“Experimental-theoretical study of the interplay between deformation mechanisms and secondary phases in metastable β titanium alloys”

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Abstract

Metastable β titanium alloys are essential materials for biomedical implant and aerospace applications. Their properties can be adjusted by tailoring the β phase instability, which not only results in the precipitation of secondary phases but also leads to the activation of additional deformation mechanisms besides dislocation slip. Aiming at an improved understanding of the deformation mechanisms associated with the β phase instability, especially the effects of secondary phases on the deformation mechanisms, three groups of β Ti–Nb–Ta–Zr–O alloys with varied β phase stability were produced, which correspond to the occurrence of dislocation slip, {211}<111> twinning and {332}<113> twinning, respectively. The interplay between these deformation mechanisms and the secondary phases (ω and α”) was investigated experimentally and theoretically.

In slip-dominated alloys, the prevailed deformation mechanism is found to be modified into dislocation channeling by the presence of homogeneously distributed nanometer-sized ω phase. A {112}<111> dislocation dissociation mechanism is proposed to account for the formation of dislocation channels. The dissociation and passage of {112}<111> dislocations can render the ω phase reversely transform into the β phase and thus create a softening channel for the movement of the following dislocations.

The relative phase stability between β and ω is found to be governed by the chemical contribution involved in the lattice rearrangement, while the elastic contribution associated with the lattice parameter mismatch plays a minor role. An energy barrier is revealed on the energetic pathway of the β → ω transition. The {211}<111> shear associated with {211}<111> twinning
or $\beta \rightarrow \alpha''$ transition plays an important role in overcoming this barrier, promoting local formation of the $\omega$ phase along the $\{211\}<111>$ twin boundary and $\alpha''/\beta$ interface.

For the first time the surface-to-bulk microstructures of $\{332\}<113>$ twins are systematically characterized. In addition to high densities of straight dislocations within the twin, a stress-induced $\alpha''$ martensite band is found near the surface adjacent to the twin. The $\alpha''$ martensite band transforms into the adjacent twin rather than into the matrix during annealing at 900 °C, based on which an $\alpha''$-assisted twinning mechanism is proposed, i.e., the $\{332\}<113>$ twin nucleates within the $\alpha''$ martensite. This mechanism is supported by the constitution of the initially formed twin, where the first portion formed consists of $\alpha''$ martensite.
Zusammenfassung

Metastabile β-Ti-Legierungen finden Anwendung in bio-medizinischen Implantaten und im Bereich der Raumfahrt. Die mechanischen Eigenschaften können durch die Instabilität der β-Phase eingestellt werden, sodass sich nicht nur eine Zweitphase ausscheidet, sondern auch weitere Deformationsmechanismen neben Versetzungsgleiten auftreten. Um die damit verbundenen, verschiedenen Deformationsmechanismen besser zu verstehen, wurden drei β-Ti-Nb-Ta-Zr-O Legierungen mit variierender β-Stabilität produziert, die jeweils Versetzungsgleiten, so wie {211}<111> - und {332}<113> - Zwillingsbildung hervorrufen. Das Zusammenwirken dieser Deformationsmechanismen mit den Zweitphasen wurde in dieser Arbeit sowohl experimentell, als auch theoretisch untersucht.

In der Legierung mit Gleitverformung tritt kanalförmige Versetzungsbewegung auf, was in der Ausscheidung von homogen verteilter, nm-großer ω-Phase begründet ist. Die ω-Phase wird aufgrund gezielter Versetzungsbewegung entlang {112}<111> aufgelöst, da sie in die β-Phase rücktransformiert und damit die Hindernisse zur Versetzungsbewegung verschwinden lässt.

Die relativen Phasenstabilitäten von β und ω werden vom jeweiligen chemischen Beitrag zur Gitterumverteilung bestimmt, und nicht so sehr von der elastischen Verzerrung durch Änderungen des Gitterparameters. Es wurde herausgefunden, dass die β → ω Umwandlung eine Energiebarriere beinhaltet. Das Überschreiten der Barriere wird entscheidend durch {211}<111> Scherung während der {211}<111> Zwillingsbildung oder während der β → α'' Umwandlung begünstigt, da die Bildung von ω-Phase entlang der {211}<111> Zwillingsgrenzen und α''/β Phasengrenzen erleichtert wird.
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Chapter 1  Introduction

Titanium has two primary phases, i.e., high-temperature body-centered cubic (bcc) β phase and low-temperature hexagonal close-packed (hcp) α phase. These phases can be stabilized by the addition of alloying elements. For example, Al and Sn stabilize α phase, while most of the transition metal elements, such as V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni and Mn, stabilize β phase. They are termed α-stabilizing elements and β-stabilizing elements, respectively. By controlling the concentrations of alloying elements, we can tailor the relative amounts of α and β phases, based on which titanium alloys have been categorized into three broad groups: α, α+β and β titanium alloys. All three groups of titanium alloys are extensively used in aerospace applications due to their high strength to weight ratio and excellent corrosion resistance [1]. In addition, these alloys also exhibit superior biocompatibility, rendering them excellent candidates for implant materials in biomedical applications [2].

