Mo-5Zr-3Al which has higher tensile and fatigue strength than Ti-6AI-4V and has a reduced elastic modulus of 80 GPa which is much close to that of bone. Figure 1.10 presents the biocompatibility of various elements in titanium alloys and Young's modulus for various β-titanium alloys with comparison of human bone. Therefore, there are multiple requirements in terms of using biocompatible alloying components only, achieving low Young's modulus as much as possible, and simultaneously reaching sufficient strength and ductility. As shown in Figure 1. 10, Nb, Ta, Zr, and Mo are regarded as the most biocompatible ones whereas V, Cr, and Al must be avoided to use for alloying. Basically, pure titanium shows approximately 100 GPa of elastic modulus, which is still five times higher than that of human bone (10–30GPa) [43]. It has been reported that different phases have different elastic modulus (E) and found to be related as:

 $E_{\beta} \approx E_{\alpha''} \approx 60-90GPa < E_{\alpha'}100GPa < E_{\omega} 130-220GPa [46-48].$ 

The least stable  $\beta$ -phase can be seen the lowest Young's modulus, but the precipitation of  $\Box$  or

 $\alpha'$  phases in the alloy make it significantly increasing the Young's modulus. Therefore, it is essential to suppress their formations and keep the Young's modulus low plausible explanation.

According to the previous reports, the oxygen significantly affects mechanical and elastic properties of biomedical  $\beta$ -titanium alloys, resulting in employing a certain amount of oxygen as an "alloying element." There are two main mechanisms as:

(1) Oxygen atoms cause strong interstitial strengthening

(2) Oxygen can control the phase stability in Ti alloys, which subsequently influences the resulting Young's modulus for final products

Generally, oxygen atoms in titanium and titanium alloys occupy interstitial sites, where is known as tetrahedral voids with  $r_{void}/r_{atom} = 0.225$  ratio and larger octahedral voids with  $r_{void}/r_{atom} = 0.414$  in a hexagonal closed packed structure ( $\alpha$ -titanium). Therefore, it is energetically favored for the oxygen atoms to occupy larger octahedral sites where is surrounded by six titanium atoms [2]. For a body-centered cubic structure,  $\beta$ -phase titanium, oxygen atoms tend to be placed at tetrahedral sites rather than octahedral ones due to the difference in the occupation volume with  $r_{void}/r_{atom} = 0.291$  and 0.155, respectively [3]. In regard, interstitial oxygen introduced in the alloys is considered to cause a significant asymmetric distortion of the lattice, which is attributed to unique elastic properties and exceptional mechanical properties in  $\beta$ -titanium alloys.

#### 1.5.1 Oxygen and elastic modulus

Elemental oxygen plays an essential role in achieving the low Young's modulus by retarding  $\alpha^{\prime\prime}$  martensite and  $\omega$  phase formation. The  $\omega$  phase is a hexagonal phase (but not hexagonal close packed) that is most responsible for the high values of Young's modulus and hardness of  $\beta$ -Ti alloys [49]. It was found that the formation of  $\omega$  phase is accompanied by a

diffusionless displacive transformation [50, 51], particularly upon quenching. There are three types of  $\omega$  phases; 1) nano-sized spherical particles in  $\beta$ -matrix (referred to athermal  $\Box$  phase), 2) lamellae-shape  $\Box$  in  $\beta$  matrix, 3) lath-like  $\Box$  with deformation twins (stress-induced martensite phase).

It has been widely reported that interstitial oxygen suppresses martensite transformation from the  $\beta$  matrix to athermal  $\Box$  phase. In Ti - (17-19)V - (0.025–0.125)O alloys, Paton et al. [52] reported that the martenstic  $\omega$  phase can be reduced by addition of oxygen element, which is attributed to decreasing  $M_s$  temperature below the room temperature, and consequently, the decreasing in Young's modulus through keeping the  $\beta$  phase whose modulus is much lower than that of other martensite phases. It has indicated that various metastable decomposition occurred at atomic level, which includes the Bain distortion for the martensitic transformation is strongly connected to the softening of shear modulus c' and a {110}<110> transverse phonon wave that is related to the shuffle [3]. Moreover, oxygen creates a hysteresis of the non-diffusional  $\beta$  to  $\omega_{ath}$  phase transformation, suggesting that interstitial oxygen can enhance the shuffle associated with the martensite temperature. It has been also observed during cold-rolling processes that metastable  $\beta$ -phase can be transformed to  $\Box$ -phase by plastic deformation, which referred to stress-induces martensite transformation. The elastic modulus in the studied alloys can be varied by the amount of cold deformation, but it can be suppressed by interstitial oxygen in the alloy [3,42].

In terms of alloying design to low-modulus titanium alloy, martensitic  $\beta$ - $\alpha$ " transformation seems to be crucial, due to the fact that the formation of  $\alpha$ " phase, an orthorhombic martensitic phase formed by lattice displacement, is significantly affected by oxygen contents in the alloy [53, 54]. As widely reported in Ti-Nb-base alloys, based on numerous experimental and theoretical studies [47, 54], oxygen elements act as a  $\beta$  stabilizing element by shifting the *M*<sub>s</sub> temperature of

 $\alpha''$  to lower temperatures. Moreover, the theoretical analysis with first principles calculations indicated that Zr-O bonding is energetically favorable, resulting in Zr-O nanoclustor. It was confirmed that the coexistence of Zr and oxygen atoms can enhance the elastic stability of the  $\beta$  phase as shown in Gum Metal [55]. For instance, the formation of stress-induced martensite  $\beta$  to  $\alpha''$  phase transformation, which is fully reversible upon unloading, causes a significant nonlinear elastic behavior, referred to as superelastic behavior. On the other hand, when oxygen is added to such finely tuned superelastic alloys, the  $\beta$  stability is more stable, and resulting in either fully or partially suppressed the martensite transformation upon loading. Furthermore, in Ti-30Nb-12Zr-(0.08–0.50)O alloys, the double yielding behavior is diminished with increasing oxygen contents, due to increasing the critical stress for activating the stress-induced martensite transformation during loading [56]. There are two mechanism on how to influence the oxygen on martensite transformation [57]:

#### (1) Enhance the critical stress for $\alpha$ "-phase formation and reducing ultimate $\alpha$ "-phase fraction

(2) Decrease in the transformation strain of displacive  $\beta$  to  $\alpha$ " transformation due to structural convergence of parent  $\beta$  and martensite  $\alpha$ " phases with increased interstitial content

The effect of oxygen for stabilizing  $\beta$  phase was used in  $\beta$  Ti alloys subjected to cold rolling, in which the stability of the  $\beta$  phase at room temperature is unstable (i.e., very close to  $\beta$  to  $\alpha$ "transformation). For example, It was reported that Ti-38Nb-0.14O alloy after 90% of cold rolling was successfully achieved the relatively low elastic modulus (approximately 54GPa), attributed to none of apparent SIM transformation [57].

Figure 1. 11 exhibits the various moduli obtained from theoretical results of single crystals [53, 57, 59-61] with electron/atom ratios, indicating that the shear modulus, c', decreases as a function of e/a ratio, while  $c_{44}$  is constant irrespective of the e/a ratio. It is apparent that both c' and  $c_{44}$  drop with decreasing temperature until the athermal  $\Box$  phase start temperature or the  $M_s$
are reached. More importantly, c' is an indicator of the  $\beta$ -stability so that the softening of c' presents the basis for the martensitic transformation. It should be noted that decreasing the e/a ratio also results in raising the  $M_s$  and athermal  $\Box_s$  temperature, and thereby it allows for alloy design towards low elastic modulus alloys attempts to retard martensite transformations below room temperature possibly at the lowest e/a ratio. It has been particularly agreed when one of the alloying additions is presented as an interstitial, such as O or N. As indicated in Figure 1. 11, the compositions based on the Ti–Nb–Ta–Zr and Ti–Nb–Ta–Zr–Sn with the lower c' and c44 values suggest that in terms of the e/a ratio, the composition of Gum Metal, which additionally contains deliberate additions of oxygen, falls into this class [54]. This is apparently because oxygen, even with Zr and Sn can retard martensitic transformation during post treatment. Unfortunately, elastic constants obviously depend in a complex manner on the variety of instabilities that  $\beta$  phase is subject to the given ranges of e/a ratio [3].

#### 1.5.2 Oxygen and mechanical strength

In terms of a strengthening effect, the anisotropy of lattice distortion is accompanied by interaction of interstitial atoms with dislocations, consequently promoting hardening. The strengthening by interstitial atoms introduced is much more effective in alloys with body-centered cubic structure rather than in materials with face-centered cubic structure. With increasing solute concentrations, the interstitial atoms, occupying one of three types of octahedral sites, lead to long-range lattice distortion and transform the lattice from body-centered cubic to body-centered tetragonal [62].

In β-titanium alloys, oxygen significantly influences on its mechanical strength by solute strengthening effect. Interstitial oxygen atoms mainly promote Cottrell atmosphere and Snoek atmosphere around dislocations and thus dislocation is hindered to move by the atmosphere,

resulting in increasing strength [63, 64]. For example, Gum Metals, which often are compositionally close to Ti-23Nb-0.7Ta-2Zr-O (at%), exhibit extremely low Young's modulus (50-70GPa) and a high strength (~1.0GPa) with oxygen content from 0.8 to 2.0(at%). Basically, there are several mechanisms on oxygen dependent plastic deformation, such as slip dislocation, twinning, stress-induced  $\Box$  and  $\alpha''$  martensite phases in  $\beta$ -titanium alloys. Given that the dominant mechanisms of plastic deformation are strongly related to with phase stability as discussed in Section 14, the strength values can be varied by the oxygen contents even during tensile plastic deformation. Table 1.1 unambiguously documents the mechanical strength enhancement by interstitial oxygen. It can be found that ultimate tensile strength in most titanium alloys would be over 800MPa with approximately 0.4wt% oxygen addition in the alloys. However, there is a drastic loss of ductility owing to oxygen solute strengthening effect [64-66], referred to strength-ductility trade-off. In particular, uniform tensile elongation decreases by the addition of oxygen, as described in Figure 1.12, which reflects the dilemma of low Young's modulus and a poor formability in metastable  $\beta$ -titanium alloys with high oxygen content [68]. Despite the fact that interstitial oxygen shows adverse effects on ductility and formability, two exceptions can be found in Table 1.1 for Ti-35Nb-5.7Ta-7.3Zr alloy [69] and the Ti-35Nb-2Ta-3Zr alloy [70], where the elongation was found to improve even when the oxygen content was increased from approx. 0.3 to 0.7wt%. Furthermore, it exhibits that work hardening is dramatically enhanced with a certain oxygen contents, which is attributed to suppressing the early necking induced by strain localization. It has been investigated that the oxygen introduced in βtitanium alloys may help retard athermal  $\Box$  or/and  $\alpha''$  martensite transformation, which are beneficial to achieved its unique elastic properties, whereas ductility and formability of the materials are significantly decreased by the addition of oxygen, which is mainly due not only to oxygen solute strengthening, but also suppression of the deformation twinning mechanism by increasing  $\beta$ -phase stability [67-69].

## 1.6 Motivation and goals

The emergence of Gum metal [65] as a super elasto-plastic titanium alloy displaying a super-elastic behavior has spurred considerable interest in understanding inelastic behavior in this class of alloys [3]. In addition to the super-elastic properties, Gum metal also exhibits low Young's modulus (30-60GPa) and high strength that cannot be obtained from conventional metallic materials, as indicated Figure 1.13. Importantly, the unique properties including good cold-workability (over 99%) can be only achieved when all three of magic numbers are satisfied simultaneously, such as (i) the valence electron number (e/a of around 4.24), (ii) the bond order (Bo value of around 2.87), (iii) the "d" electron-orbital energy level (Md value of around 2.45) [64]. When originally announced, it was proposed that each alloy system requires significant cold working, then the strength of cold-worked Gum metal approaches the ideal shear strength of the alloy determined by the shear modulus along the <111> direction [3, 64]. More importantly, it must contain a certain amount of oxygen, at 0.7 at%. Basically, the composition of the developed alloy is fundamentally expressed as Ti - 24(Ta+Nb+V) - (Zr, Hf) - O. Various alloying compositions are investigated, such as Ti-23Nb-0.7Ta-2Zr-O and Ti-12Ta-9Nb-3V-6Zr-O (at%), wherein each alloy has a simple body-centered crystal structure. As stated earlier, oxygen content, as well as cold working, influences the elastic properties of Gum metal alloys. Figure 1.14 shows the variations of elastic properties as function of oxygen content and cold working of the Ti-23Nb-0.7Ta-2Zr-O alloy before and after cold working with a 90% reduction in area. The attainable elastic strain increases with increasing oxygen content and is enormously accelerated by the cold working. Additionally, the strength of  $\beta$ -titanium alloys is remarkable increased by increasing oxygen; it reached 1500 MPa with approximately 3 mol% oxygen, and even it can be achieved over 2000MPa after aging treatment. Owing to these unique physical properties and further good biocompatibility, Gum metals are expected to be promising biomaterials such as artificial hip and knee joints, etc. However, the alloy development effort has not focused on

improved plastic deformation behaviors related to higher ductility and better formability. Due to the fact that Gum Metal has the poor formability and the relatively low strength (no precipitation) compared to the other commercial titanium alloys, Gum metal alloys translation into commercial applications has been hindered.

With progress in improving formability, a prominent approach has been considered to stimulate activation of multiple deformation modes, such as mechanical twinning or stress-induced transformation, along with dislocation slip, and thus significantly improve upon the poor ductility caused by rapid strain localization in slip-dominated  $\beta$ -titanium alloys. Unfortunately, it is difficult to separately manipulate the mechanical properties of these alloys, without affecting the Young's modulus variation (avoiding increasing the modulus), which is the most prominent property of these metastable  $\beta$ -titanium alloys for consideration in biomaterial implants. Therefore, the current research supplements the preliminary characterization and microstructure design to investigate the possibility of controlling mechanical properties of a metastable  $\beta$  phase Ti-Nb based Gum metal and is outlined below.

The next three chapters give the results and discussions of this dissertation. Each of the three chapters incorporates a detailed introduction into the literature pertinent to the issues to be clarified. Chapter 2 presents the possible deformation mechanism with respect to the  $\beta$ -phase stability. The Bo-Md phase stability diagram was adopted to evaluation the  $\beta$ -phase stability and to discuss the deformation modes with elemental distributions, resulting in different deformed microstructure. This chapter is a modified version of the present author's published paper "Sumin Shin, Cheng Zhan, Kenneth S. Vecchio. Phase stability dependence of deformation mode correlated mechanical properties and elastic properties in Ti-Nb gum metal. Materials Science & Engineering A 702 (2017) 173-183." (Courtesy of Elsevier Ltd)

In Chapter 3, thermomechanical-cycling process were developed to design pre-twinned

microstructure and delve deeply into the formation of {332}<113> twinning responsible for the microstructure evolution and hardness. Highly twinned misstructure in Ti-Nb Gum metal was achieved, and possible deformation mechanism was established for activation of twinning-induced plasticity effect. This chapter is a modified version of the present author's published paper *"Sumin Shin, Chaoyi Zhu, Kenneth S. Vecchio. Observation on {332}<113> twinning-induced softening in Ti-Nb Gum metal. Materials Science & Engineering A 724 (2018) 189-198."* (Courtesy of Elsevier Ltd)

Chapter 4 illustrates the relationship between a volume fraction of the pre-twinned structure and mechanical properties of Ti-Nb Gum metal. Based on the observed microstructure and deformation behavior as function of the twin fraction, intentional introduced twins are strongly related to the overall softening behavior, and enhanced uniform ductility, attributed to well-distributed twins throughout the entire microstructure based on the 'composite effect'. This chapter is a modified version of the present author's published paper "Sumin Shin, Chaoyi Zhu, Kenneth S. Vecchio. Effect of twinned-structure on deformation behavior and correlated mechanical properties in a metastable  $\beta$ -Ti alloy. Journal of Alloys and Compounds (accepted)". (Courtesy of Elsevier Ltd)

Chapter 5 provides a background of information regarding the special-purpose β-titanium alloys and discuss a new approach toward strength-ductility synergy based on intentional structural heterogeneities introduced by conventional cold rolling and heat treatment processes. A description of the heterogeneous microstructure process will also be detailed in this chapter, including a spatial grain-size distribution and different types of grain boundaries. This chapter also identifies a back stress hardening mechanism in heterostructural Ti–Nb-based Gum metal and presents reasonable explanations to the special deformation features observed in Gum metal. This chapter is a modified version of the present author's published paper *"Sumin Shin, Chaoyi*"

Zhu, Cheng Zhang, Kenneth S. Vecchio. Extraordinary strength-ductility synergy in a heterogeneous-structured  $\beta$ -Ti alloy through microstructural optimization. Material Research Letter, **7** (2019) 467-473." (Courtesy of Taylor & Francis)

Table 1.1: Overview of mechanical properties of Ti-Nb-based biomedical alloys with increased

Composition (wt%)	Oxygen (wt%)	SIM	Elastic modulus	Yield stress (MPa)	UTS (MPa)	Elong. (%)	Thermomechanical treatment
Ti-35Nb-5.7Ta-7.3Zr	0.06	NO	-	530	590	21	ST 850°C 1h WQ
Ti-35Nb-5.7Ta-7.3Zr	0.46	NO	-	937	1014	19	ST 850°C 1h WQ
Ti-35Nb-5.7Ta-7.3Zr	0.68	NO	-	1081	1097	21	ST 850°C 1h WQ
Ti-29Nb-13Ta-4.6Zr	0.12	NO	58	500	600	27	ST 790°C 1h WQ
Ti-29Nb-13Ta-4.6Zr	0.20	NO	70	600	700	20	ST 800°C 1h WQ
Ti-29Nb-13Ta-4.6Zr	0.42	NO	75	840	900	17	ST 820°C 1h WQ
Ti-35Nb	0	YES	-	350	500	38	CR (98.5%)+ST 900°C 0.5h WQ
Ti-35Nb	0.14	YES	-	170	700	27	CR (98.5%)+ST 900°C 0.5h WQ
Ti-35Nb	0.28	YES	-	350	850	27	CR (98.5%)+ST 900°C 0.5h WQ
Ti-35Nb	0.41	YES	=	450	900	9	CR (98.5%)+ST 900°C 0.5h WQ
Ti-35Nb	0.55	YES	-	500	1050	6	CR (98.5%)+ST 900°C 0.5h WQ
Ti-36Nb	0.04	YES		180	250	-	CR (98.5%)+ST 900°C 0.5h WQ
Ti-36Nb	0.28	YES	-	350	500	-	CR (98.5%)+ST 900°C 0.5h WQ
Ti-38Nb	0	YES	60	300	445	32	CR (90%)+ST 850°C 0.5h WQ
Ti-38Nb	0.14	YES	54	665	810	21	CR(90%)+ST 850°C 0.5 h WQ
Ti-30Nb-2Ta-3Zr	0.49	YES	58	-	1500	8	Hot rolled + cold worked (90%)
Ti-33Nb-2Ta-3Zr	0.49	NO	50	-	1250	14	Hot rolled + cold worked (90%)
Ti-36Nb-2Ta-3Zr	0.47	NO	60	-	1100	15	Hot rolled + cold worked (90%)
Ti-30Nb-12Zr	0.08	YES	67	-	545	48	ST 850°C 0.5h WQ
Ti-30Nb-12Zr	0.20	NO	67.4	-	675	37	ST 850°C 0.5h WQ
Ti-30Nb-12Zr	0.29	NO	68.2	-	720	30	ST 850°C 0.5h WQ
Ti-30Nb-12Zr	0.37	NO	68.9	-	850	25	ST 850°C 0.5h WQ
Ti-30Nb-12Zr	0.50	NO	72	-	995	18	ST 850°C 0.5h WQ

# oxygen content [68].

Composition (wt%)	Oxygen (wt%)	SIM	Elastic modulus	Yield stress (MPa)	UTS (MPa)	Elong. (%)	Thermomechanical treatment
Ti-35Nb-2Ta-3Zr	0.26	NO	65	650	750	17	ST 780°C 30 min AC
Ti-35Nb-2Ta-3Zr	0.38	NO	59	750	770	10	ST 780°C 30 min AC
Ti-35Nb-2Ta-3Zr	0.52	NO	60	800	840	4	ST 780°C 30 min AC
Ti-35Nb-2Ta-3Zr	0.59	NO	90	860	883	1	ST 780°C 30 min AC
Ti-35Nb-2Ta-3Zr	0.14	YES	60	350	600	21	Hot rolled + ST 730°C 1h WQ
Ti-35Nb-2Ta-3Zr	0.33	NO	65	700	800	13	Hot rolled + ST 810°C 1h WQ
Ti-35Nb-2Ta-3Zr	0.70	NO	75	1050	1050	19	Hot rolled + ST 970°C 1h WQ
Ti-35Nb-2Ta-3Zr	0	YES	55	280	400	33	ST 850°C 0.5h WQ
Ti-35Nb-2Ta-3Zr	0.32	NO	60	830	880	12	ST 850°C 0.5h WQ
Ti-35Nb-2Ta-3Zr	0.44	YES	45.3	880	940	5	Cold-worked (96%)



Figure 1.1: Applications of Ti alloys: (a) alpha Ti alloy in tubing for heat exchangers, (b) near  $\alpha$  + $\beta$  alloys in aeroengines, (c) high strength beta alloys in airframes, as percentage of overall aircraft weight and in landing gear of the Boeing 787 [5], (d) a Ti based hip replacement [6].



Figure 1.2: The influence of various alloying additions on  $\alpha$ - and  $\beta$ -phase stability. The  $\alpha$  and  $\beta$  phases are shaded in each case to illustrate solubility and stability: (a) stabilizers, (b)  $\beta$  stabilizers with continuous solubility, (c)  $\beta$  stabilizers with an immiscibility gap in the  $\beta$  phase, (d) eutectoid systems with intermetallic compound formation [3].



Figure 1.3: A scheme of "titanium– $\beta$ -stabilizing element" phase diagram illustrating the effect of the  $\alpha$ -stabilizing element on the boundaries of phase regions in binary (1) and ternary (2) alloys.



Figure 1.4: Pseudo-binary  $\beta$ -isomorphous phase diagram showing location of metastable and stable  $\beta$ -titanium alloys [11].



Figure 1.5: Change of phase composition for titanium–β-stabilizing element alloys as a

function of the quenching temperature [2].







Figure 1.7: Schematic phase diagram of binary titanium alloys.  $M_s$  and  $M_f$  represent the  $\alpha''$  martensite transformation start temperature and finish temperature, respectively.



Figure 1.8: The Bo-Md diagram [32].



Figure 1.9: The e/a-∆r diagram in which the Twinning/SIM and Slip regions are distinguished according to the reviews of published works. The use of empty and full bullets represents the Slip- and Twinning/SIM-dominated deformation mechanisms, respectively. SIM means stress induced martensite [38].



Figure 1.10: (a) The biological impact of metals [44]. (b) The modulus of various alloys in relation to bone [45].



Figure 1.11: [3] a) The variation of Young's modulus with  $\beta$ -stabilizing elemental addition (from Ref. [53]). (b) The variation of c' as function of e/a ratio. (c) The variation of c<sub>44</sub> with e/a ratio. (d) The variation of Young's modulus (deduced from single crystal constants) with e/a ratio. (b–d) are adapted from Ref. [59] with data included from Ti–15Mo–5Zr–3Al (red) [60], Ti–24Nb–4Zr–8Sn (green) [61] and gum metal (blue) [57].



Figure 1.12: Uniform tensile elongation vs. oxygen contents plot of the studied materials in comparison to literature data [25-28], where the uniform tensile elongation of other materials was obtained from engineering stress-strain curves.



Figure 1.13: Comparison of Young's modulus and strength of Gum metal [65].



Figure 1.14: Change in elastic properties oxygen content and cold working [64].

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# **Chapter 2**

# Phase stability dependence of deformation mode correlated mechanical properties

This chapter presents a comprehensive investigation on the phase stability dependence of deformation behavior of Ti-Nb based Gum metal. The evolution of microstructure and deformation modes in metastable Ti-23Nb-0.7Ta-2Zr-0.8O (at%) alloys with accumulated strain to 0.15 are investigated, where different solution treatments were applied to control both elemental distributions and the bcc  $\beta$ -phase stability. Based on the experimentally observed results, the  $\beta$ -phase stability dependence of deformation features can explain the possibility of manipulating the mechanical properties without the evident elastic properties variation in Ti-Nb Gum Metal. This chapter is a modified version of a paper that has been published in the journal Materials Science & Engineering A [1].

### 2.1 Literature review

Recently, tailoring chemical bonds has been considered an important methodology to the bottom-up design of metastable  $\beta$  titanium alloys [2]. This is achieved by controlling the stability of the bcc  $\beta$  phase at room temperature to a critical range, i.e., via manipulating compositional ranges in the phase diagram close to the phase boundary between  $\beta$  and  $\beta$  +  $\alpha$ " [3, 4]. This essentially renders the elastic limit (ideal shear strength) of the bcc  $\beta$  crystal to be comparable to the applied stress [5, 6], leading to non-conventional elastic and plastic deformation mechanisms

[5, 7, 8] and exceptional mechanical properties [4, 7]. With progress in developing multifunctional  $\beta$ -Ti alloys, therefore, tailoring the chemical stability of the  $\beta$ -phase has been an essential approach, which is strongly dependent on chemical composition of the alloys [9-11].

Gum Metals are the most well known metastable  $\beta$ -phase Ti alloy, developed by controlling chemical composition [12], which fundamentally consist of Ti + [Nb or V] + Ta + [Zr or Hf] elements and oxygen. It is well documented in the literature [12-14] that these alloys possess "super-properties" such as low elastic modulus with high strength, and high ductility accompanied by little or no work hardening during cold working. These combinations of properties are rarely present in a single alloy. For these unique characteristics of the alloys, three critical electronic parameters are simultaneously satisfied [12]; (a) an average valence electron/atom ratio e/a ~ 4.24; (b) a bond order (Bo-value) ~ 2.87, and (c) d-electron orbital energy level (Md-value)  $\sim$ 2.45eV. Furthermore, oxygen, with a range from 0.7 to 2.0 at.%, is an essential element in the chemical composition [12]. The specific composition required for Gum Metal's unique properties suggests that the characteristics of the alloys strongly correlate with their β-phase stability. Moreover, exceptional physical properties, such as nonlinear elastic behavior with an extended elastic limit, Invar-like thermal expansion, and Elinvar-like thermal dependence of the elastic modulus, can be achieved only after a certain amount of cold deformation [12]. This implies that the chemical composition of Gum Metal is not only related to the  $\beta$ -phase stability, but also to plasticity, which is considered as the most important factor to determine its characteristics. Plastic deformation of the Gum metal in processing is necessary to realize their unique properties.

Accordingly, there have been extensive studies investigating the deformation mechanism of Gum Metals to elucidate plastic deformation behavior [15-20]. Saito et al. [12, 19-21] reported that the above unique properties are attributed to a dislocation-free deformation mechanism, which is characterized by a distorted lattice containing nanodisturbances (referred to as "giant

faults"). It supported in the literature [22, 23] that the ideal strength of Gum Metal is achieved by means of a non-conventional plasticity mechanism, accommodated by with low resistance to shear along certain crystallographic planes, where the trigger stress for bulk shear is smaller than the critical resolved shear stress to move dislocation on their slip planes. However, several studies have recently shown that conventional deformation mechanisms are operative during plastic deformation in Gum Metals [16, 17, 22-27]. For example, mechanically induced twinning [17, 23] and stress-induced phase transformation [16, 22, 23] have been reported to be active in a deformed typical Gum Metal, Ti-23Nb-0.7Ta-2.0Zr-1.2O (at.%) alloy. In addition, Yang et al. observed dislocation glide on slip planes with increased oxygen content in Ti-22.4Nb-0.73Ta-2.0Zr-1.34O (at.%), whose  $\beta$  phase stability is slightly higher than that of nominal Gum Metal [16, 24-27]. Oxygen is considered a  $\beta$  stabilizing element in metastable  $\beta$  alloys [12, 26]. Therefore, these results imply that not only are multiple deformation mechanisms activated in Gum Metals, but also the main mechanism operative can be controlled by the  $\beta$ -phase stability.

It was found that the deformation behavior of metastable  $\beta$ -Ti alloys is closely related to the  $\beta$ -phase stability [9, 10, 13, 28-30], characterized by the ability to transform into martensite phase by cooling or external stress [31]. As discussed in the literature [10, 27, 28], deformation in stable  $\beta$ -Ti alloys is mainly accompanied by dislocation slip, while the activated deformation modes are changed with decreasing the  $\beta$ -phase stability, including mechanically-induced {332}<113> twinning, {112}<111> twinning, or stress-induced  $\alpha$ " martensitic transformation [15-17,30]. It has also been observed that multiple deformation mechanisms can co-exist, which results in a complex deformation behavior of metastable  $\beta$ -Ti alloys [16, 24, 30-32]. To establish the relationship between plastic deformation behavior and  $\beta$ -phase stability, two-dimensional phase stability diagrams have very recently been applied [31-34], utilizing the electronic parameters: bond order (Bo) and d-orbital energy level (Md). Morinaga et al. [35, 36] suggested that the two electronic parameters (Bo and Md) connect with the relative chemical stability of the

 $\beta$  phase, where Bo is the covalent bond strength between Ti and each alloying elements, and Md represents the electronegativity. These values were calculated using the following equations [35]:

$$\overline{Bo} = \sum_{i=1}^{n} x_i (Bo)_i \tag{2-1}$$

$$\overline{Md} = \sum_{i=1}^{n} x_i (Md)_i$$
(2-2)

Here,  $x_i$  is the atomic fraction of an alloying element and (Bo)<sub>i</sub> and (Md)<sub>i</sub> are the Bond order values and metal d-orbital energy level for element i, respectively. Furthermore, this phase stability map provided correlation of the chemical stability of the  $\beta$ -phase with the occurrence of the dominant deformation mechanism using experimental data from a wide variety of alloying system [35], which is experimentally corresponding to the preferred activation of mechanicallyinduced twinning, stress-induced martensitic transformation and dislocation slip [30, 31]. The Bo-Md phase stability diagram is therefore a very useful tool for investigating how plastic deformation behavior is affected by alloy composition that corresponds the phase stability of  $\beta$ -Ti alloys.

Compositional optimization has been widely used to achieve a superior combination of mechanical properties in metastable  $\beta$ -Ti alloys [12, 33, 37-39], because it is strongly linked with the presence of multiple phases that can be manipulated by materials processing and optimized alloy design. Based on this methodology, earlier reports [30, 32-34] suggest that the various deformation modes operative in a given alloy play a crucial role in enhancing the work hardening rate, and thus significantly improving the poor ductility caused by strain localization in conventional slip-dominated  $\beta$ -Ti alloys. The improvement in mechanical properties is attributed to the simultaneous occurrence of TRansformation-Induced Plasticity (TRIP) effect and

TWinning-Induced Plasticity (TWIP) effect [33, 34]. As such, compositional optimization is considered an approach to potentially control microstructure and optimize mechanical properties in  $\beta$ -Ti alloy.

Given the remarkable effects of Gum metal's composition on its physical properties, it is surprising how few studies have examined this approach to control the mechanical properties of Ti-Nb Gum Metal. Therefore, this study is aimed to improve and/or control the mechanical properties of Gum metal through manipulating deformation behavior in association with the chemical stability of the  $\beta$ -Ti phase. Different solution treatments were employed to achieve various  $\beta$ -phase stabilities through homogenizing the elemental distributions in a metastable  $\beta$ , Ti-23Nb-2Zr-0.7Ta-0.8O (at.%) alloy. The evolution of deformation mechanisms with respect to the  $\beta$ -phase stability is investigated, as well as discussion of the possibility of manipulating the mechanical properties without evident elastic modulus variation in this Ti-Nb Gum Metal.

#### 2.2 Experimental procedure

A master alloy with a nominal composition of Ti-23Nb-2Zr-0.7Ta-0.8O (at.%) was produced using a mixture of pure elements Ti, Nb, Ta Zr and powder TiO<sub>2</sub>. Owing to the difference in the melting point and density of raw materials, two kinds of ingots were first fabricated by arc-melting under argon atmosphere: *i*) Ti+Zr+TiO2, and *ii*) Nb+Ta. After melting these two ingots separately, they were combined together by arc melting, also under argon atmosphere. The resulting ingot was melted at least five times to avoid in-homogeneity due to un-melted elements or a lack of molten mixing. To minimize elemental segregation adjacent to grain boundaries, the ingot was held in an inert-gas induction furnace for 30 minutes in its liquid state. The chemical composition of the as-cast alloy is listed in Table 2-1. In order to achieve different elemental distribution in each sample, the solution treatment was performed for 100, 1,000 or 3,000 minutes at 1273K (above the  $\beta$  transus) under vacuum followed by quenching into water. These solution-treated specimens are referred to hereafter as ST100, ST1000, and ST3000, respectively. The microstructure of the as-solution treated alloys consists of large equiaxed grains whose average size was ~1200µm shown in Fig 1(a), irrespective of the different solution treatment times used in this study. For investigating the evolution of the deformation microstructure with accumulated strain, the samples for cold rolling were prepared with the following dimensions: 35mm in length, 10mm in width and 10mm in thickness. These samples, following the solution-treatment, were cold-rolled to a strain from 0.02 to 0.15, at room temperature. These cold-rolled samples were cut with a slow cutting speed to minimize any heating effects on the samples.

Specimens for structural investigations were first ground using SiC papers and then mechanically polished with  $3\mu$ m,  $1\mu$ m diamond, and  $0.05\mu$ m SiO2 solutions. The polishing process was performed under a load of 5N to avoid the formation of stress-induced  $\alpha$ " martensite phase on the surface; no subsequent etching was applied. Electron backscattered diffraction (EBSD) and scanning electron microscopy (SEM) were carried out on the plane parallel and normal to the rolling direction (RD) using a Bruker e-Flash EBSD detector on a FEI Quanta 600 SEM at 20 kV. Scans for EBSD were performed with a step sizes between 0.5-1.0 $\mu$ m and working distance around 20mm. In order to determine the local misorientation of deformed structures, the Kernel averaged misorientation (KAM) analysis was applied with misorientation ranges from 0 to 5°. The element composition of the microstructure was measured quantitatively by energy dispersive spectroscopy (EDS) using point-spot analysis as show Figure 2.1(a). To identify phase structures, X-ray diffraction (XRD) was conducted with Cu K $\alpha$  radiation. The body-centered cubic  $\beta$  phase was the only phase detected in the as-solution treated specimens shown in Figure 2.1(c).

Microhardness measurements were performed on the polished samples by Vickers hardness tester with a load of 1.0 kg. for 20s. An average of the microhardness measurements was obtained from six indentations (the measured error was within 2%). The elastic modulus of the specimens was determined with acoustic wave-speed measurements obtained from ultrasonic sound speed and the material's density measured by Archimedes' principal. The measurements of wave speed and density of pure Ti (99.99 at.%) was utilized for a calibration.

#### 2.3 Results and discussion

#### 2.3.1 Elemental distribution and phase stability

Figure 2.2 shows the distributions of the elements Ti, Zr, Nb and Ta in the three samples obtained by different solution treatments (ST100, ST1000, and ST3000), where the composition of each element was determined by EDS analysis, at locations represented as dots in Figure 2.1(b). Both the ST100 sample (Figure 2.2a) and the ST1000 sample (Figure 2.2b) displayed significantly broader ranges of elemental distributions compared to that of the ST3000 sample. These EDS results were repeated several times on different locations in each sample. Table 2.2 presents the average compositions of Ti, Zr, Nb and Ta, and the variation of elemental distribution in the ST100, ST1000 and ST3000 samples. The results indicate that all samples have almost the same average values of each element in the as-solution treated samples. On the other hand, the difference between the maximum and minimum composition of Ti, Zr, Nb and Ta was 6.8%, 0.69%, 5.7% and 0.61%, respectively, in the ST100. The variation in composition of Ti, Zr, Nb and Ta in the ST1000 was 5.8%, 0.62%, 4.6% and 0.53%, respectively, showing a narrower range compared to that in the ST100. As shown in Figure 2.2(c), the ST3000 sample has a very small variation of elemental distributions, indicating that composition homogeneity was

achieved by increasing the solutionizing time to 3000 minutes. Therefore, the EDS analysis indicates that both the ST100 and ST100 were clearly heterogeneous, which results from the sluggish diffusion of these refractory,  $\beta$  stabilizing elements and insufficient solutionizing time, while a fully homogenized structure was achieved by increasing the solutionizing time to 3000 minutes for the ST3000 sample. Furthermore, this suggests that elemental distributions in Ti-Nb Gum metal can be controlled by the solution treatment process, which influences the  $\beta$ -phase stability of this alloy.

As shown in Figure 2.3, the Bo-Md phase stability diagrams, derived from the work by Morinaga et al. [35], was adopted here to evaluate the  $\beta$ -phase stability of various microstructures in this study, where the  $\beta/\beta+\omega$  phase boundary, represented by a solid line, indicates a region of the least stable single phase  $\beta$ . Martensite phases such as  $\omega$ ,  $\alpha'$  or  $\alpha''$ , depending on the alloy composition, could exist predominantly below the boundary for the martensite start temperature, for samples at room temperature (Ms = RT) as given by a dotted line in Figure 2.3. It should be noted that the boundaries used for this diagram have been proposed by M. Abdel-Hady and coworkers [36], which showed some discrepancies with Morinaga's diagram [35, 40]. As is mentioned by others [26, 36], the addition of oxygen to metastable  $\beta$ -Ti alloys have been shown to suppress hexagonal  $\omega$  phase formation upon quenching, and decreases the Ms transition temperature, illustrating that oxygen works as a  $\beta$ -phase stabilizer in Ti-Nb Gum Metal. Based on this observation and the results found in this study, it is thus reasonable to adopt modified boundaries for both the  $\beta/\beta+\omega$  phase and the Ms transition, when considering the alloying effect of oxygen on the  $\beta$ -phase stability.

The composition data shown in Figure 2.3 is derived from the EDS data (in Figure 2.2) and the Bo and MD values of alloying elements (Table 2.3), and indicates the  $\beta$ -phase stability variation in the alloys as function of solution treatments, where the alloying vectors (Bo and Md)

were calculated for different locations within the microstructures. Position of each point, presented by the symbol  $\blacksquare$  on the phase stability map, is related with the relative  $\beta$ -phase stability, which corresponds to the EDS point-spot results represented for example in Figure 2.1(b). In addition, the Bo-Md diagram indicated the preferred activation of deformation mechanisms with the β-phase stability [35, 36]. The nominal composition of this Ti-Nb Gum Metal, with the values Bo=2.869 and Md=2.452, falls in the twinning region of Bo-Md map, as indicated by a red point in each part of Figure 2.3. Accordingly, the predominant deformation mode activated in the alloy is expected to be mechanical twinning during the initial stages of deformation, which correspond well with experimental results reported by others [22-26, 41, 42]. On the one hand, the ST100 and ST1000 samples exhibit a wide region of  $\beta$ -phase stability from a region of stable  $\beta$  phase to a region of martensitic phase dominated, resulting from the heterogeneous elemental distributions. These results imply that the constituent  $\beta$  phase of these alloys possessed varying chemical stability, which is compositionally dependent. Previous reports [10, 13, 26, 43] showed that the dominant deformation mechanism in metastable  $\beta$ -Ti alloys strongly rely on the  $\beta$ -phase stability, similar to the stacking fault energy in FCC metals. Based on existing theories and experimentally observed results, there is a strong possibility of multiple deformation mechanisms operative in these heterogeneous sample, rather than deformation by a single mechanism.

With increasing solutionizing time, however, the data points (black squares) scatter decreases and converge toward the red circle data point (representing the bulk Ti-Nb Gum metal composition) shown in Figure 2.3(c). This implies that the  $\beta$ -phase stability in the ST3000 sample was more uniform, resulting from a more homogenized elemental distribution, as previously shown in Figure 2.2(c). This result suggests that one single deformation mechanism would be primarily operative in this alloy when its elemental distribution is fully homogeneous.