1.1  Motivation

In the beginning, the majority of studies focused on α and α+β titanium alloys, especially on commercially pure Ti (c.p. Ti) and Ti–6Al–4V, and they were the predominant titanium alloys used in both aerospace and biomedical applications. Over the past two decades, the studies on β titanium alloys, especially the metastable β titanium alloys (Fig. 1.1), have increased rapidly, owing to (i) their capacity of attaining a broad range of strength levels by solution and aging treatments, offering a larger processing window compared to α or α+β alloys; and (ii) their low elastic modulus, superelasticity and shape memory effect. These two characteristics convey to
Metastable β titanium alloys refer to those alloys containing sufficient amounts of β-stabilizing elements in which precipitation of α phase is fully suppressed and β phase is nearly 100% retained at room temperature after β-field solution and water quenching. In contrast to stable β titanium alloys, the β phase in metastable β titanium alloys is instable at room temperature. Depending on the instability of β phase, secondary phases such as hcp α phase, hexagonal/trigonal ω phase and orthorhombic α” martensite may precipitate during deformation or heat treatment 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
precipitating evenly distributed fine-scale $\alpha$ plates in metastable $\beta$ titanium alloys [3], where the $\alpha$ plates create a large number of $\beta/\alpha$ interfaces that act as dislocation barriers and thus strengthen the alloys. Therefore, many studies have been directed to clarifying the initiation and evolution of $\alpha$ precipitate [4]. $\omega$ phase has long been considered to be a deleterious precipitate to mechanical properties despite its strengthening effect, because it results in severe embrittlement. Nevertheless, $\omega$ precipitates normally homogeneously distribute within the $\beta$ matrix and can act as initiation sites of $\alpha$ phase [5], providing a promising route for attaining evenly distributed $\alpha$ plates. $\alpha''$ martensite is the origin of superelasticity and shape memory effect in metastable $\beta$ titanium alloys. Considerable effort has been devoted to investigating the $\beta \rightarrow \alpha''$ martensitic transformation in the past decade [6-12].

In addition to the secondary phases, the deformation mechanism of metastable $\beta$ titanium alloys is also dependent on the instability of $\beta$ phase [13-16]. In the stable $\beta$ titanium alloys, only dislocation slip can be activated. Such alloys suffer from limited ductility [15, 17]. This drawback is also present in some $\alpha$-hardened metastable $\beta$ titanium alloys. Since the $\beta \rightarrow \alpha$ transformation involves the diffusion of $\beta$-stabilizing elements from $\alpha$ domain into $\beta$ matrix [5], the precipitation of $\alpha$ phase is accompanied by the enrichment of $\beta$-stabilizing elements in the $\beta$ matrix. As a consequence, the $\beta$ matrix of some $\alpha$-hardened metastable $\beta$ titanium alloys is very stable, analogous to the stable $\beta$ titanium alloys. Thus, the plastic deformation of such a stabilized $\beta$ matrix is prevailed by dislocation slip. For less stable $\beta$ titanium alloys, $\{112\}<111>$ twinning, $\{332\}<113>$ twinning and stress-induced phase transformations ($\beta \rightarrow \alpha''$ and $\beta \rightarrow \omega$) may be activated, as illustrated in Fig. 1.1. It has been revealed that the activation of these additional deformation mechanisms can significantly improve the poor ductility associated with the slip-dominated deformation mechanism [15, 17-23]. Therefore, tailoring the $\beta$ phase stability
or equivalently the deformation mechanisms has become an important approach of designing metastable β titanium alloys. This necessitates a deeper understanding of the deformation mechanisms associated with the β phase instability in metastable β titanium alloys.

A well-known example of the alloys designed by tailoring the β phase stability is gum metal, which was proposed by Saito et al. [24] in 2003. Gum metal represents a group of multifunctional β titanium alloys containing group IVa and Va elements and oxygen and with the composition close to the phase boundary between β and β+α” [24, 25]. In their pioneering paper [24], Saito et al. reported that gum metal assumes “super” properties, including ultralow elastic modulus, ultrahigh strength, superelasticity and superplasticity, and they attributed all of the “super” properties to a dislocation-free plastic deformation mechanism (termed giant fault) which results from the extreme instability of bcc β lattice. Their work triggered a marked increase in the study of deformation mechanisms of metastable β titanium alloys in the past decade [26-46].

Most of the follow-up studies focused on the typical composition of gum metal, Ti–23Nb–0.7Ta–2Zr–1.2O (at.%) / Ti–36Nb–2Ta–3Zr–0.3O (wt.%). In contrast to the original reports [24], conventional deformation mechanisms, including {112}<111> twinning, dislocation slip and stress-induced phase transformations (β → α” and β → ω), have been claimed to be present in this alloy [32, 34, 40, 41]. The scatter in the literature may be due to the critical position of gum metal composition in the phase diagram (close to the β/β+α” boundary), i.e., small differences in chemical composition (e.g., arising from different processing conditions) will cause the alloy to be in a different stability regime, leading to different deformation mechanisms. It is also revealed that decrease in the amount of β-stabilizing elements (e.g., 0.6 at.% Nb or 0.3 wt.% O) can enhance the instability of β phase and thus result in the activation of {332}<113> twinning [35,
39, 40, 43]. Thus, gum metal exemplifies an interesting alloy system in which a small change in the constituent concentration will result in quite different phase constitutions and deformation mechanisms. This paves a promising way for developing new metastable β titanium alloys of improved mechanical performance, which make use of the combination of different deformation mechanisms as well as secondary phases (ω and α”).