#### 2.3.2 Phase stability dependence of deformation microstructures

Figure 2.4 shows the representative microstructures of three samples after cold-rolling ( $\epsilon$ = 0.02), which were observed using EBSD analysis. The crystallographic orientation is presented by inverse pole figure (IPF) coloring scheme as indicated in the inset in Figure 2.4(a), in which the observed plane is parallel to the rolling direction (RD). The same color scheme was applied to all of the orientation maps used in this study. The small amount of black in the IPF maps indicate areas with little or no indexed patterns, which may be due to difficulty in indexing SIM  $\alpha$ " with EBSD mapping. The observed microstructures show localized deformation bands formed in the equiaxed grains after plastic deformation. The IPF maps (Figure 2.4a and b) for the ST100 and ST1000, respectively, depict similar microstructures that were composed of numerous plate-like features  $\sim 1 \mu m$  in size. The initiation of these deformation bands appears to start from one boundary and stopped at another grain boundary or by other band structuresdeformation bands. These deformation bands do not propagate though grain boundaries to neighboring grains. It has been reported that the deformation bands in Ti-Nb Gum Metals result from primarily mechanical twinning [10, 41, 42]. However, it will be shown later that the bands can be composed of mechanical twinning or martensite  $\alpha$ "phase. On the other hand, Figure 2.4(c) reveals that only a few deformation bands with parallel thin lines were observed in the ST3000 sample, illustrating that each sample deformed differently with the different solution treatment times (ST). The results in Figure 2.4 indicate that the deformation bands in strained grains significantly decreased with increasing ST time, where the average number of the bands in a grain is about 25.8, 12.7 and 6.5 in the ST100, ST1000 and ST3000 samples, respectively. Clearly the extent of the deformation bands varies with the degree of compositional homogeneity, with longer solutionizing times and therefore greater homogeneity resulting in fewer deformation bands.

The dominant deformation mechanism, including SIM, twining and dislocation slip, may be dependent on the  $\beta$ -phase stability, which is strongly related to chemical composition of the alloys [9, 10, 13]. It is thus conceivable that deformation microstructure would significantly be influenced by the  $\beta$ -phase stability of the alloy. In particular, previous reports [29, 39] found that the critical stress to trigger SIM ( $\alpha$ ") decreased when the chemical composition was close to the Ms transition line, implying that the SIM transformation was easily activated by a small amount of external stress in the less stabilized  $\beta$ -Ti alloys, resulting in a high fraction of SIM  $\alpha$ " in the alloy. Therefore, it is essential to consider the β-phase stability in the specimens, to correlate to different fractions of deformation band in the microstructures. As shown in Figure 2.3, the relatively lower β-phase stability was found in the ST100 and ST1000 samples, compared to that in the ST 3000 sample, can be correlated to a higher fraction of deformation bands in the microstructures, caused by the evident SIM  $\alpha$ " formation. In addition, Min et al. [43] have reported that different level of homogeneity in  $\beta$ -Ti alloys led to various deformation features, especially enhancement of mechanical twinning rather than dislocation slip. This suggests that the existence of the heterogeneous elemental distribution results in the formation of low  $\beta$ -phase stability regions. which can be the nucleation site for mechanical twinning [34, 43, 44]. Consequently, the occurrence of a heterogeneous twin formation was attributed to a high fraction of the deformation bands in grains [43]. As shown in Figure 2.4, similar to previous work [43], a heterogeneous elemental distribution led to a high fraction of the bands in the ST100 and ST1000 samples, demonstrating that the fraction of deformation bands in an early stage of deformation was highly dependent on elemental distributions. Based on experimentally observed results in the present study, it is reasonable to correlate the difference of the band numbers in the deformation microstructure to  $\beta$ -phase stability, associated with alloying elemental distributions.

#### 2.3.3 Characteristics of deformation band

In order to identify the internal structure of the deformation band, ST100 and ST3000 samples were further characterized by EBSD analysis with the areas highlighted in Figure 2.4(a) and Figure 2.4(c) corresponding to ST100 and ST3000 samples, respectively. The IPF map (Figure 2.5a) shows several intragranular bands, tens of micrometers in size, formed in the inhomogenized  $\beta$  matrix, with parallel thick laths induced by deformation. The deformation bands exhibit different color with that of the parent phase, which implies that their crystallographic orientations differ from each other. Figure 2.5(b) shows that most of the bands were indexed as  $\{332\}<113>\beta$  twins (indicated with blue lines) that corresponds to the crystal crystallographic misorientation of 50.5° between the  $\beta$ -matrix and {332}<113> $\beta$  twin along the <110> $\beta$  direction [45]. These observations indicate that the deformation structures are twin bands. However, some part of bands was not delineated as  $\{332\}<113>\beta$  on the image quality (IQ) map, especially in the dark color area shown in the Figure 2.5(b). It is worth noting that the image quality map reflects lattice distortion in accordance with lattice imperfection [46]. Hence, dark contrast in the bands indicates higher lattice distortion, which means that the band was not purely composed of only  $\{332\} < 113 > \beta$  deformation twins. To characterize the deformation bands in more detail, the local lattice distortion was analyzed by the Kernel average misorientation (KAM) as shown in Figure 2.5(c), where the KAM values represent the density of geometrically necessary dislocation (GND) [47, 48]. Observation of darker regions in the image guality map (Figure 2.5b) correspond higher KAM values. This suggests there are additional deformation mechanisms operative beyond the  $\{332\}<112>\beta$  twins during deformation. Figure 2.5(d) shows the point-to-origin and point-to-point misorientation profile along the arrow, presented in Figure 2.5(a), illustrating the strain was mainly activated by multiple deformation modes. This figure shows that stressinduced martensite (SIM)  $\alpha$ " was formed along the distance between 12µm and 16µm, corresponding to the point-to-point misorientation of 15.6°. The corresponding point-to-point

misorientation of 59.9° was identified as {112}<111> twins [45], while {332}<113> twinning was defined with the characteristic 50.9° point-to point misorientation angle, as shown in Figure 2.5(d). Superimposing the misorientation and twin boundaries onto the IQ map, reveals that the deformation band was composed of  $\alpha$ " / {112}<111> $\beta$  twin / {332}<113> $\beta$  twin /  $\beta$  matrix in sequence. Therefore, these images shown in Figure 2.55 indicate that the strain in the inhomogenized sample was accommodated by multiple deformation mechanism, including stress-induced martensitic transformation and mechanically induced twins during the early stages of deformation.

Figure 2.6 shows EBSD analysis of the deformation bands formed in ST3000, corresponding to a homogeneous elemental distribution in the specimen. These images illustrate that, in the homogenized  $\beta$  matrix, mechanical twinning was the only mechanism activated at a strain of 0.02. In the image quality map (Figure 2.6b), the bands were fully indexed as {332}<113> $\beta$  twins, where the image contrast color of the whole deformation band is nearly the same along its entire length. In addition, no obvious additional misorientations with the  $\beta$  matrix were observed by the KAM analysis as shown in Figure 2.6(c). In addition, the misorientation profile (Figure 2.6d) clearly shows that {332}<113> $\beta$  mechanical twinning was solely activated as the deformation mechanism. This suggests that Ti-Nb Gum metal, when compositionally homogeneous, deforms by mechanical twinning at the initial stages of strain.

Based on the above results, the operative deformation mode was obviously different between the ST100 and ST3000 samples, even with the same bulk chemical composition. According to previous studies [10, 32, 49, 50], the deformation mechanisms in metastable  $\beta$ titanium alloys strongly rely on the matrix conditions such as grain orientation, grain size and phase stability, and should be considered. In the present study, all samples, even with different solution treatments, were shown to have essentially the same grain size, and possessed no
obvious texture, as presented in Figure 2.4. Hence, it is reasonable to consider only the phase stability affecting the deformation mechanism in the alloys. Recall that a single master alloy was cast from which all the different solutionizing samples were created. Lai et al. [48] reported that the deformation behavior was accompanied by multiple deformation mechanisms in Ti-23Nb-0.7Ta-2.0Zr (at.%) with no oxygen included, an alloy with lower  $\beta$ -phase stability than a nominal composition of Gum Metal (since oxygen works as  $\beta$  stabilizer by retarding  $\omega$  phase formation). It was found that the deformation bands formed in the less stable  $\beta$ -Ti alloys were composed of  $\{332\}<113>\beta$  twinning,  $\{112\}<111>\beta$  twinning and SIM  $\alpha$ ", in good agreement with our results obtained from the ST100 sample, as shown in Figure 2.5. It suggests that the deformation bands formed in a compositionally heterogeneous sample was attributed to the relatively lower β-phase stability, which was mainly observed in the ST100 deformed at a strain of 0.02. On the other hand, it is found by others [22, 51] that Gum metal undergoes a reversible stress-induced martensitic phase transformation  $(\alpha \rightarrow \beta)$  during the unloading process at the initial stage of strain. The above result demonstrated that mechanical twinning was the primary deformation mechanism in Ti-25Nb-0.7Ta-2Zr-1.2O (at.%) alloy, which is well supported by the deformation bands formed in the ST3000 sample. This study thus highlights the fact that the deformation behavior of Ti-Nb Gum metals is closely related to the  $\beta$ -phase stability that can be controlled by alloying element distributions as shown in Figure 2.3.

## 2.3.4 Effect of β-phase stability on deformation mechanism

To investigate the effect of chemical stability on the deformation behavior, the microstructure of individual grains in the ST1000 sample were observed after cold-rolled to 5% reduction ( $\epsilon$ =0.05). Figure 2.7(a-c) shows the typical deformation microstructures corresponding to the  $\beta$ -phase stability (Figure 2.7d) in the deformed ST1000. Clearly different deformation

features, with different fractions of parallel thin bands and thick lathes, were revealed in strained grains (Figure 2.7a-c). This implies that the deformation behavior was accompanied by different plastic deformation mechanisms in β-grains. It should be state that deformation bands nucleated at one grain boundary and propagated either to the middle of the grain intersecting with other bands or terminated at another grain boundary. Hence, the deformation mode occurring in one grain has little or no influence on the deformation mechanisms of neighboring grains. In the micrograph of grain A, shown in Figure 2.7(a), a few deformation bands 0.1-1.5µm in width were observed. As described in the previous section, the thick-lath features were characteristic of mechanical twinning, and the thin bands were either considered as stress induced martensite (SIM,  $\alpha$ ") or slip lines [24]. In grain B, shown in Figure 2.7(b), the numbers of bands significantly increased and were thicker compared to grain A. It is clear that the bands formed in the grain B are comprised of both mechanical twins and SIM ( $\alpha$ "), as indicated in Figure 2.7(b). Finer band features of the microstructure were observed in Figure 2.7(c), corresponding to grain C, and no thick laths were present. The observed thin bands whereas identified by SIM  $\alpha$ " with 5-20nm in width, indicating that the occurrence of stress-induced martensite  $\alpha$ " transformation led to a dense network of nanoscale thin band structures [52]. These observations (Figure 2.7 a-c) demonstrate that different  $\beta$  grains respond to plastic behavior in different way in a heterogeneous specimen. Composition differences between grains directly alter the deformation mode of individual grains.

Figure 2.7(d) displays the  $\beta$ -phase stability of each grain, corresponding to the grain A (Figure 2.7a), the grain B (Figure 2.7b) and the grain C (Figure 2.7c), on the Bo - Md diagram, where the Bo and Md values of individual grains were calculated as described in Section 2.3.1. The obtained  $\beta$ -phase stabilities in three grains were obviously different due to a heterogeneous elemental distribution shown in Figure 2.3(b), which can lead to various deformation mechanisms. The corresponding  $\beta$ -phase stability in grain A shows most points were located near or above the  $\beta/\beta+\omega$ -phase boundary (i.e. in the stable  $\beta$ -phase region), illustrating that plastic deformation in

this grain was mainly accommodated by mechanical twins or dislocation glide on slip planes, which is in close agreement with the micrograph of grain A. Furthermore, the relatively stable  $\beta$ -phase was strongly correlated with a small number of visible deformation bands in grain A. On the other hand, lower stability of the  $\beta$ -phase was revealed in grain B, where composition measurements yield Bo - Md values that mostly fall in the area between the  $\beta/\beta+\omega$ -phase boundary and the  $M_s$  transition line. Observation of the microstructure indicates characteristics of mechanical twins and SIM ( $\alpha$ "), with a high number of deformation bands within grain B, as shown in Figure 2.7(b). In the Bo - Md diagram, the  $\beta$ -phase stability obtained from grain C was mainly located near the Ms transition line, where the SIM  $\alpha$ " transformation was predominantly taking place during plastic deformation, as was pointed out in Section 2.3.2. These observations indicate that the preferential activation of a deformation mechanism in different  $\beta$ -grains is closely linked to the chemical stability of the  $\beta$ -phase. In addition, it also plays a significant role in determining deformation behavior of the alloy as a whole, as different deformation mechanisms lead to different levels of ductility and homogeneity of deformation.

## 2.3.5 Effect of phase stability on phase constitution

Figure 2.8 presents IPF maps of typical microstructures observed in the ST100 (Figure 2.8a and c) and ST3000 (Figure 2.8b and d) specimens after cold rolling to 15% reduction ( $\epsilon$ =0.15). In a general view of the deformed microstructures shown in Figure 8(a) and (b), there were obvious changes in the band number and their volume fractions between an in-homogenized specimen (ST100) and a homogenized specimen (ST3000). As mentioned in Section 2.3.2, this is likely a result of differences in the elemental distributions between the ST100 and the ST3000 samples. In the IPF map of the ST100 sample, at a strain of 0.15, a high fraction of deformation bands was observed with activation of second deformation products in the primary bands as

shown in Figure 2.8(c). According to Sun et al. [32], the primary band would provide a modified orientation area, where secondary deformation products including secondary twins and SIM  $\alpha^{\prime\prime}$  were favored over continued deformation of the  $\beta$  matrix, resulting in a dense network of deformation bands. The feature shown in Figure 2.8(c) depicts that with further plastic deformation, multiple deformation mechanisms, including secondary mechanical twins and SIM  $\alpha^{\prime\prime}$  were simultaneously operative, which was strongly correlated with multiplication of deformation bands. Figure 2.8(b) and (d) show corresponding IPF maps of the ST3000 sample, indicating that a large fraction of un-deformed area was still shown in individual grains. The observed primary band with ~100µm in width was much thicker than that in the ST100 sample. Few secondary deformation bands were found in the microstructure at a strain of 0.15. This implies that the plastic deformation in the ST3000 sample was mainly accommodated by the primary bands being denser and thicker, rather than multiplication of the bands, as shown in Figure 2.8(d).

To further investigate the deformation band in Figure 2.8(d), detail EBSD was carried out with careful misorientation analysis. In the IPF map, the primary band shows slightly different colors along its width as indicated by a line A to B in Figure 2.9(a). This illustrates that the crystallographic features were obviously different from each other, including crystallographic orientations or crystal structure, which might be a result of multiple phases. The KAM map (Figure 2.9b) shows that the boundaries were clearly visualized in the primary band, which is attributed to different lattice distortions. Figure 2.9(c) displays the misorientation profile of the line from A to B in Figure 2.9(a), indicates that the crystallographic misorientation between the  $\beta$ -matrix and the band was less than 20°, corresponding to SIM  $\alpha$ " phase. On the other hand, the point-to-point misorientation of the band along the distance between 58µm and 112µm were 59.7° and 59.2°, respectively, which correspond to the {112}<111> $\beta$  twinning system as revealed in Section 3.3. The above results indicate that the deformation bands were characterized by SIM  $\alpha$ " / {112}<111> $\beta$  twin / SIM  $\alpha$ ", in sequence. Figure 2.9(d) corresponds to the misorientation

profile of the bands as indicated by a line from C to D in Figure 2.9(a). It shows the crystallographic misorientation between  $\beta$ -matrix and the bands were less than 20°, illustrating that the bands were only composed of SIM  $\alpha$ " phase. This suggests that SIM  $\alpha$ " phase would be developed either at boundaries between the matrix and the primary twin or in the  $\beta$ -phase matrix, which might be a result of their orientation caused by high lattice distortion with accumulating strain [32]. Therefore, this demonstrates that the deformation bands were composed of both mechanical twins and SIM  $\alpha$ " or only SIM  $\alpha$ " phase in cold rolling to a strain of 0.15.

Figure 10 shows XRD patterns of the ST100, ST1000 and ST3000 samples subject to cold rolling ( $\epsilon = 0.15$ ) and solution-treated. Only the peaks of the  $\beta$  phase (body centered cubic, bcc) were indexed in the solution-treated ST100 sample, as shown in Figure 10. It is worth noting that none of the  $\omega$  phase, {thermally-induced martensitic transformation ( $\beta \rightarrow \omega$ )} during quenching [48], was detected in the three solution-treated samples, even though it has been previously observed in TEM analysis [53-56] in metastable Ti-Nb alloys. This may result from the nano-scale size and low volume fraction of the martensite phase, making it difficult to detect by conventional XRD analysis. With accumulating strain to 0.15, peaks corresponding to the  $\alpha$ " phase were observed in the ST100 and the ST1000 samples, both having a heterogeneous elemental distribution. This demonstrates the occurrence of the stress-induced martensitic transformation  $\beta \rightarrow \alpha^{"}$  in the heterogeneous specimens during plastic deformation. Comparing the intensity of  $\alpha$ " phase peaks between the cold rolled ST100 and ST1000 samples, higher intensity and more evident  $\alpha$ " peaks were indexed in the ST100 specimen. This might be due to a higher volume fraction of  $\alpha^{n}$  phase in the ST100 sample, resulting from the enhancement of the SIM transformation with increasing cold deformation. On the other hand, no orthorhombic  $\alpha$ " peaks were found in the ST 3000 sample, even though SIM  $\alpha$ " was identified in microstructures deformed to 15%, as shown in Figure 2.9. This might be due to fact that a negligibly amount of

SIM  $\alpha$ <sup>"</sup> formed in a homogenized sample compared to that in a heterogeneous sample. Therefore, this illustrates that the fraction of deformation bands has a significant influence on the phase constitution of the alloys.

#### 2.3.6 Influence of β-phase stability on hardness and elastic modulus

In order to establish the dependence of mechanical properties and elastic properties on the  $\beta$ -phase stability, as well as confirm the effect of plastic deformation on these properties, hardness and elastic modulus were measured by Vickers hardness and acoustic wave method, respectively. Figure 2.11(a) shows the variation of microhardness of three specimens strained from 0 to 0.15, indicating that the hardness in three specimens increases slightly with accumulated strain, regardless of structural state ( $\beta$ -phase stability), with only about 8% increase in hardness with a cold-rolling reduction to 15%. This suggests that the alloys would show a relatively low work hardening behavior compared to conventional β-Ti alloys, which is in agreement with previous studies [12, 57]. According to other studies [12-15, 58], little or no work hardening has been observed during over 90% cold-deformation in Ti-Nb based Gum metals, which was attributed to non-conventional dislocation-free deformation mechanisms. Based on these theoretical and experimentally results, it would appear that dislocation activity has little effect on the mechanical behavior of these alloys. In the ST3000 sample, the measured hardness values, at different strain levels, were significantly higher than that of the ST100 and ST1000 specimens. The analysis presented in Section 2.3.2 shows that the ST100 and ST1000 specimens possess in-homogenized structures having relatively large volume fractions of deformation bands composed of mechanically induced twins and SIM  $\alpha^{\prime\prime}$ , as compared to samples with a homogenized structure (e.g., in the ST3000). As is mentioned in several other studies [6, 7, 30-34, 58], strain-hardening processes are presumably linked to the occurrence of multiple

deformation mechanisms in metastable  $\beta$ -Ti alloys, which may result from transformation-induced plasticity (TRIP) effect and twinning-induced plasticity (TWIP) effect. This means that the mechanical behavior of  $\beta$ -Ti alloys largely depend on the interaction between these different deformation mechanisms. Therefore, the enhancement of twinning deformation and/or SIM  $\alpha^{\prime\prime}$  for achieving better ductility can be expected in the heterogeneous specimens like the ST100 and ST1000 samples. In addition, Hao et al. [59] suggested that SIM  $\alpha^{\prime\prime}$  possesses a lower hardness compared with the  $\beta$ -phase, which is well supported by the results of XRD analysis and hardness measurement in this study. As shown in Figure 2.10, a relatively high volume fraction of SIM  $\alpha^{\prime\prime}$  phase was observed in the ST100 and ST1000, which can result in lower hardness values compared to that of ST3000. Therefore, these observations suggest that the deformation mechanism activated during plastic deformation has a significant effect on the mechanical properties in these alloys, which can be manipulated by the extent of  $\beta$ -phase stability, as discussed in Section 2.3.1.

Figure 2.11(b) shows the elastic moduli of the three specimens subjected to solution treatment and cold rolling to 15%. The data reveals that the elastic modulus in all specimens decreased gradually with accumulating deformation to 15%, from 109GPa to 91GPa in the ST100 sample, from 96GPa to 78GPa in the ST1000 sample, and from 98GPa to 76GPa in the ST3000 sample which is in good agreement with the typical mechanical behavior of Ti-Nb Gum metal [13, 14]. Furuta et al. [14] has reported that the elastic modulus of Gum Metals decreases with increasing cold working to 90% due to its highly textured microstructure (strong <110> texture) and/or a significant amount of stored elastic energy after deformation. In addition,  $\omega$ -precipitates in solution treated alloys gradually disappear within the primary deformation band in the early stages of strain. Lai et al. [15] reported that the initiation and propagation of the deformation band leads to the deformation-induced transformation from  $\omega$ -phase to  $\beta$ -phase, which is shown to lead to the formation of the channel depleted of athermal  $\omega$ -phase. However, the mechanism

for cold-deformed Gum Metal is still under discussion. Although the trend in elastic modulus with accumulated cold-deformation is similar to the trends observed for typical Gum Metals, the ST100 shows the highest elastic modulus of these three specimens. It is worth noting that the elastic modulus in metastable β-Ti alloys is highly dependent on the constituent phases of the alloy, resulting from the clear differences in elastic modulus of individual phases [59-61], and found to be related by the following approximations:  $E\omega \approx 2.0E\beta$  and  $E\alpha'' \approx E\beta$  [59, 62]. Therefore, it is important to clarify that as the volume fraction of the athermal  $\omega$ -phase increases in the microstructure, the elastic modulus of the alloy would be increased ( $\alpha$ " phase has little effect on the elastic modulus of the  $\beta$ -phase Ti alloys [59]). As shown in Section 2.3.1, the ST100 specimen has the most heterogeneous elemental distribution and the least  $\beta$ -phase stability, being located under the Ms transition line. By comparison, the more homogeneous specimens, ST1000 and ST3000, relatively few points representing the  $\beta$ -phase stability were observed under the  $M_s$ transition line. This implies that in more stable  $\beta$ -Ti alloys, the appearance of  $\omega$ -phase was limited or absent, which results in lower elastic modulus of as-solution treated alloys. Although the volume fraction of the  $\omega$ -phase in each alloy cannot be obtained quantitatively with our XRD analysis, due to its small fraction and size in the nanoscale, the formation or presence of athermal  $\omega$ -phase in the three alloys is associated with both the chemical stability of the alloy and its deformation behavior. Furthermore, the ST1000 and ST3000 exhibit similar values of elastic modulus even with strain to level of 15%. It should be noted that between the ST1000 and ST3000, significantly different  $\beta$ -phase stability and mechanical behavior were characterized as can be observed in Figure 4 and Figure 11(b). These results lead to a very important conclusion, that mechanical properties of the alloys can be controlled without elastic properties variation in the same chemical composition of Ti-Nb Gum Metal.

## 2.4 Summary

- (1) For the solution treated Ti-23Nb-0.7Ta-2Zr-0.8O (at.%) alloy, the extent of β-phase stability was dependent on elemental distributions, which was controlled by the solution treatment process.
- (2) The effect of  $\beta$ -phase stability on the deformation behavior of the alloy was related to the deformation mechanism and could be described on the basis of characterization of deformation band at the initial stage of strain. In the ST3000 specimen, a fully homogenized structure, only mechanically-induced {332}<113> $\beta$  twinning was observed, whereas in both the ST100 and ST1000 samples, having heterogeneous structures, were accompanied by multiple deformation mechanisms operative, including {112}<111> $\beta$  twinning, {332}<113> $\beta$  twinning and stress-induced  $\alpha''$  martensite during the early stages of deformation.
- (3) The preferential activation of the deformation mode was highly dependent on the chemical stability of the β-phase during an early stage of deformation, which plays a significant role in determining deformation behavior and constitute phase of the alloy.
- (4)  $\beta$ -phase stability plays an important role in determining the mechanical properties and the elastic properties of metastable Ti-alloys. The microhardness results revealed that the enhancement of the twinning deformation (TWIP) and/or SIM  $\alpha^{"}$  (TRIP) for achieving better ductility can be expected in the heterogeneous specimens or homogeneous samples slightly off the current composition. It was also found that the elastic modulus of the alloys decreased with accumulating strain, which was highly dependent on phase constitution before and after cold working.

# 2.5 Acknowledgements

Chapter 2, in full, is a reprint of the material as it appears in S. Shin, C. Zhang, K.S. Vecchio. Phase stability dependence of deformation mode correlated mechanical properties and elastic properties in Ti-Nb gum metal. *Materials Science & Engineering A* **702** (2017) 173-183. The dissertation author was the primary author of this paper.

Element	Ti	Nb	Та	Zr	0
at.%	Balance	22.8	0.71	2.02	0.80
wt.%	Balance	35.5	2.15	3.09	0.21

Table 2.1: Chemical composition of as-cast Ti-Nb-Ta-Zr-O alloy.

Samples	Ti		Zr		Nb		Та	
Avera (at.%)	Average	∆content	Average	∆content	Average	∆content	Average	$\Delta$ content
	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)
ST100	74.32	6.8	2.03	0.69	22.89	5.7	0.76	0.61
ST1000	74.45	5.8	2.05	0.62	22.72	4.6	0.78	0.53
ST3000	74.10	0.7	2.00	0.06	23.16	0.9	0.74	0.03

Table 2.2:Measured contents of each element and calculated variation of elemental distributionin the ST100, ST1000 and ST3000 samples.

Element	Ti	Nb	Та	Zr
Во	2.790	3.099	3.144	3.086
Md (eV)	2.477	2.424	2.531	2.934

Table 2.3: List of the Bo and Md values for each of the alloying elements in bcc Ti [36]





Figure 2.1: (a), (b) Microstructure, (c) XRD pattern of the solution-treated alloy for 100 minutes. The white spots in (b) represent locations for EDS analysis depicted in Figure 2a for the ST100 sample.



Figure 2.2: Elemental distributions of Ti, Nb, Ta and Zr in samples of the same alloy melt, but solutionized for different times (a) ST100, (b) ST1000 and (c) ST3000. Arrows depict the elemental ranges within each plot.



Figure 2.3:  $\beta$ -stability as function of solution treatments: (a) ST100, (b) ST1000 and (c) ST3000. Each point superimposed on the (Bo)<sup>-</sup>(Md)<sup>-</sup>diagram corresponding to a specific EDS point-spot result shown in Fig. 2. The red point on the map represents the  $\beta$ -phase stability of the Ti-23Nb-0.7Ta-2.0Zr-1.2O (at.%) overall alloy composition.



Figure 2.4: Inverse pole figure maps of deformation microstructures in specimens with a strain of 0.02: (a) ST100, (b) ST1000, (c) ST3000. The observed plane is nominal to the rolling plane.



Figure 2.5: EBSD analysis of deformation bands formed in the ST100, a heterogeneous structure: (a) IPF map, (b) IQ map superimposed with boundaries for {332}<113> twins delineated by the blue lines, (c) KAM map and (d) Misorientation profile along the arrow in (a).



Figure 2.6: EBSD analysis of deformation band formed in the ST3000, a fully homogenized structure: (a) IPF map, (b) IQ map superimposed with boundaries for {332}<113> twins delineated by the blue lines, (c) KAM map and (d) Misorientation profile along the arrow in (a).



Figure 2.7: (a, b and c) SEM images of the ST1000 subject to 5% cold rolling ( $\epsilon$ =0.05), (d)  $\beta$ -phase stability relative to the Grain A (a), Grain B (b), and Grain C (c) superimposed on the (Bo)<sup>-</sup> (Md)<sup>-</sup> diagram. The red point on the map represents the  $\beta$ -phase stability of a Ti-23Nb-0.7Ta-2.0Zr-1.2O (at.%) alloy.



Figure 2.8: IPF map of deformation structure in the specimen subject to cold rolling to 0.15 (a) and (c) ST100 and (b) and (d) ST3000.



Figure 2.9: EBSD analysis of deformation microstructure in the ST3000 ( $\epsilon$  = 0.15): (a) IPF map, (b) KAM map, (c) and (d) Misorientation profiles relative to the first points along the arrows A-B (c) and C-D (d).



Figure 2.10: XRD patterns of Ti-Nb-Ta-Zr-O alloys subject to solution treatment (ST100) and 15% cold rolling (ST100, ST1000, ST3000).



Figure 2.11: (a) Micro-hardness and (b) Elastic modulus of Ti-Nb-Ta-Zr-O alloys (ST100, ST1000, ST3000) subject to solution treatment and cold-rolling to strains of 0.05 and 0.15.

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# **Chapter 3**

# Design of twinned structure in Ti-Nb Gum metal

In this chapter, thermomechanical-cycling processes were applied to a metastable Ti-23Nb-0.7Ta-2Zr-1.0O (at%) alloy to design twinned structure composed of mechanical twins, resulting from activation of twinning-induced plasticity effects. The fraction of twins was significantly increased with increasing the number of the cycles in the process, resulting in a pronounced softening effect. To shed a light on the relevant micro-scale features (e.g., geometric orientation and stress concentrations) responsible for the microstructure evolution and mechanical response, the local Schmid factor of grains and geometrically-necessary dislocation densities were evaluated from experimentally observed results, and correlated with deformation twinning. A good correlation between the local geometric Schmid factor and softening behavior, due to texture evolution within twins was established, as well as the effect of local stress concentrations on microstructure evolution of this Ti-Nb Gum metal. This chapter is a modified version of a paper that has been published in the journal *Material Science & Engineering A* [1].

## 3.1 Literature review

Recently, the development of metastable  $\beta$ -titanium alloys, which can be defined as the least stable  $\beta$ -phase Ti alloys, are known to possess a good combination of extremely low elastic modulus and a high specific strength. These alloys have been widely considered to be utilized as promising biomaterials in artificial hip and knee joints, etc to reduce the stress shield which is

caused by high Young's modulus of the implant, compared with that of human bone (max. 30 GPa) [2, 3]. In recent years, several new  $\beta$  alloys such as TNS (Ti–25Nb–11Sn (wt.%) [4], Ti-2448 (Ti-24Nb-4Zr-8Sn (wt.%)) [5] and TNTZ (Ti-29Nb-13Ta-4.6Zr (wt.%)) [2, 6] have been developed for applications as metallic structure implants as well as a replacement for hard tissue [4-7]. However, due to the relatively poor formability compared to other conventional alloys, their translation into commercial applications has been hindered. As a result, further investigations have been undertaken to open new possibilities to expand the material property window between the relatively low Young's modulus, which is related to chemical composition optimization [1] and better formability [8,9], which is linked to improved ductility and enhanced strain hardening [8-11]. With progress in improving formability, a prominent approach has been considered to stimulate activation of multiple deformation modes, such as mechanical twinning or stress-induced transformation, along with dislocation slip, and thus significantly improve upon the poor ductility caused by rapid strain localization in slip-dominated  $\beta$ -Ti alloys [10,11]. However, it is difficult to separately manipulate the mechanical properties of these alloys, without affecting the Young's modulus variation (avoiding increasing the modulus), which is the most prominent property of these metastable  $\beta$ -Ti alloys for consideration in biomaterial implants.

For example, Gum metals, which fundamentally consist of Ti-Nb-Ta-Zr elements, along with intentional amounts of oxygen, have been developed by optimized alloy design for "super-properties" such as low elastic modulus (50-90GPa), very high strength (~1.1GPa) and superelasticity (~2.5%) [11-17]. Owing to its unique physical properties and good biocompatibility, gum metals are expected to be potential biomedical materials. However, this alloy development effort has not focused on improved plastic deformation behaviors related to higher ductility and better formability. As an example, the oxygen introduced in the gum metal chemical composition may help retard athermal  $\alpha$ "-martensite and  $\omega$ -phase transformations, which are beneficial to achieve its unique elastic properties [13, 14], whereas ductility and

formability of gum metal are significantly decreased by the addition of oxygen, which is mainly due not only to oxygen solute strengthening [15], but also suppression of the deformation twinning mechanism by increasing  $\beta$ -phase stability [16].

Twining is an important deformation mode in several metastable  $\beta$ -Ti alloys, and it is well documented in the literature that the origin of {332}<113> twinning strongly depends on crystallographic orientation [17, 18], which was substantiated based on Schmid's law. In addition, Marteleur et al. [10] reported that deformation twining plays a crucial role in exhibiting a large uniform elongation and significant straining hardening, as evident from Twinning-Induced Plasticity (TWIP) steels [19-21]. Although the improvement in these mechanical properties has not yet been fully understood or utilized, the activation of multiple {332}<113> twinning is an essential key to enhance formability in metastable Ti alloys [10, 18, 22]. It is worth noting that, whereas the occurrence of mechanical twining in these alloys has been extensively studied, twin fraction/mechanical property relationships have received little attention and not optimized due to a lack of experimental information on highly twinned structures of  $\beta$ -Ti alloys.

As a consequence, this study was focused to achieve multiple twinning in a Ti-23Nb-2Zr-0.7Ta-1.0O (at%) alloy, attributed to an optimized microstructure design approach. Significant decrease in hardness without evident Young's modulus variation was achieved through the formation of highly twinned structure, and a possible deformation mechanism was discussed. To understand the microstructure evolution during plastic deformation, stress concentrations were estimated qualitatively with geometrically-necessary dislocation (GND) densities derived from electron backscattered diffraction (EBSD) measurements. In addition, different fractions of twins were employed to elucidate the relevant microstructure features responsible for the variation in mechanical properties, based on the global Schmid factor analysis. Therefore, the main objective of this study was to understand the effect of microstructure features on deformation

evolution and the mechanical properties in the Ti-Nb Gum metal resulting from extensive plastic deformation processing.

# 3.2 Experimental procedure

## 3.2.1 Twinned structure design

In order to achieve twinning-induced microstructural features, a unique cycling process (CP) composed of a small pre-strain step and subsequent heat treatment was adopted in this study. A fully homogenized Gum metal alloy was first cold-rolled to 5% reduction ( $\epsilon$ =0.05) leading to the formation of the primary deformation twins, attributed to the presence of different crystallography orientation within the parent grain and lattice distortions caused by local stress concentrations. This pre-strain level provided a sufficient trigger stress for the nucleation of the primary twin bands in the grains, and neither the secondary bands, generally formed into the primary band, nor significant the primary band growth were found with the 5% reduction. Next, a heat treatment step was carried out at 973K for 30 minutes, with sufficient time at temperature to relieve local stress concentrations adjacent to the deformation bands and grain boundaries, but still avoid detwinning of the deformation twins by recrystallization and/or boundary migration. The presence of athermal martensitic phases can lead to undesired properties, such as embrittlement and increases in Young's modulus [23]. Therefore, a rapid water cooling step was selected to maintain a homogenized structure, which is beneficial to suppress growth of recrystallized grains and limit precipitation of athermal  $\omega$  and/or  $\alpha$ <sup>"</sup> martensitic phases. The process was implemented as a sequence of up to four cold-rolling/heating/cooling cycles able to achieve varying twin fractions in the microstructure of the Gum metal. These thermomechanicalcycling processed specimens are referred to hereafter as CP1, CP2, CP3 and CP4, respectively.

### 3.2.2 Experimental details

Gum metal with a nominal chemical composition of Ti-23Nb-2.0Zr-0.7Ta-1.3O (at.%) was prepared by arc-melting under argon atmosphere, with a mixture of pure elements Ti, Nb, Ta, Zr, and TiO<sub>2</sub>. For the preparation of fully homogenized specimens, the ingots were held in an inertgas induction furnace for 30-min in its liquid state, then solution-treated for 2000-min at 1273K (above the  $\beta$  transus), followed by water quenching [24]. The measured chemical composition of the as-cast alloy is presented in Table 3.1. It is shown that the microstructure of the assolution treated alloy consists of random oriented grains with an average size of ~650µm (Figure 3.1a). Phase identification was conducted by X-ray diffraction (XRD) using Cu-K $\alpha$  radiation. The body-centered cubic  $\beta$ -phase was the only phase detected in the alloy as shown in Figure 3.1(b). For these experiments, all samples were subjected to mechanical polishing with SiC papers and SiO<sub>2</sub> solutions under a load of 5N. Microstructure observations of the polished surfaces were carried out via optical microscopy (OM) and electron backscatter diffraction (EBSD) on the crosssection parallel to the rolling-direction (RD) using a Bruker e-Flash EBSD detector on a FEI Quanta 600 SEM at 20kV. To investigate the effect of deformation twinning on the mechanical and elastic properties, as well as establish the dependence of these properties on the cycling process, micro-hardness and elastic modulus measurements were conducted using Vickers hardness and acoustic wave method, respectively. The experimental methods and conditions for these mechanical tests were described in our previous work [24].

### 3.2.3 Schmid factor and GND

To further explore the orientation information, Schmid factor (SF) and geometrically necessary dislocation (GND) densities were analyzed using EBSD results. Data were collected from four distinct 38µm x 50µm scans at different locations on the same cross section of samples.

Based on orientation of parent grains and {332}<113> twin variants, it was possible to obtain Schmid factor values using the available Bruker EBSD software. The Schmid factor presented in this study is the global Schmid factor, which ignores the complex internal stress state variation It is calculated for every pixel of the EBSD image in the following manner. First, the [25]. orientation matrix is used to rotate individual twin variants from crystal coordinates to sample coordinates. Next, the global Schmid factor of individual twin variants in the sample coordinates can be calculated as a product of the direction cosines between the loading direction and individual twinning direction/plane. GND density is calculated based on measured orientation data from Hough-based EBSD through the Nye tensor, while ignoring the relatively insignificant elastic strain gradients. From the orientation descriptor, i.e. Euler angles, lattice misorientation matrices can be extracted from pairs of neighboring pixels, which are used for computing lattice orientation gradients to populate the Nye tensor [26]. A traction free boundary condition is reasonably assumed for the interrogated surface material, therefore only five terms of the Nye tensor are directly accessible from the measured data ( $\alpha_{12}$ ,  $\alpha_{13}$ ,  $\alpha_{21}$ ,  $\alpha_{23}$ ,  $\alpha_{33}$ ), plus an extra difference term ( $\alpha_{11}$ - $\alpha_{22}$ ) [27]. Through Frank's loop construction, the measured Nye tensor can be equated with the unknown dislocation density vector and the dislocation configuration matrix formed by dyadics of the Burgers vectors and unit line directions. Erroneous GND density data points are then filtered out, including those below the noise floor and those adjacent to sub-grain or grain boundaries. In this study, the dislocation density statistics are generated through lognormal probability density function fitting of the data distribution [28].

## 3.3 Results

#### 3.3.1 Mechanical properties

Figure 3.2 shows the variation of microhardness and Young's modulus with increasing the number of cycling process (CP) steps compared to those of specimens subjected to coldrolling reductions (CR) to 5%, 15% and 20%, corresponding to the same amount of thickness reduction with CP1, CP2 and CP4, respectively. Young's modulus measurements reveal that there was little or no difference in the specimens subjected to the cycling process versus coldrolling alone to 15%. On the other hand, Young's modulus with cold-rolling to 20% reduction decreased slightly from 78GPa to 69GPa, which was beneficial for cold-worked Gum metal [11]. For mechanical properties, typical process methods or deformation mechanisms that accumulation of strain are associated with an increase in hardness and strength of polycrystalline, a phenomenon commonly known as work hardening behavior. This was observed in the gum metal with cold-rolling reduction to 20%, although with a relatively low work-hardening rate, based on the hardness measurement shown in Figure 3.2, as compared to conventional β-Ti alloys, which is attributed to non-conventional dislocation-free deformation mechanisms [11, 29, 30]. However, the Gum metal samples subjected to the thermomechanical-cycling process exhibit a different hardness trend compared to the cold-rolled specimens. The data reveal that microhardness significantly decreased with increasing number of CP steps, with approximately 20% decrease in hardness even with a thickness reduction to 20% from the solution-treated alloy. These results appear to be in conflict with the dynamic Hall-Petch mechanism for strengthening by deformation twinning as previously described in the literature [19-21, 28], since twin boundaries are generally considered to be obstacles to dislocation-based plasticity. The present study is thus focused particularly on this softening behavior induced by the cyclic processing, and establish and validate the mechanism associated with this softening effect depicted in Figure 3.2.
### 3.3.2 Phase constitution

Figure 3.3 shows XRD results of the 20% cold-rolled Gum metal and thermomechanicalcycling processed Gum metal. Only the peaks related to the body centered cubic (bcc)  $\beta$ -phase were indexed in the Gum metal after 20% reduction (20CR in Figure 3.3), implying that cold deformation has no obvious influence on phase constitution of the single phase  $\beta$  microstructure. However, evidence for the C-centered orthorhombic  $\alpha^{"}$  martensitic formation was found in CP-Gum metals, as indicated in Figure 3.3. This demonstrates the occurrence of thermally-induced martensitic transformation  $\beta \rightarrow \alpha''$  during heat treatment, which was mainly attributed to a lower process temperature (923K) than  $\beta$ -transus temperature, as it has been reported earlier for numerous metastable  $\beta$  Ti alloys [31-34]. Comparing the intensity of  $\alpha$ " phase peaks among the samples, the highest intensity and more evident  $\alpha$ " peaks were observed in CP4 specimen. This suggests a higher volume fraction of  $\alpha^{"}$  phase in the CP4, which may be correlated to the enhancement of the thermally-induced martensitic transformation by increased total heat treatment time with each cycle. It is worth noting that constituent phases of the alloy are closely linked to Young's modulus and hardness of metastable  $\beta$ -Ti alloys [24], and it has been observed previously that β-phase microstructure possesses a lower hardness and Young's modulus compare to those of  $\alpha''$  phase-dominated structures [35-37]. Based on the results as depicted in Figure 3.2, however, the amount of  $\alpha^{n}$  phase formed during the CP had a negligible effect on mechanical and elastic properties of the processed Gum metal in this study. In addition, it has been reported previously that the precipitation of isothermal martensitic phases in β-phase dominated Ti alloys, such as  $\omega$ - and/or  $\alpha$ "-phase, would significantly influence its deformation mechanism, which is mainly dependent on  $\beta$ -phase stability [38, 39]. From the microstructure observations (it will be shown in Section 3.3.3), it can be seen that plastic deformation induced by the thermomechanical process was mainly attributed to mechanical twinning, irrespective of phase constitution. This also supports the conclusion that neither deformation mechanism in

Gum metal nor  $\beta$ -phase stability would be influenced by the precipitation of isothermal  $\alpha$ " phase.