By using the Ti–Nb–Ta–Zr–O alloys (with compositions the same as or close to gum metal) as a model system, this dissertation aims at clarifying the interplay between the initial presence or mechanically-induced formation of secondary phases (ω and α”) and the deformation mechanisms, including \{111\} dislocation slip, \{112\}<111> twinning and \{332\}<113> twinning.

1.2 Organization of dissertation

This dissertation contains six chapters. Chapter 2 presents the experimental and theoretical tools employed in the studies. The electron microscopes for microstructure characterizations and the apparatuses for tensile tests are described first. The theoretical tools, including phenomenological theory of martensitic transformation and ab initio exact muffin-tin orbitals method, are introduced later.

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 3 identifies a dislocation channeling mechanism in ω-enriched 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 “M.J. Lai, C.C. Tasan, D. Raabe. Deformation mechanism of ω-enriched Ti–Nb-based gum metal:
Dislocation channeling and deformation induced \( \omega-\beta \) transformation. Acta Materialia 100 (2015) 290–300". (Courtesy of Elsevier Ltd)

Chapter 4 illustrates the relationship between stress-induced \( \omega \) phase and \{112\}<111> atomic shear associated with \{112\}<111> twinning and \( \beta \rightarrow \alpha'' \) martensitic transformation. This chapter is a modified version of the present author’s published paper “M.J. Lai, C.C. Tasan, J. Zhang, B. Grabowski, L.F. Huang, D. Raabe. Origin of shear induced \( \beta \) to \( \omega \) transition in Ti–Nb-based alloys. Acta Materialia 92 (2015) 55–63”. (Courtesy of Elsevier Ltd)

Chapter 5 sets off with the oxygen-free gum metal composition and delves deeply into the origin of \{332\} twinning by characterizing the surface-to-bulk microstructures of \{332\} twins and investigating their initiation and propagation during tensile deformation and their evolution during high-temperature annealing. An intimate relationship between \{332\} twinning and stress-induced \( \beta \rightarrow \alpha'' \) transformation is revealed. This chapter is a modified version of the present author’s published paper “M.J. Lai, C.C. Tasan, D. Raabe. On the mechanism of \{332\} twinning in metastable \( \beta \) titanium alloys. Acta Materialia 111 (2016) 173–186”. (Courtesy of Elsevier Ltd)

Chapter 6 summarizes the entire results and gives some suggestions for future work on the deformation mechanisms of metastable \( \beta \) titanium alloys.
Chapter 2  Experimental and theoretical tools

In order to investigate the deformation mechanisms of metastable β titanium alloys, tensile tests and cold rolling were performed to induce the deformation microstructures and a series of characterization tools including scanning electron microscopy, transmission electron microscopy and synchrotron X-ray diffraction were used to examine the deformation microstructures. For gaining deeper insight into the stress-induced phase transformations (β → ω and β → α") occurred during deformation, some theoretical tools including the phenomenological theory of martensitic transformation and the ab initio exact muffin-tin orbitals method were used when analyzing the experimental results. This chapter presents descriptions to these tools.

2.1 Scanning electron microscopy

Analogous to optical microscopy (OM), scanning electron microscopy (SEM) is an approach for imaging of surfaces. The SEM uses a focused beam of high-energy electrons to scan the surface of solid samples and collects the generated signals, including Auger electrons, secondary electrons (SE), backscattered electrons (BSE), characteristic X-rays, etc., by using a variety of detectors. These signals can provide detailed information on the chemistry and topography near the surface. Since the 1970s, another SEM-based technique that provides the crystallographic information of crystalline samples, i.e., the electron backscatter diffraction (EBSD), has been developed rapidly [47]. This technique can be used for revealing phase constitution, grain morphology, local crystallography, texture, etc. More recently, SEM is also used for the direct observation of crystal lattice defects, such as dislocations, stacking faults and nano-twins, with the development of the electron channeling contrast imaging (ECCI) technique [48].
In the studies of this dissertation, SE and BSE imaging as well as EBSD mapping were employed. All SEM experiments were carried out using a Zeiss-Crossbeam XB 1540 FIB-SEM instrument (Carl Zeiss SMT AG, Germany). This instrument has a high resolution GEMINI® field emission column and is equipped with an EDAX/TSL system (Draper, UT, USA) for acquiring EBSD data. TSL OIM softwares (versions 6.5–7.0) were employed for analyzing the EBSD data. Prior to SEM experiments, all samples were subjected to mechanical grinding and polishing on the surface to be scanned. Silicon carbide grinding papers with 220–4000 grits were used for grinding. After grinding the samples were mechanically polished using a colloidal silica suspension neutralized to pH ~ 7 by hydrogen peroxide.

2.2 Transmission electron microscopy

Transmission electron microscopy (TEM) uses the electrons that pass through an ultra-thin specimen for imaging. The TEM instrument used in the studies of this dissertation is JEOL JEM-2200FS. The JEOL JEM-2200FS is equipped with a 200 kV field emission gun, a high-precision digital CCD camera and an omega-type energy filter. Conventional scanning transmission electron microscope (STEM) image detectors including bright-field detector and high-angle annular dark-field (HAADF) detector are installed as well. The double-tilt specimen holder is capable of going up to ±30° for Y tilt and up to ±35° for X tilt.

Five imaging modes were employed in the current studies, including bright-field (BF), dark-field (DF), selected area diffraction (SAD), high resolution TEM (HRTEM) and STEM bright-filed [49]. The energy filter was used to enhance the contrast when taking BF, DF, SAD and HRTEM images [50]. The width of the energy-selecting slit was 5 eV for HRTEM imaging, 10–20 eV for BF imaging and DF imaging and 20–25 eV for SAD imaging.
Two types of TEM specimens were used, i.e., conventional 3 mm diameter discs and focused ion beam (FIB) lift-out TEM lamellae. The disc specimens were punched off thin foils with ~150 μm thickness. They were further mechanically ground to attain a thickness of 70–100 μm using 4000 grit silicon carbide grinding papers. Such discs were then subjected to twin-jet electropolishing until perforation in a Struers TenuPol-5 equipment.

FIB lift-out TEM lamellae were prepared using a FEI Helios Nanolab 600 FIB workstation. The FEI Helios Nanolab 600 has a high-resolution SEM column and a fine-probe Gallium ion source, allowing for simultaneous SEM imaging and FIB milling. It is also equipped with an OmniProbe AutoProbe 200.2 nano-manipulator, enabling the preparation of site-specific TEM samples. The following steps were made to prepare a FIB lift-out TEM lamella:

1) A Pt layer of 10–15 μm length, 1–1.5 μm width and 3–5 μm thickness was deposited on top of the lamella to be milled.

2) Two regular cross section trenches were made on either side of the Pt layer to attain the lamella (Fig. 2.1a).

3) The lamella was lifted out using the OmniProbe AutoProbe 200.2 nano-manipulator (Fig. 2.1b).

4) The lamella was welded to an OmniProbe TEM lift-out copper grid (Fig. 2.1c) and further milled to electron transparent.

Fig. 2.1. Procedure of preparing a FIB lift-out TEM lamella.
2.3 Synchrotron X-ray diffraction

Synchrotron X-ray diffraction (SXRD) was employed to identify the presence of ω phase and to measure the lattice parameters of β and α” phases in the current studies. All SXRD experiments were carried out on beam-line P02.1 at PETRA III (DESY Hamburg, Germany). This beam-line operates at a fixed energy of 60 keV and the generated X-rays have a wavelength of 0.20727 Å. The samples under study were ~1 mm thick and were transmitted by a 500 × 500 μm² sized X-ray beam. The diffraction patterns were collected on a fast area detector PerkinElmer XRD1621 (2048 × 2048 pixels, 200 μm² and 16 bit resolution) which was placed at a distance of 800 mm behind the sample under measurement. The center of the diffraction patterns and the sample–detector distance were calibrated using the software Fit2D [51] and a silicon calibration sample. Fit2D was also used to output the intensity/2θ spectra from the two-dimensional diffraction patterns. Rietveld refinement was performed to attain the lattice parameters by using the software MAUD [52].

2.4 Tensile test device

Two types of tensile stages were employed for tensile tests: (i) Kammrath and Weiss tensile stage and (ii) in situ SEM tensile stage. Fig. 2.2a and b show the dimensions of the tensile samples for these two stages, respectively. The tensile samples were cut by using electrical discharge machining (EDM) and their thicknesses were 0.5–2.0 mm. Some of the samples were subjected to grinding and polishing before tensile test for microstructure observation.

The maximum load of the Kammrath and Weiss tensile stage is 5 kN. This stage is integrated with two cameras and the Aramis software (version 6.3.0-6 © 2011, GOM mbH, Germay) for
digital image correlation (DIC) analysis [53]. Prior to tensile test, a continuous white layer was painted on the sample and then graphite particles were sprayed onto the white layer. During tensile testing, the movements of graphite particles were recorded by the two cameras, which were then correlated to the local strain field by the Aramis software. The maximum load of the in situ SEM tensile stage is 300 N. This stage was mounted in the Zeiss-Crossbeam XB 1540 FIB-SEM instrument, allowing for simultaneous tensile testing and SEM observation.