### 3.3.3 Microstructure

the То compare the microstructures between cold-rolled specimens and thermomechanical-cycling processed specimens, EBSD analysis was carried out. The microstructures in the Gum metal samples exhibit significantly different features between these two processes after the as-solution treated state. Figure 3.4(a) and (b) show the representative microstructures of the specimens after cold-rolling to 5% ( $\epsilon$ =0.05) and 20% ( $\epsilon$ =0.2) reduction, respectively. The color code was used for grain orientation in all IPF maps is given in the upper right corner of Figure 3.4(a). In the deformed Gum metal, at 5% reduction, a few deformation bands, tens of micrometers in size, were observed with different fractions in each grain, shown in Figure 3.4(a). In addition, crystallographic orientations identified in the elongated deformation bands differ from that of the  $\beta$ -parent phase, caused by twinning deformation. This implies that a lattice reorientation of the twinned regions would make it change the condition of plastic deformation, based on geometric factors. The crystallographic orientation obtained from EBSD analysis will be discussed in the Section 3.4 to interpret the deformation behavior in Gum metal. In our previous work [24], mechanical  $\{332\}<113>_{\beta}$  twinning was preferred as the active deformation mechanism, especially at the early stages of cold deformation, suggesting that the deformation bands formed during the cold rolling process are mainly consistent with  $\{332\} < 113 >_{B}$ twins induced by plastic deformation. The microstructure features shown in Figure 3.4(b) show that the fraction of deformation bands identified as  $\{332\}<113>_{\beta}$  twins was unchanged with increasing reduction from 5% to 20%, although strain localization was observed in a few grains, which is in good agreement with the typical deformation behavior of Ti-Nb Gum metal [11, 14, 15]. This implies that plastic deformation with further cold rolling proceeds mainly through the

activation of other mechanisms, such as dislocation slip, kinking, and shear band formation, resulting in significant strain hardening [16] when compared to twinning-dominated plastic deformation. Conversely, in the specimens that were processed by a combination of pre-strain and subsequent heat treatment (CP samples) shown in Figure 3.4(c), a large fraction of deformation bands was observed. In the inset of Figure 3.4(c), which is the enlarged microstructure, several recrystallized grains, with the size of a few micrometers, were also found in the deformation bands, resulting from the combined effects of localized strain in the bands and heat treatment. From the misorientation analysis (along the line inset of Figure 3.4c), the platelike features were confirmed to be typical  $\{332\}<113>_{\beta}$  twins (indicated with blue lines) that corresponds to the crystallographic misorientation of 50.5° between the β-matrix and  $\{332\}$  <113><sub> $\beta$ </sub> twin along the <110><sub> $\beta$ </sub> direction [17]. The IPF maps shown in Figure 3.4 indicate that mechanical twinning was induced by not only pre-strain, but rather enhanced by further deformation in the thermomechanical-cycling process. Furthermore, the obtained results demonstrate that microstructure features in Gum metals were strongly linked to its mechanical properties, especially the softening behavior associated with the twinning, as mentioned in Section 3.3. A better assessment of the effect of multiple twinning on the mechanical response was achieved using a Schmid factor analysis, which will be discussed in Section 3.4.

# 3.3.4 Microstructure evolution in the thermomechanical-cycling processed Gum metal

To uncover the microstructure evolution in the thermomechanical-cycling processed Gum metal, microstructures corresponding to the CP1 and CP2 were characterized by EBSD analysis, and the results obtained are displayed in Figure 5. Dramatic changes in the microstructure

features were apparent as the number of CP increased. In Figure 3.5(a) and (b), the observed microstructure in CP1 shows numerous plate-like bands consisting of  $\{332\}$  <113  $>_{B}$  twins, which were identified with the misorientation profile shown in Figure 3.5(c). These bands were introduced by plastic strain to 5% reduction ( $\epsilon$ =0.05) by the first CP, and the width of the primary twins are approximately 10-20µm determined from the Figure 3.5(c). It should be noted that the initially induced twins appear to nucleate from one boundary and terminate at another grain boundary. In addition, the majority twin bands formed in the same grain exhibited the same orientation as shown in the IPF map (Figure 3.5a), implying that they were formed under the same geometrical deformation condition. The secondary twins were also observed within the primary ones, in which the secondary deformation, formed by the first cold-rolling, was preferred to be active within the primary twin due to the modification of the geometrical orientation in the twinned  $\beta$  zones, as reported earlier [40]. In the microstructure of CP2 shown in Figure 3.5(d) and (e), more densely distributed deformation features were observed compared to that of CP1. A few deformation twins appeared to have different orientations from others in the same grain, as seen in the IPF map (Figure 3.5d). As seen in Figure 3.5(e), the number of deformation bands were significantly increased as evident by the abundance of the dark areas which are heavily deformed regions. Further observations reveal that some grains were also deformed sufficiently to have a wavy structure of bands, demonstrating that grain rotation and twisting occurred with further deformation, resulting in new twins as indicated with arrows in Figure 3.5(d). According to the misorientation analysis shown in Figure 3.5(f), the occurrence of newly formed deformation bands present in the CP2 were also identified as  $\{332\}<113>_{\beta}$  twins. Furthermore, the new twins with the width of only a few micrometers were mainly introduced in un-deformed  $\beta$  regions of the CP1. The reason for the discrepancy in twin thickness between CP1 and CP2 was considered to be strain localized in the un-deformed ß zones during the second CP, which is associated with increasing activation energy for twin nucleation.

In Figure 3.6, the representative microstructures of CP3 (a and b) and CP4 (c and d) observed of etched surface with optical microscopy are displayed. Numerous deformed lamella structure as well as several recrystallized grains a few microns in size were observed. It should be noted that these features were observed throughout the specimens, irrespective of location; however, it was not possible to evaluate accurately the number of deformation band and their thickness due to highly deformed structure. Indeed, the variation of bands was found to be increased and more pronounced as the cycling process proceed to CP4. It was also seen in Fig. 6b and 6d that the fine deformation traces within the twins exhibit consider waviness between the twin bands in the un-deformed zones (indicated as bright area in the observed microstructures), which is a different deformation behavior compared with CP1 and CP2. These results demonstrate that the highly twinned structure induced by the thermomechanical-cycling process was obviously derived from the different deformation condition when compared to when only cold rolling deformation was applied. The microstructure evolution sequence associated with the thermomechanical-cycling process will be discussed further in Section 3.4.

### 3.4. Discussion

### 3.4.1 Effect of the geometric Schmid factor on softening behavior

Experimental observations from this study illustrate a highly twinned microstructure in a metastable Ti-Nb Gum metal can be achieved by the thermomechanical-cycling process described herein, composed of repeated cycles of a pre-strain and subsequent heat treatment. In addition to twin-induced plasticity (TWIP) effect, exhibiting low yield strength and large uniform elongation through significant work hardening, which have been reported previously [7-11, 18, 40, 41], it was found that the multiple twins significantly affect microstructure evolution and

mechanical response in this study. The trend of decreasing hardness, shown in Figure 3.2, in the Gum metal, with increasing twin fraction, can be well explained by softening mechanism in terms of a crystallographic orientation of deforming crystal structure. Earlier reports [38, 45-47] suggest that deformation twinning can induce a structural softening in the twinned region, due to texture evolution associated lattice reorientation, as indicated in Figure 3.5. The modified orientation in the twinned structure is ascribed to a favorable geometrical condition for the secondary deformation twins. Hence, it implies that the contribution to softening will be significant the larger the fraction of deformation twins in the microstructure.

In order to clarify the effect of orientation-dependent on twinning activation, the Schmid factor (SF) was calculated with EBSD data, considering the resolved external stress on the twinning plane and in the twining shear direction [17]. Combining the hardness results of CP specimens in Figure 3.2, with the mean Schmid Factor analysis, reveals that the trend of the measured hardness with the number of CP steps was strongly related with the variation of SF values, as depicted in Figure 3.7(a). It should be noted that the fine newly formed twins observed throughout the microstructures of CP3 and CP4 (Figure 3.6) were not considered as part of the mean SF values due to the inability of the EBSD technique to resolve these features, where thickness of the twins were smaller than the step size (~0.85 µm) used for EBSD analysis or the corresponding interaction volume. Only absolute SF values larger than 0.3 were considered to activate plastic deformation, as reported by Bertrand et al. [17]. During the thermomechanicalcycling process, the average Schmid factor increased mainly due to a larger volume of twinned regions with increasing the number of CP steps. Figure 3.7(a) and (b) present the distribution of Schmid factors on the population of observed twins, for the CP1 and CP2 samples respectively. For the CP1 sample, the average SF values increase from 0.403 to 0.429, while for the CP2 samples the values are demonstrably higher with a range from 0.45 to 0.49, close to the maximum value of 0.5. It is noted that more twins were found with higher Schmid factors. In Figure 3.7(c)

and (d), the representative microstructure in the CP1 and CP2 obtained by EBSD image quality maps reveal that the volume fraction of deformation twin increased as the cycling process proceeded, due to not only pre-strain, which induced the primary twins in the CP1, but also further deformation, which introduced newly formed twins in CP2, as illustrated in Figure 3.5. This result demonstrates that the variation of Schmid factor with the number of the CP steps was strongly linked to microstructure features, correlated with the fraction of deformation twins.

Figure 3.8 show inverse pole figure (IPF) maps of the CP1 and CP2 with the corresponding Schmid factor (SF) distribution maps, illustrating that reorientation was accompanied by deformation twin. According to the SF maps shown in Figure 3.8(b) and (d), the twinned region has a much higher SF value than that of the  $\beta$ -matrix. The results are in agreement with previous literature [41, 48] in  $\beta$ -Ti alloys, where the secondary deformation was preferentially activated in the twinned regions because of a modified orientation factor, based on the Schmid factor. This also supports the conclusions that the mechanical softening in Ti-Nb Gum metal is governed by the initial twin fraction in the microstructure, which might be attributed to orientation dependence of the critical resolved shear stress in twin-dominated deformation [17, 48-50].

### 3.4.2 Effect of local stress concentrations on microstructure evolution

The results in this study lead to a question of why twin formation would be further enhanced in the cyclically processed Gum metal. From Schmid factor analysis, it can be expected that further plastic deformation is likely to be active in twin bands rather than in untwinned regions. Based on Figure 3.5 and Figure 3.6, however, the observations demonstrate that the activation of new deformation twins induced by the cyclic process preferentially occurred in the un-twinned regions, implying that the microstructural evolution correlates to a different deformation behavior when compared to that of the cold-rolled Gum metal. Indeed, numerous studies on the nucleation of deformation twin in a polycrystalline material have been suggested non-Schmid factor behavior associated deformation twin formation [51-53]. The postulated non-Schmid factor mechanism has been explained by local stress concentrations. For instance, a twin variant formed in a grain is not always related with the highest Schmid factor, and some of the twins were shown to form in regions of the second highest or even much lower SF values, for example in [17, 41, 51]. In addition, Guo et al. [25] reported deformation twins can cause a localized stress field at the twin tip and at the interface between the twin and parent grain, which was highly correlated with the lengthening and thickening of the twins by further external stress. This implies that the twining process, including nucleation, propagation and thickening, would be strongly dependent on the localized event (or stress concentration), based on a resolved shear stress that is determined by the stress tensor in the twinning region rather than the Schmid factor alone. To elucidate this point further, the Kernel average misorientation (KAM) was analyzed by the EBSD data, which can represent relative strain concentration; misorientations greater than a tolerance of 3° were excluded. Figure 3.9 display the IPF maps (a and c) and the corresponding KAM maps (b and d) of the specimen subject to cold-rolling to 15% (a and b), and cyclic processed (CP2) (cold-rolled + annealing). The IPF map shows from the cold-rolled sample (Figure 3.9a), the relatively coarse deformation twins, with approximately 50~70µm wide, represents a thickening dominated phase of the twinning process. The misorientation analysis shown in Figure 3.9b demonstrates that a stress concentration was significantly localized at the twin tip and at twin-parent interface, resulting in a very heterogeneous stress distribution. From these results, it can be stated that, with only cold deformation (no annealing step), an external stress applied after the primary twin formation would mainly assist thickening of the twins through local stress concentrations around the twin-parent interface (thickening state) rather than nucleation of new twins. On the order hand, clearly different microstructural features, with a large number of parallel

thin twins (see Figure 3.9c), were revealed in the cyclically processed specimen, as compared to the twins in Figure 3.9a. This implies that nucleation of new twins predominantly occurred in the deformation process rather than thickening of existing twins, which might be attributed to lower strain (and hence stress) concentrations. As depicted in Figure 3.9(d), the CP2 sample, having undergone annealing before the additional cold-rolling, was identified with almost the same KAM values throughout the whole grain, indicating that the level of stress concentrations from strained (cold-rolled only) state to annealed (CP) state change sharply.

A better assessment of the effect of local stress concentrations on twin formation was achieved by the determination of the density and distribution of geometrically necessary dislocations (GND), which are associated with non-uniformly deformed regions of a material [54]. GND density is calculated based on measured orientation data from Hough-based EBSD through the Nye tensor, while ignoring the relatively insignificant elastic strain gradients. Figure 3.11 shows the GND density of strained state (5CR) (by cold rolling to 5%) was higher than that of the annealed state (5CR+annealing) by subsequent heat treatment. The comparison between the two GND densities reveals that the local stress concentration might have been modified slightly by recovery of the distorted lattice after heat treatment (annihilation of dislocations). Accordingly, it demonstrates that small stress gradients, which could drive the nucleation of new twin at grain boundaries, and enhanced local stress concentrations (e.g., at twin tips and grain boundaries), which would be beneficial for twin thickening, were strongly dependent on the microstructure state of the Gum metal. These results lead to a very important conclusion that controlling stress states (particularly dislocation densities and their distributions) is an essential key to achieve the highly twinned structure that contribute to the softening behavior in the mechanical response of Ti-Nb Gum metals.

### 3. 5 Summary

In order to investigate the effect of twin fraction (after being deformed) on mechanical properties in a Ti-23Nb-0.7Ta-2Zr-1.3 (at%) alloy, a microstructure design approach was utilized, which incorporated both highly twinned structures and highly strained structures. The geometric Schmid factor and GND density of the resulting microstructures were analyzed following a study of texture softening and microstructure evolution. The main results in this work are summarized as:

- (1) The goal of a highly twinned microstructure was successfully obtained through the thermomechanical-cycling process by a combination of pre-strain (5% cold-rolling) and subsequent heat treatment (973K, 30min), which was mainly composed of  $\{332\}<113>_{\beta}$  twinning.
- (2) Microhardness measurement revealed that the twinning structure was strongly related to the overall softening behavior, showing that more twins result in lower hardness in the Gum metal. However, Young's modulus was largely unaffected by twin fraction and isothermal α"-phase present in these alloys.
- (3) The Schmid factor analysis demonstrated that there was structural softening in twinned regions, caused by texture reorientation associated with a more favorable orientation for plastic deformation.
- (4) Local stress concentrations mainly induced by twin formation plays an important role in determining the deformation evolution of Ti-Nb Gum metal. It was found that reduced localized stress variation facilitates the nucleation of new twins at grain boundaries. Whereas, in the cold-rolled condition, propagation and thickening of pre-existing twins were enhanced due to the higher stress concentrations at the twin tips and/or the

interface between twins and  $\beta$ -parent phase.

### 3. 6 Acknowledgement

Chapter 3, in full, is a reprint of the material as it appears in S. Shin, C. Zhu, K.S. Vecchio. Observation on {332}<113>twinning-induced softening in Ti-Nb Gum metal. *Materials Science & Engineering A* **724** (2018) 189-198. The dissertation author was the primary author of this paper.

Element	Ti	Nb	Та	Zr	0
at.%	Balance	22.8	0.72	2.05	1.0
wt.%	Balance	35.5	2.18	3.13	0.27

Table 3.1: Chemical composition of as-cast Ti-Nb-Ta-Zr-O alloy.



Figure 3.1: (a) Microstructure and (b) XRD patter of the solution-treated alloy.



Figure 3.2: Variations of microhardness and Young's modulus with the number of cycling process and cold-rolled ratio.



Figure 3.3: XRD patterns of Ti-Nb-Ta-Zr-O alloys subject to 20% cold rolling and the thermomechanical cycling process from one to four cycles (CP1, CP2, CP3 and CP4).



Figure 3.4: Inverse pole figure maps showing the deformation microstructures of specimens with a strain of (a) 0.05; (b) 0.2, and (c) microstructure of CP4. (d) Misorientation profile along the along the arrow AB of the inset image in (c).



Figure 3.5: EBSD results of CP1(a-c) and CP2(d-f): (a), (d) IPF maps, (b), (e) the corresponding IQ maps and (c), (f) misorientation profiles along AB in (b) and CD in (e), respectively.



Figure 3.6: Optical micrographs showing the microstructures of (a), (b) CP3 and (c), (d) CP4. Micrograph plane is parallel to the rolling direction (RD).



Figure 3.7: Deformation twinning dependence of Schmid factor (SF): (a) variations mean Schmid factor and Vickers hardness with the number of CP with the error bars showing the standard deviation, (b) SF distributions of CP1 and CP2, and IQ maps of (c) CP1 and (d) CP2, respectively. Measured surface is parallel to the rolling direction.



Figure 3.8: Twinning structures of (a) CP1 and (c) CP2, and the corresponding Schmid factor distribution maps of (b) CP1 and (d) CP2. The scale indicates the calculated SF value.



Figure 3.9: EBSD analysis of specimens subject to (a), (b) cold-rolling to 15% and (c), (d)CP2: (a), (c) IPF maps and (b), (d) the corresponding Kerner average misorientation maps, The scale indicates the misorientation value excluding greater than a pre-set tolerance value of 3°.



Figure 3.10: Comparison of GND density as a function of stress states between strained structure (5CR) and annealed structure (5CR+Annealing) in the Ti-Nb Gum metals.

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### **Chapter 4**

# Effect of pre-twinned structure on mechanical behavior of Ti-Nb Gum metal

In this chapter, the mechanism of {332} twinning was studied in a metastable  $\beta$ -titanium alloy. A microstructure design approach, which leads to twinning-induced plasticity (TWIP) effects through twinned structures, is investigated in this study to tune deformation mechanism and correlated mechanical properties in Ti-23Nb-0.7Ta-2.0Zr-1.50O. To shed light on the underlying deformation mechanism responsible for the mechanical response under tensile stress, a global Schmid factor and a Kernel average misorientation, related to geometrically-necessary dislocation densities, are evaluated from experimentally observed results by electron backscattering diffraction (EBSD) analysis. These findings open new possibilities to expand the materials property window between the relatively low Young's modulus and better formability for metastable  $\beta$ -Ti alloys as structural biomaterials. This chapter is a modified version of a paper that has been submitted in Journal of Alloys and Compounds.

### 4.1 Literature review

Mechanical twinning is one of the fundamental plastic deformation modes in crystalline solids. In materials with low crystal symmetry such as hexagonal close-packed (hcp) metals, metastable titanium alloys or high manganese steel, twinning is dominantly activated during plastic deformation [1-3]. In materials with high crystal symmetry such as face-centered cubic (fcc) and bcc metals, where dislocation slip commonly prevails, deformation twinning is also of high relevance, since the twin boundaries that progressively form with increasing strain are

effective obstacles to gliding dislocations [4]. It illustrates that deformation twinning provides a substantial work hardening, referred to twinning-induced plasticity (TWIP) effect, for these materials. As a result, the introduction of deformation twinning, e.g., by tailoring the stacking fault energy in TWIP steels [5], has been an essential approach for enhancing mechanical properties of steels.