![Fig. 2.2. Dimensions (in mm) of the tensile samples for (a) Kammrath and Weiss tensile stage and (b) in situ SEM tensile stage.](image)

**2.5 Phenomenological theory of martensitic transformation**

When the bcc $\beta$ phase (austenite) transforms into the orthorhombic $\alpha''$ martensite, the difference in their crystal structures generates large amounts of local strain. Normally, this strain is accommodated by producing a twinned martensite structure on a lattice invariant plane (habit plane) of the $\beta$ phase, as schematically illustrated in Fig. 2.3. Thus, the macroscopic shape change associated with the $\beta \rightarrow \alpha''$ martensitic transformation is equivalent to a simple shear on the habit plane plus a contraction perpendicular to the habit plane. The phenomenological theory
of martensitic transformation (PTMT) as outlined by Lieberman et al. [54] or Bowles and Mackenzie [55-58] provides a practical tool for predicting the relative amounts of the two twin-related variants, \( x \) and \( 1 - x \), the habit plane normal \( n \), the shear direction \( s \), the angle of shear \( \theta \), the orientation relationships between \( \beta \) and \( \alpha'' \), etc. The inputs to this theory are the lattice parameters of \( \beta \) phase \((a_\beta)\) and \( \alpha'' \) martensite \((a_o, b_o, c_o)\) as well as the twinning relationship between martensite variants.

Fig. 2.3. Schematic illustration of a twinned martensite structure formed within austenite.

The orthorhombic \( \alpha'' \) martensite has six crystallographic variants (designated as \( V1, V2, V3, V4, V5 \) and \( V6 \)), which may be twin-related to each other via \( \{111\}_B \) type I twinning, \( <211>_0 \) type II twinning or \( \{011\}_B \) compound twinning when forming in the \( \beta \)-matrix, as illustrated in Fig. 2.4.\(^1\) The twinning relationship between the \( \alpha'' \) martensite variants is dependent on the specific alloy composition [8]. Here, the \( V1–V2 \) pair is taken as an example to delineate the PTMT by Lieberman et al., which has been demonstrated to be equivalent to the theory by Bowles and Mackenzie [59].

\(^1\) The subscript “O” following the indices represents the orthorhombic \( \alpha'' \) martensite.
The twinning relationship between V1 and V2 is $(01\bar{1})_{V1}$ compound twinning. The Bain strain associated with the $\beta \rightarrow \alpha''$ transformation is

$$B = \begin{bmatrix}
a_0 & 0 & 0 \\
a_\beta & 0 & 0 \\
0 & \frac{b_0}{\sqrt{2}a_\beta} & 0 \\
0 & 0 & \frac{c_0}{\sqrt{2}a_\beta}
\end{bmatrix}. \quad (2.1)$$

The lattice deformation matrices of V1 and V2 with respect to the coordinate system of $\beta$ phase are represented by

$$T_1 = R_1 B R_1^T \quad (2.2)$$

and

$$T_2 = R_2 B R_2^T, \quad (2.3)$$

respectively. $R_1$ and $R_2$ are two rotation matrices determined by the crystallographic correspondences between the $\beta$-matrix and the martensite variants (V1 and V2), which are given by

$$R_1 = \begin{bmatrix}
1 & 0 & 0 \\
0 & 1/\sqrt{2} & -1/\sqrt{2} \\
0 & 1/\sqrt{2} & 1/\sqrt{2}
\end{bmatrix}, \quad (2.4)$$

and

$$R_2 = \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/\sqrt{2} & 1/\sqrt{2} \\
0 & 1/\sqrt{2} & 1/\sqrt{2}
\end{bmatrix}. \quad (2.5)$$

The total deformation matrix $E$ (called shape strain) caused by the martensitic transformation is represented by

$$E = \Phi_1 F = \Phi_1 [(1 - x)T_1 + x\Phi T_2], \quad (2.6)$$

where $\Phi_1$ and $\Phi$ are two rotation matrices describing the rotation of V1 with respect to $\beta$-matrix and the rotation of V2 with respect to V1, respectively. $F$ is an asymmetric matrix, so it can be
expressed as the product of a symmetric matrix $F_s$ and a rotation matrix $\Psi$. The symmetric matrix $F_s$ can be diagonalized by a rotation matrix $\Gamma$, so that

$$F_s = \Gamma F_d \Gamma^T,$$  \hspace{1cm} (2.7)

where $F_d$ is a diagonal matrix,

$$F_d = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}.$$  \hspace{1cm} (2.8)

![Fig. 2.4. Lattice correspondence between bcc $\beta$ phase and six orthorhombic $\alpha''$ martensite variants.](image)

The sufficient and necessary condition that a lattice invariant plane exists is that one of the principal strains, $\lambda_i$, is unity. Under this condition, the following equation is attained

$$\det(FF^T - I) = 0,$$  \hspace{1cm} (2.9)
where $I$ is a $3 \times 3$ identity matrix. It has been proved that Eq. (2.9) can be solved only when one of the following conditions is satisfied [60]:

(i) One of the other two $\lambda_i$’s is larger than 1 and the rest is smaller than 1 (e.g., $\lambda_1 > 1$, $\lambda_2 < 1$ and $\lambda_3 = 1$).