In metastable  $\beta$ -Ti alloys, significant theoretical and experimental developments have been achieved in optimizing alloy design to meet the crucial demands for industrial application such as metallic biomaterial implants: extremely low Young's modulus (<50GPa) and significant large elastic strain (>2%), necessary to overcome the stress shield effect that cause bone degradation and absorption [6]. For instance, several new  $\beta$  alloys such as Ti-4.7Mo-4.5Fe [7], Ti-32Nb-2Sn [8], Ti-24Nb-4Zr-8Sn [9], Ti-19Nb-2.5Fe [10] and Ti-12Mo [11] have been introduced for biomedical applications as they offer high strength (~1.6GPa) and good bio-compatibility by precipitation of secondary phases ( $\alpha$ " and/or  $\omega$ ) during aging heat treatment. However, in general, owing to low work hardening rate and low ductility (elongation to fracture less than 10%), their translation into commercial field has been hindered. Unfortunately, the formation of  $\alpha$ " and/or  $\omega$  phases inevitably increases the Young's modulus of the alloys. Consequently, further investigations have been undertaken to open new possibilities to expand the materials property window between the relatively low Young's modulus and improved strength through a chemical composition optimization [10-14].

Interstitial oxygen in metastable  $\beta$ -Ti alloys plays an essential role in achieving low Young's modulus by suppressing  $\alpha$ <sup>"</sup> martensite and  $\omega$  phase formation through increasing  $\beta$ phase stability, which also leads to improving ultimate strength attributed to solid solution strengthening effect [13-18]. However, an increased oxygen level in general does not result in improved ductility, specifically the uniform elongation necessary for good formability. The most

well-known example of such metastable β-Ti based-alloys having high oxygen content is Ti-Nb based gum metal (GM), which fundamentally consist of Ti-Nb-Ta-Zr along with intentional amounts oxygen (~3.0 at%) [14]. This alloy is also reported to exhibit low elastic modulus (50-80GPa), high ultimate strength (~1.0GPa) and superelasticity (~2.5%), which is achieved by tailoring β-phase stability, based on three critical electronic parameters [14, 19]: *(i) an average valence electron ratio (e/a) of ~4.24; (ii) a bond order (Bo value) of about 2.87; and (iii) d-electron orbital energy level (Md-value) of about 2.45 eV.* However, a drastic loss of ductility and uniform tensile elongation with the addition of oxygen element has been reported, which reflects the dilemma of low Young's modulus and a poor formability in metastable β-Ti alloys having high oxygen content [18, 20, 21]. For a given chemical composition optimized for a low Young's modulus, therefore, must also impart enhanced plasticity without significant Young's modulus variation: one of the important challenges in metastable β-Ti alloys [22].

Recent studies suggest that the twinning mode plays an important role in enhancing the work hardening and ductility, and thus improving the mechanical properties in metastable  $\beta$ -Ti alloys [23-26]. Multiple twins with hierarchical structure in grains is linked to microstructural evolution and work hardening behavior progressively during tensile deformation, as evident from Twinning-Induced Plasticity (TWIP) steels [27, 28], and thus can potentially improve the poor ductility caused by rapid strain localization in slip-dominated  $\beta$ -Ti alloys. Although the improvement in these mechanical properties has not yet been fully understood or utilized, such investigations suggest that improved formability in metastable Ti alloys can be achieved by introducing twins as a second-level structural refinement [11, 15, 23-25].

The present paper focuses on a new thermos-mechanical processing method to tune mechanical properties, particularly enhancing uniform elongation in a Ti-23Nb-2Zr-0.7Ta-1.5O (at%) alloy without significant increases in Young's modulus by introducing multi-scale twins.

The microstructure evolution created by this cyclic-thermomechanical processing follows well known mechanical metallurgy principles for enhancing uniform strain (the microstructure suppresses localized strain concentration and encourages a well-distributed plastic deformation throughout the entire microstructure) enabling a high work hardening capability to be achieved. To better understand the effect of the twinned structure on subsequent deformation behaviors and mechanical properties, different fractions of twins are introduced into the microstructure of the Ti-Nb-based Gum Metal. The developed microstructure features, mechanical response, and corresponding deformation microstructure of multi-scale twinned Gum Metal alloys are systematically examined by comparing the characteristics with those of the solution-treated material. Therefore, the main objective of this study is to provide insights into the origin of the deformation features, especially based on twinning deformation, and show the feasibility of controlling mechanical properties in metastable  $\beta$ -Ti alloys, attributed to an optimized microstructure design proposed herein.

### 4.2 Experimental procedure

### 4.2.1 Twinned structure design

In this study, a deformation-twin-induced microstructure is achieved through a unique cycling process (CP) composed of a pre-strain step (twin formation) and subsequent heat treatment (dislocation recovery). To accurately control twin fractions in the microstructure, the cyclic process was implemented as a sequence of cold-rolling/heating/cooling cycles. For the thermomechanical-cycling process, a fully homogenized gum metal was first subject to cold-rolled (CR) at room temperature (RT) to 5% ( $\epsilon \approx 0.05$ ) thickness reduction leading to a formation of primary twins in grains. At this strain level, the twin bands formed in each grain indicated

different crystallographic orientations within its parent grains and a lattice distortion caused by local stress concentrations. It should be noted that, with this level of strain, the trigger stress was sufficient to nucleate the primary twin bands, but neither the secondary twin band, generally formed within the primary band, nor significant primary twin growth was found in the microstructure. Following this small deformation step, a heat treatment was performed on the pre-strained material (5% CR) at 700°C for 30min. Note that at this temperature, the twinned samples is able to relieve the residual stresses localized adjacent to the deformation bands and grain boundaries, but still avoids recrystallization and/or boundary migration necessary to cause detwinning of the bands or precipitation during the process. After heat treatment, the sample was rapidly quenched in water to maintain a homogenized structure by limiting precipitation of athermal  $\omega$  and/or  $\alpha^{\prime\prime}$  martensite phases. In general, the presence of martensite phases in metastable  $\beta$ -Ti alloys lead to undesired properties, such as embrittlement and significant Young's modulus variation [29]. To investigate the effect of twin fractions on the mechanical properties, the cyclic process was performed up to three times on specimens, which are referred hereafter as CP1 (one cycle), CP2 (two cycles) and CP3 (three cycles), respectively.

#### 4.2.2 Experimental details

Gum metal with a nominal chemical composition of Ti-23Nb-2.0Zr-0.7Ta-1.5O (at%) was prepared by arc-melting under argon atmosphere. Owing to the difference in melting points and density of raw materials, two different types of ingots were first fabricated: *i*)*Ti* + *Zr*+ *TiO*<sub>2</sub> *and ii*) *Nb* + *Ta*. Then, these ingots were mixed and melted at least five times in the furnace, also under argon atmosphere. To form a fully homogenized  $\beta$ -phase microstructure, the resulting ingot was cold rolled to thickness reductions of up to 75%, from 10.0mm to 2.5mm in thickness. This rolled sample was then solution treated (ST) at 900°C for 60 minutes, followed by water quenching.

The as-solution-treated sample was subjected to the thermomechanical-cycled process to achieve the twin-induced microstructure.

Cyclically-twinned Gum Metal and an as-solution-treated specimen (for comparison) were machined to a standard dog-bone tensile shape, then mechanically polished to remove surface layers, to a depth of 0.5mm from each side of a specimen. Uniaxial tensile tests were carried out at ambient temperature along the rolling direction (RD) at a strain rate of  $2.4 \times 10^{-4} s^{-1}$  with a gauge section of 20mm x 2.5mm x 2.0mm; three tensile samples were tested for each condition. Young's modulus was determined by acoustic wave-speed measurements obtained from ultrasonic sound speed, coupling longitudinal and transversal waves, with a plate specimen 2mm in thickness.

Specimens for microstructural investigation were first mechanically polished with SiC papers and SiO<sub>2</sub> solutions. The polishing process was carried out under a load of 5N to avoid the formation of stress induced martensite phases on the surface; no subsequent etching was applied. Microstructure characterization was performed in a Thermo-Scientific Apreo FEG-SEM equipped with an Oxford Instrument's Symmetry-EBSD detector. The collected data from the EBSD analysis was utilized to determine global Schmid Factors (SF), based on orientation of β-parent grains and {332}<113> twin variants [30]. The average area fraction of twins induced by the cyclic processing was estimated with Inverse Pole Figure (IPF) maps and image analysis, collected from four distinct 500μm x 350μm scans at different location on the same cross section of each sample. After tensile testing, the necked regions of the samples were observed by EBSD and scanning electron microscopy (SEM) on the plane parallel and normal to the rolling direction (RD). The chemical composition of the as-solution-treated alloy was evaluated quantitatively by energy dispersive spectroscopy, and the results are presented in Table 4.1.

### 4.3. Results

## 4.3.1 Microstructure evolution in the thermomechanical-cycling processed Ti-Nb Gum metal

The microstructures of the as-solution treated and cyclic-processed samples are presented in Figure 4.1, exhibiting significantly different features as the number of cyclic processing steps is increased from the as-solution-treated condition. Figure 4.1(a) shows that the microstructure of as-solution-treated alloy consists of randomly oriented grains, attributed to being fully recrystallized after the solution treatment. No precipitation or macro-segregation are observed in the equiaxed β-grains. EBSD images of the samples subject to the cyclic processing steps are found to be heterogeneous microstructures consisting of grains with lamellae deformation bands and those without, as depicted in Figure 4.1(b-d). In the CP1 sample, at 5% thickness reduction, the IPF map of Figure 4.1(b) reveals that only a few of grains, less than 5% (determined from EBSD images of approximately 300 grains), contain deformation features, which are nucleated from one boundary and stopped at another boundary, or by other band structures in a grain. It can also be seen that crystallographic orientations identified in the elongated deformation bands differ from that of  $\beta$ -parent phase in each grain, which is indicative of mechanical twinning. This implies that the lattice reorientation of the bands would change locally the geometrical conditions, in terms of Schmid factor. Figure 4.1(c) reveals that increasing strain to 10% thickness reduction (CP2) leads to a significant increase in the number of bands and their area fraction. At this strain level, most grains contain at least one band (around 70%), and grains with no deformation structure are rarely observed. In addition, one crystallographic orientation, with little the secondary deformation features, is mainly observed with the deformation bands formed in the same grain, irrespective of CP1 or CP2, and the twins are mostly active in un-twinned regions rather than in twin bands. It demonstrates that new twins

introduced by the second CP are also developed under the same geometrical deformation condition with the existing deformation bands in CP1, which is the most desired deformation behavior to achieve the twinned structure GM. It is worth noting that, with only cold deformation (no annealing step), an external stress applied after the CP1 would mainly assist thickening of the twins rather than nucleation of new twins, due to the localized event (or stress concentration) at the twin tips and the interface between the twin and parent grains [31]. As reported in the previous study [30], the specimen, having undergone annealing process before the additional cold-rolling, indicated much lower level of stress concentration compared to that of strained (cold rolled only) state, and consequently able to obtain the highly twinned structure GM by the cyclicthermomechanical process, as depicted in Figure 1(c). In the microstructure of CP3 shown in Figure 4.1(d), more densely distributed deformation bands are seen with increasing strain to 15%. Only less than 5% of the grains contains no deformation bands. Although a few grains appear to have bands with more than one crystallographic orientation (as seen in the IPF map of Figure 1d), the microstructure developed by the thermomechanical-cyclic process is mainly composed of grains containing lamellae deformation bands, predominantly with the primary twin system activated. Thus, one potential mechanism that may explain the influence of twinned structure on deformation is that lattice reorientation observed in the bands, potentially caused by twinning deformation, will change the slip geometry for a subsequent plastic deformation (i.e. alter the Schmid factors), which strongly influences the deformation behavior of the Ti-Nb Gum Metal.

### 4.3.2 Characteristics of mechanical twins

To further understand the nature of the internal structures in the alloys subject to the cyclic processing, the lamellae deformation bands are characterized by EBSD analysis, and the results obtained are displayed in Figure 2. From the misorientation profile (along the arrow path from A

to B in Figure 1b) as seen in Figure 2(a), the plate-like features introduced by the first cyclic processing step are identified as {332}<113> twins, corresponding to a misorientation of 50.5° around <110> [24], with approximately 15-30µm width. This demonstrates that the mechanical {332}<113> twinning system is preferred as the active deformation mechanism during the prestrain in the cyclic processing, which is in good agreement with deformation behavior observed in metastable titanium alloys [15, 32-34]. Figure 2(b) shows the misorientation analysis of the CP3 sample along the arrow path from C to D in Figure 1(d). The occurrence of new twins present in the CP3 sample are also identified as {332}<113> twins. Furthermore, the new twins introduced by CP2 and CP3 are mostly nucleated in un-twinned  $\beta$  regions with a width of around 10µm and  $3\mu m$ , respectively. This may be attributed to strain localization in the un-deformed  $\beta$  zones during subsequent cyclic processing steps, which is associated with increasing activation energy for twin nucleation [30]. Accordingly, as seen in Figure 2(c), the average number of twins per grain gradually increases to 4.3.2 with the second cyclic processing step, then significantly increases to 10.1 in the third cyclic processing step, suggesting the higher the number of stress concentrations introduced by further strain of the cyclic processing steps, the higher number of twins nucleated in grains. In addition, the average twin width (measured by image analysis) decreases with increasing number of the cyclic processing steps, accompanied by interleaved thinner twins than previously existed in the grain. Figure 2(d) shows the area fraction of twins that is calculated as twin area divide by observed area, covering more than 400,000µm<sup>2</sup> (as measured by EBSD). The twinned area fraction rapidly increased to 0.25 (25%) by CP2, and with further cyclic processing increased to 0.30 (30%) for CP3, suggesting a saturation condition [30]. Due to the fact that twins can act as barriers to dislocation movement, the twin fraction results in a reduced dislocation mean free path ( $\lambda$ ), which can be estimated with Eq. (1) [35, 36]:

$$\frac{1}{\lambda} = \frac{1}{L} + \frac{1}{D} \tag{1}$$

where, L is the mean twin spacing and D is the grain size. Thus, the mean twin spacing plays a significant role in determining the dislocation mean free path. Furthermore, the mean twin spacing (L) can be obtained from the volume fraction of twins and the twin thickness as expressed by Eq. (2) [36]:

$$\frac{1}{L} = \frac{f_v}{2d(1-f_v)} \tag{2}$$

Here, the volume fraction ( $f_v$ ) of twin is approximated from the area fraction of twins, and the half of the average twin width, shown in Figure 2(c), is taken for the twin thickness (d), based on stereological relations [37]. As seen in Figure 2(d), the dislocation mean free path is rapidly decreased as increasing the number of the cyclic processing steps, attributed to increasing the number of twins and its fraction in grains. Thus, the obtained results imply that the microstructural refinement associated with mechanical twins introduced by the cyclic processing steps would significantly influence deformation behavior and thus enables the ability to tune mechanical properties of the alloys

### 4.3.3 Mechanical properties and strain hardening response

The representative tensile engineering stress-strain curves of the Ti-Nb Gum metal alloys with different microstructures (CP1, CP2 and CP3) are displayed in the Figure 3(a). For comparison, the engineering stress-strain curve of the as-solution-treated specimen is also shown in Figure 3(a). The true stress-strain curves and the corresponding work hardening rate (WHR) curves of the alloys are presented in the inset of Figure 3(a). The 0.2% offset yield strength (YS :  $\Box$ ), ultimate tensile strength (UTS:  $\circ$ ) and uniform elongation (UE:  $\diamond$ ) of each curve are marked with corresponding symbols, and these obtained mechanical properties are summarized in Table
2.2, along with Young's modulus (as measured by an acoustic wave method). For the CP3 sample, with the highly multi-scale twinned structure, a good combination of yield strength (739 MPa), ultimate tensile strength (894 MPa), ductility (24%) and uniform elongation (17.5%) was attained. Furthermore, the limited Young's modulus variation in the cyclic processed samples suggests that the twinned structure has a negligible effect on elastic properties of metastable  $\beta$ -Ti alloys.

Figure 3(a) reveals a strong softening effect for the cyclic processed samples: the yield strength decreases with increasing the number of cyclic processing steps, from 855 MPa for the as-solution-treated sample to 809, 776 and 739 MPa for CP1, CP2 and CP3 samples, respectively, which is in good agreement with hardness trends reported in our previous study [30]. This softening behavior in the cyclic processed samples can be explained by a structural softening effect associated with lattice reorientation in the twinned regions (Figure 1). Given that twins can provide a favorable geometrical structure for a subsequent deformation based on dislocation slip or mechanical twinning [26, 32, 38], this trend implies that a structural softening is strongly correlated with texture evolution formed in the twinned areas of the cyclic processed specimens (which will be discussed in Section 4.3.4). On the other hand, the UTS for the CP3 sample decreases slightly when compared to that of the as-solution-treated sample (903 MPa - 894 MPa). This indicates that an increase in the twin density results in a monotonic decrease in the yield strength, yet a more pronounced work hardening behavior (UTS-YS) in the cyclic processed specimens, from 48 MPa for as-solution-treated to 155 MPa for CP3, as indicated in Table 4.2. As expected from sacrificing some of the yield strength by increasing twin structures, the ductility is substantially improved from 14% in as-solution-treated sample to 24% in the CP3 sample. These improvements in ductility and work hardening ability can be attributed to the twin structure achieved by the cyclic processing (deformation + annealing), especially increasing the number of twins and their fraction in the microstructure. It is also found that not only the uniform elongation

(4.5%-17.5% as determined by  $d\sigma/d\epsilon = \sigma$  [39]), but also the work hardening rates ( $d\sigma/d\epsilon$ ) are substantially enhanced by the cyclic processing. As shown in the inset of Figure 3(a), the work hardening rate of the as-solution-treated sample linear drops to the point of necking, less than 5% uniform elongation, which can be due to a lack of twin formation and localized deformation [15, 24]. According to Considére criterion, a uniform deformation is possible to continue without localized necking deformation unless the work-hardening ability caused by strain hardening of material is surpassed by the evolved true stress,  $d\sigma/d\epsilon \leq \sigma$  [40]. This implies that the work hardening rate of the as-solution-treated sample is insufficient to prevent the early necking instability, resulting in limited uniform deformation. Conversely, a multi-stage strain hardening response appears in the cyclic processed samples, with a particularly obvious three-stage deformation behavior exhibited by the CP3 sample. Similar work hardening processes are reported in other  $\beta$ -Ti alloys, based on the TWin-Induced Plasticity (TWIP) effect [8, 11, 37]. As seen in the work hardening rate curves of Figure 3(a), a sharp downward trend in Stage 1 is related to the transition from elastic to plastic deformation with activation of dislocation slip. In Stage 2, no obvious drop in work hardening rate is found in the CP3 sample throughout the plastic deformation process. The relatively high work hardening increment of ~1500MPa, enhances the uniform deformation, and consequently a good combination of strength and ductility is achieved. This is expected to promote a high incidence of mechanical twinning during tensile deformation [41]. In Stage 3, the work hardening rate rapidly decreases until necking takes place, due to the greater propensity for dislocation-twin or dislocation-dislocation interactions, rather than the formation of new twins. Given that the work hardening behavior in the twin-dominated deformation is controlled by the active twinning mechanism [42], the greatly enhanced uniform deformation achieved in the cyclic processed specimens can be accompanied by the maintenance of adequate work hardening capability during tensile deformation, mainly attributed to the multi-scale, highly twinned structure developed by the cycling process.

Figure 3(b) shows the uniform tensile elongations as a function of oxygen contents for these Ti-Nb Gum Metal alloys, and compares the results to those of other  $\beta$ -Ti alloys containing high oxygen content [18, 43-46]. From this comparison, it is revealed that the pronounced improvement in the uniform elongation is achieved at little expense of strength in the highly twinned Gum Metal (CP3 sample). It is noted that the improved mechanical properties of the current Ti-Nb Gum Metal are strongly linked to the twinned structure developed by repeating the cyclic-processing.