(ii) Two of the three $\lambda_i$’s are unity.

By solving Eq. (2.9), the volume fraction of V2, $x$, can be obtained. This in turn allows $F, F_d, n, E, s, \theta$ and all of the rotation matrices mentioned above to be determined [54]. Regardless of the usually small volume change (contraction perpendicular to the habit plane) [60], the shape strain can be expressed as

$$E = I + msn^T,$$

(2.10)

where $m$ is the magnitude of shear. The transposes of the rotation matrices $\Theta$ and $\Omega$ that define the orientation relationships between the $\beta$-matrix and the martensite variants V1 and V2, respectively, can be calculated by normalizing each column of the matrices $\Phi_1 T_1$ and $\Phi_1 \Phi T_1$.

2.6 Ab initio exact muffin-tin orbitals method

In computational materials science, the ab initio methods refer to calculating the properties of solid materials by solving the Schrödinger equations. However, a direct solution of the Schrödinger equations for a huge number of electrons and nuclei contained in any solid material is impossible at present. The complexity of this problem is first simplified by the Born-Oppenheimer approximation, which assumes that the electrons are in their stationary states on the timescale of nuclear motion, i.e., the motion of nuclei and electrons can be solved separately [61]. Actually, the numerical solution of the remaining set of stationary Schrödinger equations for a lot of interacting electrons is still impossible. This problem is simplified by the density
functional theory [62, 63]. Most of the ab initio methods currently used are based on the density functional theory, so is the exact muffin-tin orbitals (EMTO) method [61].

Hohenberg and Kohn [62] proved that there exists a universal functional of the electron density \( n(r) \), \( F[n] \), such that the total energy of the electronic system \( E_e[n] \) has its minimum value in the ground state of the electronic system:

\[
E_e[n] = F[n] + \int v_{\text{ext}}(r)n(r)dr
\]  

(2.11)

The second term of the above expression is the interaction energy with the external potential \( v_{\text{ext}}(r) \) created by the fixed nuclei located on lattice sites \( \mathbf{R} \). The \( v_{\text{ext}}(r) \) is given by

\[
v_{\text{ext}}(r) = -\sum_{\mathbf{R}} \frac{2Z_{\mathbf{R}}}{|r - \mathbf{R}|}
\]  

(2.12)

where \( Z_{\mathbf{R}} \) is the nuclear charge. The universal functional \( F[n] \) is composed of three portions:

\[
F[n] = T_s[n] + E_{\text{H}}[n] + E_{\text{xc}}[n]
\]  

(2.13)

where the kinetic energy of non-interacting electrons \( T_s[n] \) and the Hartree energy \( E_{\text{H}}[n] \) are the major contributions and the remaining minor contribution \( E_{\text{xc}}[n] \) is the so called exchange-correlation functional [61]. Thus, the initial system of interacting electrons has been simplified into a system of non-interacting electrons, where the complexity of the initial problem is shrouded in the exchange-correlation term.

Kohn and Sham [63] proposed a self-consistent method to calculate the electron density \( n(r) \). Within the Kohn-Sham scheme, non-interacting electrons in an effective potential \( v_{\text{eff}}([n]; \mathbf{r}) \), instead of interacting electrons in the external potential \( v_{\text{ext}}(r) \), are considered. The \( v_{\text{eff}}([n]; \mathbf{r}) \) contains the effect of all the nuclei and electrons:

\[
v_{\text{eff}}([n]; \mathbf{r}) = v_{\text{ext}}(r) + v_{\text{H}}([n]; \mathbf{r}) + \mu_{\text{xc}}([n]; \mathbf{r})
\]  

(2.14)
where $v_H([n]; \mathbf{r})$ is the Hartree potential and $\mu_{xc}([n]; \mathbf{r})$ the exchange-correlation potential. The Schrödinger equation for a single electron in the effective potential takes the following form,

$$\{-\nabla^2 + v_{\text{eff}}([n]; \mathbf{r})\} \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}) \quad (2.15)$$

where $\psi_j(\mathbf{r})$ and $\varepsilon_j$ are the wave function and energy of the electron, respectively. Three important groups of methods have been developed for solving the one-electron Schrödinger equations (Kohn–Sham equations): all-electron full-potential methods, pseudopotential methods and muffin-tin methods [61]. The full-potential methods take into account the deep-lying core electrons and the valence electrons equally. Such methods are well-known for high accuracy and low efficiency. The pseudopotential methods keep the full-potential description in the interstitial region (valence electrons) but approximate the true Coulomb-like potential using a weak pseudopotential in the regions near the nuclei (core electrons). It has been demonstrated that the pseudopotential calculations can often sustain the high accuracy and enhance the efficiency of the full-potential methods [64]. Based on the observation that the exact crystal potentials are almost flat between the atoms and are atomic-like around the nuclei, the muffin-tin methods approximate the effective potentials by muffin-tin potentials $v_{\text{mt}}(\mathbf{r})$, i.e., a constant potential $v_0$ in the interstitial region plus spherically-symmetric potential wells $v_R(r_R) - v_0$ centered on the lattice sites $R$ [61]. The approximation is represented as

$$v_{\text{eff}}(\mathbf{r}) \approx v_{\text{mt}}(\mathbf{r}) = v_0 + \sum_R [v_R(r_R) - v_0] \quad (2.16)$$

where $r_R$ is the modulus of the vector $r_R = \mathbf{r} - \mathbf{R}$. In the original muffin-tin methods, the spherically-symmetric potentials are non-overlapping, leading to a rather poor description of the exact effective potential. In contrast, large overlapping potential spheres are employed and optimized for an exact solution of the Kohn–Sham equations in the EMTO method [61].
The electron density \( n(\mathbf{r}) \) can be calculated from the Kohn–Sham wave functions \( \Psi_j(\mathbf{r}) \) using the following expression,

\[
n(\mathbf{r}) = \sum_{\varepsilon_j \leq \varepsilon_F} |\Psi_j(\mathbf{r})|^2
\]

where \( \varepsilon_F \) is the Fermi level. By solving Eqs. (2.15)–(2.17) self-consistently, the equilibrium electron density, one-electron energies and effective potential in the ground state can be obtained. With these self-consistent results, the kinetic energy and Hartree energy can be calculated by

\[
T_s[n] = \sum_{\varepsilon_j \leq \varepsilon_F} \varepsilon_j - \int n(\mathbf{r}) v_{\text{eff}}([n]; \mathbf{r}) d\mathbf{r}
\]

and

\[
E_H[n] = \frac{1}{2} \int v_H([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r}
\]

respectively. In Eq. (2.19), the Hartree potential \( v_H([n]; \mathbf{r}) \) is expressed as

\[
v_H([n]; \mathbf{r}) = 2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
\]

By incorporating the nucleus–nucleus repulsion energy, the total energy of the system consisting of electrons and nuclei is obtained, i.e.,

\[
E_{\text{tot}} = E_e[n] + \sum_{RR'} \frac{Z_R Z_{R'}}{|\mathbf{R} - \mathbf{R}'|}
\]
Chapter 3  ω-modified dislocation plasticity:

Dislocation channeling

This chapter presents a comprehensive investigation on the deformation mechanism of Ti–Nb-based gum metal samples with confirmed presence of large amounts of nanometer-sized hexagonal ω particles. Deformation experiments demonstrate all the special deformation features observed in the original reports [24], such as plastic flow localization, pronounced surface steps, low work hardening, and large elongation. However, careful characterization reveals that the deformation bands (similar to the originally-reported giant faults) where plastic flow localized are "dislocation channels" that are depleted of ω phase. These channels are proposed to form by a \{1\text{1}\text{2}\}\text{<1\text{1}\text{1}>} dislocation dissociation mechanism, promoting reverse transformation of the ω phase into the β phase. The deformation induced ω → β transformation and the associated dislocation channeling process can explain the presence of the aforementioned special deformation features in the current gum metal. This chapter is a modified version of a paper that has been published in the journal Acta Materialia [65].

3.1 Literature review

Tailoring the chemical bonds has become an important methodology to the bottom-up design of multifunctional β titanium alloys [24, 66]. This is achieved by setting the stability of the bcc β phase at room temperature to a critical range, i.e., via shifting the compositional area in the phase diagram close to the phase boundary between β and β + α" [25, 67]. This essentially renders the elastic limit (ideal shear strength) of the bcc β crystal to be comparable to the applied stress [24,
leading to non-conventional elastic and plastic deformation mechanisms [24, 26-28, 30, 66, 69, 70] and exceptional mechanical properties [24, 66, 71].

The most well-known example of such β titanium alloys is the gum metal, an alloy system consisting of group IVa and Va elements and oxygen [24], which has attracted considerable attention in the past decade due to the proposal of a non-conventional plasticity mechanism therein [24, 26, 28, 30, 68]: It is claimed that these alloys sustain a metastable bcc β structure, with low resistance to shear along certain crystallographic planes, where dislocation activity is proposed to be inhibited by densely distributed Zr–O atom clusters and plasticity is accommodated by ideal bulk shear (referred to as giant faults) along the softened crystallographic planes instead. Three critical electronic parameters were proposed for tailoring the β phase stability [24, 25]: (i) a compositional average valence number (e/a) of about 4.24; (ii) a bond order (Bo value) of about 2.87; and (iii) a “d” electron-orbital energy level (Md value) of about 2.45 eV. In addition, the alloys require the oxygen concentration to be restricted to a range between 0.7 and 3.0 at.% [24]. Typical compositions that fulfill these conditions include Ti–12Ta–9Nb–3V–6Zr–1.5O, Ti–20Nb–3.5Ta–3.4Zr–1.2O and Ti–23Nb–0.7Ta–2Zr–1.2O (at.%) [24, 26, 30]. These alloys show interesting deformation features such as plastic flow localization, pronounced surface steps, and lack of work hardening, i.e., nearly horizontal engineering stress–strain curves, yet, surprisingly, high ductility (total elongation up to 19%) [24, 30]. Furthermore, the 90% cold-worked gum metal exhibits exceptional physical properties such as non-linear elasticity, Invar and Elinvar behaviors [24].