## 4.3.4. Microstructure evolution in tensile deformation

To examine the origin of the enhanced plasticity and the pronounced work hardening behavior in the twinned cyclic processed samples, EBSD investigation was performed on the deformation microstructure of the as-solution-treated and CP3 samples at different total strain levels for comparison. Drastic change in the microstructure features after plastic deformation are apparent. Figure 4.4 shows the EBSD maps of specimens deformed to 0.05 global strain. In the IPF map of as-solution-treated sample (Figure 4.4a), deformation-induced features are visible in the  $\beta$  matrix, tens of micrometers in size, with several intragranular bands having different orientations. The microstructure of the as-solution-treated sample is significantly heterogeneous compared with the single cyclic processed (CP1) sample, having only a few grains with mechanical twins and the majority of grains show no twins (see Figure 4.4b). Even though grains with twins possess a high twin fraction (around 30% area fraction), only 10% area fraction of twins are observed in the entire microstructure. The kernel average misorientation (KAM) map (Figure 4.4c) shows the local misorientation level (KAM values is higher at higher strain), corresponding to the darker regions contains a high density of deformation twins in the IQ map (Figure 4.4b). Based on the KAM values, deformation twinning is extensively activated in a few

grains at the early stage of plastic deformation, which leads to strain localization. Therefore, it can be stated that, for the as-solution-treated specimen, an external stress applied after the primary twin formation would mainly assist thickening of the twins rather than nucleation of new twins in other grains.

Conversely, it is found that more densely and uniformly distributed deformation features appear in the microstructure of the CP3 sample. In contrast to deformation behavior of the assolution-treated sample, the mechanical response of the twinned Gum metal is preceded by a non-local plastic strain, as shown in Figure 3(d-f). A few deformation twins are shown to have different orientations from other in the same grain, as seen in the IPF map (Figure 4d), indicating that different twinning systems are activated at this strain stage. Furthermore, there is a significant increase in the twin area fraction, from 28% (as-initial state) to 41% (after a global strain to 0.05). Note that some twins are thinner than the resolution limit of the EBSD map, so that it might be higher than the value estimated. In the IQ map (Figure 3e), numerous deformation twins are found in most of grains (around 90%), demonstrating that twin bands, irrespective of being induced by the cyclic processing or tensile deformation, are uniformly distributed throughout the gauge section of the sample. Based on the KAM values (indicted in Figure 3h), no significant stress concentration and a smaller strain gradient are observed, where plastic strains are enhanced not only at grain boundaries, but also in twinning regions. Accordingly, these observations imply that mechanical twins, as a microstructural variable that directly controls strain homogeneity, have a strong effect on deformation behaviors under tensile stress and lead to the improved mechanical properties of this Ti-Nb Gum metal alloy.

Figure 4.5 presents EBSD maps of typical microstructures in as-solution-treated and CP3 samples with a global strain to 0.1, exhibiting clearly different deformation features in strained grains. EBSD analysis was performed adjacent to the necking area of the samples. The IPF

map of Figure 4.5(a) shows that the microstructure after necking is composed of non-uniformly dispersed twins even with some cracks so that plastic deformation in the as-solution-treated specimen occurs heterogeneously in uniaxial tensile strain. As seen in the IQ map of Figure 5(b), there are mainly three different types of microstructure features observed: grains (G1) with several cracks, tens of micrometers in length, grains (G2) with only a limited amount of deformation, with no visible twins, and grains (G3) with the highly twinned structure. The microstructure evolution of the as-solution-treated sample implies that an unstable deformation mode can cause strain localization within a small necked region as twinning is not able to accommodate the applied strain gradient in a uniform manner, resulting in early necking or/and failure. The internal microstructure of the CP3 sample, at this strain level, is provided in Figure 5(c), and is composed of deformed lamella bands and un-twinned regions. In addition, severely deformed structures are found in the twin bands of each grain, based on multiple crystallographic orientations observed, when compared to un-twinned regions. In the image quality (IQ) map as seen in Figure 5(d), it is clearly seen that the deformation bands are evenly distributed (indicated by Twin and Matrix, respectively), and a multi-scale, highly twinned structure is created inside the primary twins through the cyclic processing. It is worth noting that the IQ map reflects lattice distortion in accordance with lattice imperfection [47]. Hence, dark contrast in a vicinity of the deformation bands indicates high lattice distortion, accompanied by further plastic deformation. As seen in these observations, plastic deformation in a twinned structure of the Gum Metal is mainly achieved by twinning (as seen in Figure 4 d-f), and lead to localized deformation in the vicinity of the twins uniformly distributed in the microstructure.

# 4.4 Discussion

## 4.4.1 Effect of twinned structure on yield strength

The main finding concerning the influence of the twinned structure on deformation behavior is that the yield strength of the Ti-Nb Gum metal decreases with a more pronounced multi-scale twinned structure, as illustrated by the tensile behavior in Figure 4.3. The nature of softening mechanism in terms of a crystallographic orientation of twining is not yet fully explained, but previous reports [31, 48-50] have suggested that deformation twinning is attributed to a structural softening in the twinned region, due to a texture evolution associated a lattice reorientation. Bertrand et al. [38] and Lilensten et al. [51] have also reported experimentally, based on Schmid factor (SF) changes, that a modified orientation in the twinned area is ascribed to a favorable geometrical condition for secondary deformation features. It is reasonable to consider that the contribution to softening can be enhanced as the deformation twin fraction increase in the microstructure. In order to clarify the effect of orientation-dependent behavior in the early stage of plasticity, a twinned structure GM (CP3) was strained to 0.03 and then systematically characterized by EBSD analysis to determine the variation in Schmid factor. The IPF map of Figure 4.6(a) reveals the presence of multiple features across band structures, i.e. the secondary bands (yellow arrows), are preferentially formed in the primary bands induced by cyclic processing (white arrows) rather than within the  $\beta$ -matrix. The IQ map of Figure 4.6(b) shows most of the deformation bands are indexed as {332}<113> twins as indicated with blue lines. Indeed, the twinned region formed by the cyclic processing has a much higher Schmid factor values than that of the  $\beta$ -matrix in the Schmid factor (SF) distribution map, as depicted in Figure 6(c). This observation implies that the secondary deformation mode is preferentially activated in the twinned regions owing to a modified orientation factor, based on the values of the Schmid factor.

From these observations, it can be stated that the twin structure plays a significant role in the yield strength of Ti-Nb Gum Metal as the hierarchical deformation behavior enables the critical resolved shear stress (CRSS) required for twin formation to decrease, even with increasing twin structure in the microstructure. Figure 7(a) shows that the distribution of global Schmid factors on the population of observed twins, for the CP1, CP2 and CP3 specimens, respectively. The global Schmid factor values increase from 0.405 for the CP1, to 0.441 for CP2, while for the CP3 samples the values are demonstrably higher with a range from 0.46 to 0.49, close to the maximum value of 0.5. Therefore, more primary twins are found with a higher Schmid factor, demonstrating that the variation of Schmid factors with the cyclic processing steps is strongly linked to microstructure features, correlated with the fraction of primary twins. Figure 7(b) shows the variation of micro-hardness and yield strength as a function of measured global Schmid factors in twinned Gum Metal alloys indicating that the softening behavior is substantially pronounced as the Schmid factor values increase. Therefore, this supports the conclusion that the mechanical softening in Ti-Nb Gum Metal alloys is governed by the initial twin fraction in the microstructure, attributed to orientation dependence of the CRSS in twin-dominated deformation [37, 49, 52].

## 4.4.2 Effect of twinned structure on uniform elongation

The results in this work lead to a question of how a uniform tensile deformation, as depicted in Figure 4.3, would be further enhanced in the cyclically processed Gum metal alloys. From the Schmid factor analysis and Figure 4.5(d), it can be expected that plastic deformation is likely to be localized in the primary twin bands rather than in un-twinned regions. However, a great deal of evidence suggests that nucleation centers for mechanical twinning are positions of highly localized strain in the lattice [27], explained by non-Schmid factor deformation mechanism with regards to local stress concentrations. As seen in Figure 4.4, the misorientation analysis demonstrates that a stress concentration is substantially localized at the twin bands and at twin-parent interfaces, resulting in a very heterogeneous stress distribution at this fine scale of the

microstructure. Hence, the activation of new deformation twins in the primary twins are affected by not only a local stress concentration, but also a geometrical orientation of grains with respect to the applied shear stress, and resulting severe deformation appears in the primary twins. Owing to greater plastically in the twinned area than the  $\beta$ -parent regions, the deformation behavior leads to subsequent formation of deformation gradients, called the *"dynamical composite effect"* [53]. Furthermore, one of the effective ways to improve the uniform elongation in twining deformation-dominated materials is to enhance the work hardening capability, which is achieved by the sequential activation of deformation twining. *Martry et al.* [23] have recently reported that, in early stages of strain, sequentially activating the secondary products, the same or different deformation mechanisms in the primary deformation twins, known as *'hierarchical deformation structure'* was attributed to improved ductility of  $\beta$ -Ti alloys. As discussed in Figures 4.1 and 4.2, a much more homogeneous distribution of the twins was achieved as the number of the cyclic processing steps increases. Consequently, the multi-scale, highly twinned structure developed by the cyclic processing leads to the heterogeneous *"Twin/Matrix"* system, in which the twins contribute to enhance uniform elongation in metastable  $\beta$ -Ti alloys.

## 4.4.3 Effect of twinned structure on work hardening

The specimens subjected to the thermomechanical-cyclic process exhibits much higher work hardening (or/and work hardening rate) compared to as-solution-treated sample, as described in Figure 4.3 and Table 4.2. This is mainly attributed to the pre-existing twins in the microstructure. It is well-known that twin boundaries act as barriers to mobile dislocations, and thereby enhanced work hardening capacity in the cyclic processed samples can be well explained by decreasing dislocation mean free path, referred to as the *dynamic Hall-Petch theory* [54]. As was shown in recent studies [23, 36, 51], the refined microstructure created by deformation twins

can significantly reduce the dislocation mean free path (shown in Figure 4.2d) resulting in not only limiting the effective gliding dislocation distance, but also blocking twin propagation by twin-twin interaction, and consequently these grains achieve a more pronounced work hardening ability. Figure 8(a) shows the deformation microstructure of the cyclic processed sample after tensile test, which shows the twins effectively serve as barriers to the deformation bands formed in the matrix, resulting in efficient work hardening. It is also found that there is a significant local strain gradient between the pre-twinned structure and the matrix. The IQ map of Figure 8(b) reveals that the relatively dark contrast in the twins when compared to the un-twinned β matrix, illustrating that the twinned area has undergone much high lattice distortion under tensile loading. Basinsski et al. [36, 55] have previously suggested that glissile dislocation in untwinned areas are converted to sessile dislocation after twinning, and thus enhancing tensile strength. This mechanism demonstrates the importance of mechanical twinning in improving strengthening effect, which is strongly linked in enhancing lattice distortion in the twinned area. The KAM map of Figure 4.8(c) exhibits a significant difference in the level of local misorientations between the twinned structure and the matrix (the higher the KAM values, the more local stress concentration [56]). Figure 4.8(d) display the misorientation profile along the arrow path in Figure 8(c), showing an obvious stress partitioning between the twin and the matrix, which can result in inhomogeneous plastic strain based on geometrically necessary density theory [57]. Previous reports in the literature have suggested that, in the heterogeneous structure composed of soft and hard regions, stress partitioning is also considered as main strengthening mechanism, attributed to strain inhomogeneity generated by local plastic strain, in addition to the strengthening inhomogeneous internal stresses i.e. long-range back stress [58]. This implies that, along with the twinned structure, there is high probability of dislocation/twin interaction, which also leads to the strain hardening effect observed in the Gum Metal alloys. Therefore, in terms of strength effects, there are three specific changes in the microstructure by twinning: i) boundary spacing reduces

(dynamic Hall-Petch effect); ii) dislocation density increases within the twins (Basinski hardening); and iii) inhomogeneous plastic strain produces (non-local strengthening effect).

# 4.5 Summary

This study investigated a microstructure design approach, which incorporated a twinned structure, to tune deformation behavior and mechanical responds in a metastable  $\beta$ -Ti alloy having high oxygen content. The developed microstructure and subsequent deformed microstructures were systemically analyzed to elucidate the effect of deformation twinning on deformation mechanism and correlated mechanical properties of Ti-Nb Gum metal. The main results in this work are summarized as:

- (1) The twinned microstructural design strategy is successfully obtained through the thermomechanical-cycling process, which is mainly composed of {332}<113> twinning. The different plastic deformation behaviors observed for each sample are derived from the evolving plastic deformation related to multi-scale deformation twins.
- (2) The multi-scale, highly twinned Gum Metal (CP3) samples exhibits an excellent uniform elongation of 17.5%, without sacrificing tensile strength and Young's modulus compared to the as-solution-treated Gum Metal. The twinning structure is strongly related to the overall softening behavior, and enhanced uniform tensile elongation, attributed to well-distributed twins throughout the entire microstructure based on the 'composite effect'.
- (3) Multiple twins introduced by repeating the cyclic-processing largely influence microstructural evolution and strain hardening behavior in tensile plastic deformation. An increase in tensile ductility with increasing the twin density is accompanied by an

enhancement of homogeneous plastic flow (delocalized deformation behavior) and work hardening rate.

(4) The twinned structure is attributed to strength effects with: i) contributions from decreasing dislocation mean free path (dynamic Hall-Petch effect); ii) enhancement of a lattice distortion, and thus an adequate work hardening capability achieved (Basinski mechanism); and iii) the presence of stress partitioning (non-local strengthening effect).

# 4.6 Acknowledgement

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Element	Ti	Nb	Та	Zr	0
at%	Bal.	22.8	0.73	2.03	1.3
wt%	Bal.	35.6	2.22	3.11	0.35

Table 4.1: Chemical composition of as-cast Ti-Nb-Ta-Zr-O alloy.

Table 4.2: Mechanical properties of as-solution treated and as-twinned samples. YS, UTS, WH, ETF, UE and YM represent 0.2% proof yield strength, ultimate tensile strength, work hardening form yield strength to tensile strength, elongation to fracture, uniform elongation and Young's modulus, respectively.

	YS (MPa)	UTS (MPa)	∆(UTS-YS) (MPa)	ETF (%)	UE (%)	YM* (GPa)
As-solution treated (ST)	855	903	48	14.5	4.5	68
As-cyclically twinned (CP)						
CP1	809	883	74	11	7.5	72
CP2	776	878	102	17	11	69
CP3	739	894	155	24	17.5	73

\*Young's modulus was estimated by an acoustic wave method.



Figure 4.1: EBSD inverse pole figure maps of the alloys with (a) as-solution stated and (b-d) asthermomechanical-cyclic processed; (b) CP1, (c)CP2 and (d) CP3, respectively, and (e) the corresponding XRD patterns.



Figure 4. 2: Misorientation profiles along the trace AB (a) and CD (b) of the Fig. 1, respectively. Evolution of twining structure in the cyclic processed specimens; (c) average number of twins and twin width and (d) area fraction and dislocation mean free path.



Figure 4. 3: Mechanical properties of the studied materials. (a) Engineering stress-strain curves of as-ST, the CP1, CP2 and CP3 GMs. The inset shows true stress-strain curves superimposed with the corresponding work hardening rate. (b) Uniform tensile elongation vs. oxygen contents plot of the studied materials in comparison to literature data [25-28], where the UE of other materials was obtained from engineering stress-strain curves.



Figure 4.4: EBSD analysis of deformation microstructures in the ST(a-c) and CP3 (d-f) specimens with a strain of 0.05; (a), (d) IPF maps; (b), (e) image quality maps; (c), (f) the corresponding Kernel average misorientation maps. The scale indicates the misorientation values excluding greater than a pre-set tolerance value of 2° (for indexed areas the higher misorientation level, the brighter green color; non-indexed areas in black).



Figure 4.5: EBSD maps of the ST (a, b) and CP3 (c, d) specimens after 8% global strain: (a), (c) IPF maps; (b), (d) the corresponding IQ maps.



Figure 4.6: EBSD analysis of the CP3 sample after 3% total tensile strain. (a) IPF map; (b) IQ map superimposed with {332}[113] twin boundaries in blue; (c) Schmid factor distribution map. The scale indicates the calculated SF value.



Figure 4.7: Deformation twinning dependence of Schmid factor: (a) global SF distributions of CP1, CP2 and CP3; (b) variation of micro hardness and YS as a function of SF values corresponding CP1, CP2 and CP3 (The error bars indicate the standard deviation).



Figure 4.8: Deformed Microstructure of the twinned structure GM: (a) IPF map; (b) IQ map; (c) the corresponding KAM map. (d) the misorientation profile along the marked arrow by yellow in KAM map.

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# **Chapter 5**

# Towards strength-ductility synergy though the design of heterostructural Ti-Nb Gum metal

Metals are used to be processed for ultra-high strength, but usually at a drastic loss of their ductility, referred to strength-ductility trade-off. In this chapter, we report a heterogeneous-structured  $\beta$ -Ti alloy with exceptional strength and ductility, resulting from optimized hierarchical features in a lamellar microstructure. The microstructure is achieved by controlling the fraction of coarse/fine domains, spatial grain-size distribution, and different types of grain boundaries. The large degree of microstructural heterogeneity leads to obvious mechanical incompatibility and strain partitioning during plastic deformation . In addition, experimental results demonstrate that the unique heterogeneous structure induces back-stress hardening and promotes dislocation accumulation, thereby achieving high yield strength ~970 MPa and exceptional uniform tensile elongation of ~16%. This chapter is a modified version of a paper that has been published in the journal *Materials Research Letters*.

# 5.1 Literature review

Despite very attractive combinations of low Young's modulus, high ductility, and superior fatigue resistance, metastable β-Ti alloy's translation into commercial applications has been

mainly hindered by its low strength, compared to conventional  $\alpha$ - and  $\alpha$ + $\beta$  Ti alloys [1]. With progress in attaining a high level of strength, a prominent approach has been considered for strengthening mechanisms, particularly exploiting precipitation hardenability to utilize dispersed nano-sized secondary  $\alpha^{\prime\prime}$  and/or  $\omega$  phases through aging heat treatments [2, 3]. However, as newly designed alloys, an intrinsic drawback of the thermo-mechanical processes is the conventional trade-off dilemma: the substantial improvement in strength by brittle secondary phases inevitably brings about a drastic loss of ductility and a significant increase of Young's modulus, which is adverse for structural- and bio-applications [4]. Thus, a new strategy for imparting strengthening, while still preserving large ductility and acceptable Young's modulus in metastable  $\beta$ -alloys is needed.

In recent years, many efforts have been devoted to design distinct microstructures consisting of heterogeneous structures to overcome the strength-ductility trade-off dilemma. Examples include producing harmonic structures with micrometer-sized grains surrounded by ultrafine grains [5-7], generating spatially grain-size gradient microstructures [8-13], designing heterogeneous materials with large-sized lamella domains embedded into a matrix of ultrafine grains [14-16], and other complex hierarchical structures [17-19]. The resulting materials, with the heterogenous features, have exhibited remarkable strength-ductility enhancement compared to their homogeneous counterparts. Therefore, an efficient strengthening and effective strength-ductility synergy are expected by deploying heterogeneous microstructure in metastable  $\beta$ -Ti alloys, which has previously received little attention.

For the heterogeneously-structured materials, enhanced strength is primarily attributed to back-stress hardening, originating from mechanical incompatibility between constituent components under uniaxial tensile stress [10, 11, 15]. In addition, the different mechanical responds to an external applied stress can induce the buildup of geometrically necessary

dislocations (GND) at interfaces between hard and soft domains, which contributes to strain hardening of the material, and thus promoting larger tensile strains [11, 17-19]. The underlying deformation behavior suggests intentional microstructural heterogeneity can induce steep stress and strain gradients across domain interfaces, which is beneficial towards a synergy between high strength and high ductility. However, it still remains a challenge to determine which type and form (lamella, gradient, level of heterogeneity) is more efficient to achieve significant enhancement in mechanical properties.

Recently, *Wu et al.* [20] have suggested that an exceptional improvement in strengthductility synergy could be accomplished by introducing microstructural lamella, such as 30 vol% soft lamella grains embedded in a hard matrix. In addition, a study on a grain size dependent harmonic structure [6, 7] reveals deformation incompatibility is required for the generation of GNDs, contributing to strength and strain hardening, especially when the structural/strain gradient is large. Consequently, the mechanical behaviors in heterogeneous-structured materials are strongly related to microstructural heterogeneity, for stimulating non-homogeneous plasticity during plastic deformation. Owing to a lack of controllable processing variables, however, the design strategy to control the spatial distribution of coarse/fine grains and optimize their volume fraction is limited [8, 16, 21].

The aim of this study is to develop the desired heterogeneous microstructure through microstructural design optimization, so as to achieve an optimized strength-ductility synergy in a metastable Ti alloy. The various microstructural heterogeneities are effectively introduced by cold-rolling and annealing of a pre-twinned Ti-23Nb-0.7Ta-2.0Zr-1.0O(at%) Gum Metal. The newly-designed Gum Metal combining lamella and hierarchical features exhibits a superior combination of strength and ductility compared to its homogenous counterpart. The microstructure heterogeneity and its relationship to the underlying deformation mechanism, which can lead to

the extraordinary strength-ductility combination is discussed in detail.

## 5.2 Experimental procedures

#### 5.2.1 Solution-treated sample preparation

The Ti-23Nb-0.7Ta-2.0Zr-1.0O(at%) Gum Metal alloys were fabricated by arc-melting under an argon atmosphere from pure raw materials Ti, Nb, Ta, Zr and TiO<sub>2</sub>, followed by a homogenization treatment at 1000°C for three hours, and subsequent water cooling (Figure 5.1a referred to the microstructure as the solution-stated (ST), with an average grain size of ~120mm). The homogenized Gum metal alloy was processed by a thermomechanical-cyclic method to form a pre-twinned microstructure (Figure 5.1b). Based on our previous results [22], the twinned Ti-Nb based Gum Metal alloy was used in the present study because a very homogeneously deformed microstructure could be attained by a twinning-preferred deformation behavior during cold-rolling. The uniformly deformed microstructure enables effective control of the area fraction of soft/hard domains without non-recrystallized grains in the microstructure (refer to Figure 5.2 for the microstructure processed in the solution-treated Gum Metal condition shown in Figure 5.1a). Detailed processing history and mechanical properties of the starting material and the pre-twinned Gum Metal have been reported previously [22, 23]. For the next step, a heterogeneous structure was effectively introduced by cold-rolling to 85%, followed by annealing at 690°C. The heavily twin-dominated microstructure reverted back to recrystallized grains during the post annealing treatment.

## 5.2.2 Heterogeneous microstructure

To design the heterogeneous microstructure showing consistent coarse-grained and fine-

grained lamella domains, strain gradient in deformation microstructure is required for heterogenous nucleation of recrystallized grains based on the accumulation of the stored deformation energy. The initial equiaxed grains are mainly deformed by mechanical twinning during cold-rolling, and the deformed grains can be divided by twining regions and matrix regions. There exist huge strain heterogeneities by further cold deformation, accompanying by the pronounced inhomogeneous plastic deformation between the twin bands and matrix, i.e. strain is normally accumulated in twins rather than in  $\beta$ -matrix, thus exhibiting the strain-gradient microstructure. During recrystallization, larger pre-straining generally accelerates nucleation rate. As a result, recrystallized grains preferentially nucleate adjacent to the twin bands, seen in Figure 5.2, which is led to a gradient structure with soft, coarse-grinned lamella layers. Conversely, the  $\beta$ -matrix undergoes sluggish kinetics caused by the relatively small number of active nucleation sites, resulting in a hard, exceptionally fine-grained lamella matrix. Based on the strain-assisted heterogeneous nucleation of recrystallized grains, the heterogeneous microstructure with well-distributed grain-sized gradient can be developed, as indicated in Figures 5.3(a) and 5.4. As shown in Figure 5.5 (a), the area fraction of fine-grained region decreases as the recrystallization proceeds. Note that the grain size regime changes gradually from finegrained domains to coarse-grained domains, consequently enabling the fraction of the finegrained region to be controlled precisely by manipulating post-annealing conditions. More importantly, twinning-mediated plastic deformation could control the important parameters of the heterogeneous geometry, such as grain size, area fractions between coarse grains and fine grains, and a spatial distribution of lamella structures. As a result, distinct microstructures combining various fractions of coarse-grained and fine-grained regions, can be obtained through the relatively sluggish recrystallization kinetics (detailed behavior during post-deformation annealing is explained in the Supplementary material). In this study, three heterogeneous microstructural Gum Metals have been prepared, and are denoted as HS80, HS45 and HS15 with the area

fraction of fine-grained domains (refer to Figure 5.5(a) for variation of coarse-grain/fine-grain area fraction as a function of annealing time, and the corresponding phase constitution shown in Figure 5.5b).

The heterogeneous microstructures were characterized by a Thermo-Fisher Apreo FEG-SEM equipped with an Oxford Instruments EBSD-Symmetry detector. Standard dog-bone shaped specimens, with the gage dimensions of 20mm x 2mm x 1mm, were subjected to uniaxial tensile tests and loading-unloading-reloading (LUR) tensile tests with an initial strain rate of  $5 \times 10^{-4}$ s<sup>-1</sup> (tensile direction parallel to the rolling direction). The GND density in the deformed Gum Metal alloys were calculated from EBSD data using an in-house Matlab code developed by Zhu et al. [24, 25].

## 5.3 Result and discussion

Similar to the near-ideal heterogeneous microstructure schematically presented in ref. [20], the tailored Gum Metal (HS80) clearly exhibits microstructural heterogeneity with three types of grains at multiple length scales, as depicted in Figure 5.3. The macro-EBSD image of Figure 5.3(a) illustrates that the heterogeneous-structured possesses heterogeneous lamella geometry with a specific spatial distribution of coarse-grained and fine-grained domains. In Figure. 5.3(b), a magnified view of the black box in Figure 5.3(a), the coarse grains, which comprise an area fraction of around 23% soft regions, (see Figure 5.5(a)), are embedded in a hard, fine-grained lamella matrix, wherein a pronounced bimodality is seen (Figure 5.3(d)). Due to a large grain size (average size is approximately 78mm), these regions will be referred to as coarse grains, and other structures will be referred to as fine- and/or ultrafine-sized grains, all with size of < 14mm in width). It is apparent that, during the post-deformation annealing process, the deformed grains are only partially recrystallized, owing to the nature of gradient deformation

between twins and matrix regions during cold working [26, 27]. An enlarged microstructure of the fine-grain domain, indicated as the yellow box in Figure 5.3(b), is presented in the Figure 5.31(c). The fine-grain regions are grouped as two types of grains with various size ranging from 0.1 to 14mm (the inset of Figure 5.3(d)): fully recrystallized grains with ultrafine-size (all with a size ~2mm) and partially recrystallized grains including subgrain boundaries (LAGB: 2~15°) are with fine scales ranging from 2mm to 14mm. According to the previous reports [15, 26 28], there is a coupling effect due to the size difference and inhomogeneous dislocation density after partially recrystallized zones and partial recrystallized zones. Note that the partially recrystallized grains dramatically decrease with increasing annealing time and are hardly observed in HS45 and HS15 samples (Figure 5.4a-f). Concurrently, the HS80 sample is a unique heterogeneous microstructure composed of lamella and hierarchical features, which are expected to provide a wide range of microstructural heterogeneity across multiple length scales in the Gum Metal.

Figure 5.6 shows the tensile properties of three heterogeneous-structured Gum Metals with distinct microstructures and the results are summarized in the table inset. To highlight the enhancement in the strength-ductility synergy achieved by the heterogeneous microstructure design, the curves of 90% cold-rolling labeled (CR90) and its fully annealing state (CG, grain size in ~73mm) are also included. The microstructural engineering of severely-deformed microstructure by cold-rolling results in the CG sample with plastic instability that develops immediately after yielding, along with higher yield strength (YS) and ultimate tensile strength (UTS), as well as the inverse strength-ductility relationship [29]. In contrast, heterogeneously structured Gum Metals exhibit a good combination of high strength (YS and UTS) and high ductility, (elongation-to-fracture and uniform elongation as determined by the *Considére-criterion* [30, 31]). Note that the relatively poor ductility of the HS15 specimen, compared to that of the CG sample, can be affected by a formation of thermally-induced  $\alpha$ <sup>*r*</sup> phase during the relatively

long annealing process [32] (see Figure 5.5b). In this study, an extraordinary strength-ductility synergy is observed in the HS80 sample, as evidence by high strength (YS: ~32% and UTS:  $\sim$ 35%) and ductility (total elongation:  $\sim$ 8.4% and uniform elongation:  $\sim$ 6.8%). It is interesting to note that its ductility is even higher than its CG counterpart. Therefore, it is apparent that the intentional microstructural heterogeneity imparted by the microstructural design is essential to enhance the strength and the strength-ductility trade-off in this metastable Ti alloy. Interestingly, heterogeneous-structured samples show a yield drop at the onset of plastic deformation, followed by a transient deformation stage, seen in Figure 5.6(a). The strain transition results in an upturn in the strain hardening rate (SHR, Figure 5.6b), wherein strain hardening rate drops rapidly first (region I), then finally reaches to its maximum (region II). This non-continuous yielding generally appears at higher oxygen concentration (above 1.2 at.%) in conventional Ti-Nb Gum Metal, owing to the interaction between dislocations and interstitial oxygen [33]. By comparison with the coarse-grained Gum Metal (1.0 at.% O), the double-yielding observed in heterogeneousstructured samples mainly originates from the inherited microstructural heterogeneity as widely reported in heterostructured metals or alloys [10, 15, 16]. This can be attributed to the varying yield stress corresponding to heterogeneous elastic-plastic deformation at interfaces between soft/hard grains, i.e. back-stress hardening [15, 34]. Moreover, the HS80 sample exhibits a remarkable feature of strain hardening rate-retention over a wide strain range (region III), leading to extraordinary strain hardening ability, thus the excellent tensile ductility of HS80.

To prove the peculiar mechanical behavior and unique stain hardening of heterogeneousstructured samples, loading-unloading-reloading (LUR) tensile tests have been performed, and the resulting curves are shown in Figures 5.6(c) and 5.7(a), respectively. The test was conducted in the strain range of the uniform elongation. All the samples exhibit a hysteresis loop, which reveals a strong Bauschinger effect [15]. Interestingly, the HS80 shows a larger hysteresis loop compared to that of thecoarse-grained sample, resulting in a stronger Bauschinger effect in

HS80 (see Figure 5.7(b)). The flow stress can be divided into the back-stress associated with the forward motion of dislocations and the effective stress required locally for activating dislocation sources [16], seen in Figure 5.7(b). Figure 5.6(d) displays the values of back stress ( $\sigma_h$ ) and the ratio of back stress to effective stress ( $\sigma_b/\sigma_f$ ), estimated by the method reported in Ref [11]. To trigger yielding, additional external stress needs to be supplied to move dislocations, so that yield strength would be enhanced by as much as the back-stress contributes. The calculated backstress of heterogeneous-structured samples near the yield point is much higher than that of the coarse-grained sample, which quantitively explains that the increased YS of heterogeneousstructured samples is elevated with increasing microstructural heterogeneity [11, 20, 35, 36]. For heterogeneous-structured materials under a uniform tensile load, the soft coarse-grain domains would deform plastically, while the hard domains would remain elastic. Therefore, there exists mechanical incompatibility due to the strain constraint by the hard fine-grain domains. Such strain gradients would generate geometrically-necessary dislocations (GNDs), which induce a long-range back-stress at the domain interface [20]. Ultimately, the strain inhomogeneity enables soft grains to become much harder by accumulating dislocations in them until hard grains start to yield, which is the so-called synergetic strengthening [10, 16]

In addition, the high back stress lead to enhancement in the strain hardening capability, and thus a high tensile ductility [20, 34]. With increasingly higher applied strain, the back stress of the HS80 sample increases linearly, showing a pronounced enhancement compared to HS15, HS45 and coarse-grain samples. The ratio,  $\sigma_b/\sigma_f$ , is indicative of the contribution of back stress to flow stress, and illustrates that the influence of back stress is much higher than the effective stress over the entire plastic range. It is evident that the strain gradient would be larger with ongoing deformation, especially when microstructural inhomogeneity increases in the materials. Since the soft coarse-grains would deform plastically more than the hard, fine grains, this plastic instability requires excess GNDs to maintain material continuity, which is expected

from non-local strengthening effects [12-16, 21]. Therefore, GND densities would be higher in HS80, which is necessary for the high flow stress, and consequently enhancing the strain hardening rate with an increase in overall plastic strain in the sample [36].

To examine the origin of the enhanced plasticity and the pronounced strain hardening behavior observed in heterogeneous-structured samples, EBSD investigation using the Kernel Average Misorientation (KAM), values ~2°, was performed on deformation microstructures of coarse-grained and heterogeneous-structured Gum Metal samples, where the average grain size is approximately 73mm and 67mm, respectively. Drastic changes in the microstructure features, with a strain of 0.05, are apparent. The EBSD micrograph of the coarse grains, Figure 5.8(a), shows that deformation-induced features are visible in a few grains, as intragranular bands with different orientations. Note that the deformation bands are characterized with misorientations of ~50.5°, which correspond to  $\{332\}<113>_{B}$  twins as the primary deformation mechanism of a Ti-Nb Gum Metal [22]. Meanwhile, no mechanical twins are observed for heterogeneous-structured sample with uniform deformation as shown in Figure 5.8(b). Based on the knowledge of the nucleation of twins at grain boundaries, it is believed that accommodation of back stresses at interfaces such as coarse-grain/fine-grain boundaries could inhibit twinning formation in coarsegrained domains by increasing the activation energy for twin nucleation [5]. Figure. 5.8(c) presents the local misorientation of the deformed coarse-grain sample (KAM values are higher at higher strain), showing that strain localization is associated with extensive deformation twinning, and thus poor ductility. In general, for most engineering applications, the microstructure should be designed to delocalize strain concentration and promote a uniform distribution of plastic flow to avoid early failure under tension [36]. Conversely, the mechanical response of the heterogeneous-structured Gum Metal is preceded by non-localized plastic strain. The calculated KAM maps of the heterogeneous-structured Gum Metal in Figure 5.9 shows little evidence of residual stress remaining in the partially recrystallized grains. With increasing plastic

strain beyond the yield point in the heterogeneous-structured Gum Metal, as shown in Figure 5.8(d), there is little evidence for stress concentrations and well-distributed strain are observed, wherein plastic strains are enhanced mainly near interfaces separating coarse-grain/fine-grain domains. Therefore, it can be stated that the designed structural heterogeneities promote uniformity of deformation by alleviating strain localization due to twinning. More importantly, the enlarged KAM image obtained from the heterogeneous-structured Gum Metal, Figure 5.8(e), illustrates that the higher KAM values are seen in the vicinity of interfaces separating coarsegrain/fine-grain regions compared to that of the grain boundary between coarse-sized grains. Since the high KAM values are a result of GNDs pile-ups, the deformation process of the heterogeneous-structured Gum Metal would produce a significantly higher level of GND density. As a result, this leads to efficient accommodation of plastic deformation by the gradual distribution of strain near the interfaces among coarse-grain/fine-grain regions [6, 18, 21]. Accordingly, these observations imply that the intentional structural heterogeneity, as a microstructural variable that directly controls strain homogeneity, is very effective in enhanced stable plastic flow, which is beneficial for sustained strain hardening up to large strain (uniform elongation values), especially when the structural/strain gradient is large.

Finally, we analyzed the distribution of the GND density in the heterogeneous microstructure, which can experimentally verify the local back stress strengthening mechanism. With a tensile test interrupted prior to the yield point of HS45, the quantification of GNDs was performed using the obtained EBSD orientation data (Figure 5.10a) [24, 25]. The calculated values that the grain average GND density versus grain area is given in Figure 5.10(b) which is based on the results of Figure 5.11. It shows that the high-density data lies primarily within the fine-grain regions, whereas the relatively low GND density is found in the coarse-grain region. Based on grain boundary strengthening, GND densities are generally higher in a small grain compared to that in a large grain. In the heterogeneous-structured sample, the strain partitioning
effect leads to even more pronounced GND distribution in the fine-grain regions to accommodate the high plastic incompatibility at the interfaces separating coarse-grain and fine-grain domains [36, 37], as shown in Figure 5.8(e). These accumulated dislocations would contribute to back stress hardening by generating long-range stresses impending dislocation movement [11, 20, 36]. Moreover, Wu [34] has suggested that, under uniaxial loading condition, the evolution of incompatible deformation can induce multiaxial stress states to keep compatibility among neighbor grains. The multiaxial stress leads to interaction with the GNDs and mobile dislocations, which effectively promote dislocation accumulation near the interfaces separating soft/hard regions [38]. This is related, not only to extra strength through forest hardening [36, 37], but to additional ductility through the activation of new slip systems (cross-slip mechanisms) [34, 36].

Based on our results with the heterogeneous-structured Gum Metal, significant microstructural heterogeneity, related with spatial grain size distribution and high interface density, leads to a high GND density, which is needed to accommodate high plastic incompatibility during deformation. In addition, creation of long-range back stresses due to GNDs serves as a strain hardening mechanism, and thus finally resulting in an extraordinary strength-ductility synergy.

## 5.4 Summary

A new methodology to design a heterogeneous microstructure, with twin-structured Gum Metal, enables manipulation of microstructural heterogeneity by controlling the fraction of coarse grains/fine grains involving lamella and hierarchical features. The heterogeneously structured Gum Metal, containing approximately 80% hard lamella matrix, exhibits an exceptional strength-ductility synergy, compared to its coarse-grain counterpart, as well as other heterogeneous-structured Gum Metals. Moreover, it can be confirmed that the microstructural heterogeneity is beneficial for improvement in both strength and ductility in Gum Metal. Based on the previous

results, the stress and strain gradients, generated between separating soft/hard domains, could induce the storage of GNDs, leading to not only synergetic strengthening crucial to increase the global yield strength of the material, but also back stress hardening essential to achieve high strength and ductility. This work ultimately suggests that the method applied in this study may be easily utilized to conventional deformation-annealing processes, hence, has a great potential for multi-scale applications.

## 5.5 Acknowledgement

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Figure 5.1: EBSD micrographs of (a) the solution-treated (ST) and (b) pre-twinned structural Gum Metals. For The crystallographic orientation, the same color scheme was applied to all of the orientation maps used in this study.



Figure 5.2: IPF map showing the recrystallized grains preferentially nucleated in twin bands. The Gum Metal was processed with 5% cold rolling, followed by annealing at 700°C for 10 minutes.



Figure 5.3: (a) EBSD map of the HS80 Gum Metal and (b) magnified image quality (IQ) map of the black box. (c) a magnified map of the fine-grained domain (in the yellow box), wherein the gray and black lines represent LAGB (2-15°) and HAGB (>15°), respectively. (d) The grain size distributions of the HS80 sample and the fine-grained domain (shown in the inset).



Figure 5.4: EBSD micrographs of (a) HS45, (b) HS15, and (c) magnified view of HS15. The corresponding IQ maps of (d) HS45, (e) HS 15, and (f) the magnified view of HS15. The gray and black lines in (f) represent low angle grain boundaries (LAGB, 2-15°) and high angle grain boundaries (HAGB, >15°), respectively.



Figure 5.5: (a) Variation of the area fraction between coarse-grained/fine-grained domains as function of annealing time, and (b) the corresponding XRD patterns of HS15, HS 45, HS 80 and the homogeneous counterpart.



Figure 5.6: Mechanical responses of the three heterostructural Gum Metals. (a) Engineering strain-stress curves where the inset table represents measured values of the mechanical properties. (b) True stress and strain hardening rate curves as function of true strain. (c) The loading-unloading-reloading behavior of the HS80 and homogeneous coarse-grained samples. (d) back stresses and ratio of back stress and effective stress values obtained from the LUR test.



Figure 5.7: (a) The loading-unloading-reloading (LUR) curves of HS15, HS45 and CG counterpart. (b) The LUR loops for the homogeneous coarse-grained and HS80 samples where back stress and effective stress represent  $\sigma_b$  and  $\sigma_{eff}$ , representatively.



<u>10μm</u> Figure 5.8: EBSD analysis of deformation microstructures in the homogeneous coarse-grained (a, c) and heterogenous-structural (b, d, e) samples with a strain of 0.05: (a), (b) IPF maps and (c), (d) the corresponding KAM maps. (e) A magnified KAM map of the heterostructured sample. The scale indicates the misorientation values excluding greater than a pre-set tolerance value of 2°.



Figure 5.9: Kernel average misorientation (KAM) map of the heterostructured Gum Metal at zero stress, illustrating the similar level of KAM values between coarse-grained and fine-grained domains.



Figure 5.10: (a) EBSD micrograph of the HS45 sample and (b) Grain average GND density (log m<sup>(-2)</sup>) plotted against grain area (log m<sup>2</sup>) with each data point colored according to the order of magnitude of grain average density.



Figure 5.11: (a) Grain area map (log10 m<sup>2</sup>, color bar:  $-12.5 \sim -8.5$ ) and (b) the corresponding GND density map (log10 m<sup>(-2)</sup>, color bar:  $13.8 \sim 14.9$ ).

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