These observations created a long-pending discussion on the reported microstructural peculiarities in gum metal. For example, regarding conventional plasticity mechanisms (i.e., dislocation plasticity, mechanically-induced twinning) and stress-induced phase transformation
that were originally claimed to be absent in gum metal [24, 26-28, 30, 72], recent studies have demonstrated different observations for the Ti–23Nb–0.7Ta–2Zr–1.2O (at.%) alloy.

As to the former, dislocations [29, 31, 40, 41, 46, 73] and deformation twinning [32, 34, 46] have been reported to be active in gum metal. Castany et al. [41] observed dislocation slip during in situ tensile tests in a transmission electron microscope and suggested that conventional dislocation slip prevailed during plastic deformation. However, the governing deformation mechanism of gum metal is still under discussion, since some of the special deformation features such as the plastic flow localization and pronounced surface steps, observed in the original reports [24, 28, 30], cannot be consistently explained by the conventional dislocation or twinning mechanisms. For the latter, secondary phases, orthorhombic α" and hexagonal ω, were extensively observed [32, 34, 36, 37, 50, 74-77] and even regarded as the origins of the exceptional physical properties in the cold-worked gum metal, i.e., the non-linear elasticity, Invar and Elinvar behaviors [34, 76, 77]. Talling et al. [34, 78] estimated the ideal shear strength of gum metal to be >2 GPa with the aid of in situ SXRD and thus suggested that it is not easy for ideal bulk shear to occur preceding the stress-induced phase transformation.

While the remarkable effects of the secondary phases on the physical properties are confirmed in the above mentioned studies, little effort has been devoted to clarifying their influence on the deformation mechanism. The importance of this point is clearly seen upon a glance at other β titanium alloys, where the secondary ω phase plays an important role in the deformation behavior: Gysler et al. [79] revealed that the dislocation arrangement in Ti–Mo alloys changed from an inhomogeneous to a homogeneous distribution with increasing precipitation of ω particles. Banerjee and Naik [80] attributed the Portevin-Le Chatelier (PLC) effect that occurred in Ti–15Mo (wt.%) alloy at 575–775 K to the interaction between matrix dislocation and
dynamically-precipitated ω phase. In solution-treated gum metal, TEM detected very diffuse streaking at the 1/3 and 2/3 \{211\}_b positions of \{110\}_b-zone selected area diffraction pattern [34, 50], resulting in ambiguity on the existence of ω phase [81]. Nonetheless, Morris Jr. et al. [36] observed clear ω diffraction streaks via SXRD (with higher diffraction intensity than yielded in TEM) in solution-treated <110> and <100> single crystals of gum metal, corresponding to the existence of ω phase. The ω phase contained in gum metal may have strongly affected the deformation mechanism. This still remains one of the most critical issues to be elucidated.

In order to provide insights into the origin of the special deformation features and the effect of ω phase on the deformation mechanism in gum metal, three compositions, Ti–23Nb–0.7Ta–2Zr–(0.87, 1.52, 1.83)O (at.%), which comply with the composition restrictions proposed by Saito et al. [24] for gum metal, were prepared. Large amounts of nanometer-sized ω particles were introduced into these alloys by furnace cooling following the high-temperature homogenization. In what follows, detailed microstructure characterization (by SXRD, TEM and SEM) following uniaxial tension and cold rolling deformation experiments of these alloys are presented to provide a full understanding of their deformation behaviors.

### 3.2 Experimental procedure

Referring to the typical gum metal composition, Ti–23Nb–0.7Ta–2Zr–1.2O (at.%), three ingots with different oxygen concentrations were melted in an arc-melting furnace under argon atmosphere and cast into a copper mold. The as-cast alloys were then homogenized at 1200 °C for 4 hours, under vacuum, followed by furnace cooling. The slow cooling rate allows enough time for the formation of embryonic ω zones and the final ω phase [82]. The measured chemical

---

\(^2\) The diffraction streaking is a hint that the ω phase may exist, but unambiguous identification of its existence is unavailable, since it is not possible to image the ω phase with such weak diffraction signals.
compositions of the three alloys are listed in Table 3.1. Apparently, the obtained oxygen concentrations comply with the range (0.7–3.0 at.%) proposed by Saito et al. [24]. For simplicity, these alloys will be respectively referred to as 0.87O, 1.52O and 1.83O hereafter. In Table 3.1, the three electronic parameters (e/a, Bo and Md) of these alloys are included as well, which show significant similarity to that of the previously-reported gum metal [24, 34]. The as-homogenized microstructures consist of fully equiaxed grains with average size of 150–550 μm (Table 3.1). In order to avoid any biased identification of the prevalent deformation mechanisms, the material was not subjected to any hot- or cold-working before the following tailored deformation tests.

Table 3.1. Measured chemical composition (at.%), electronic parameter and grain size (μm) of the Ti–Nb–Ta–Zr–O alloys.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Nb</th>
<th>Ta</th>
<th>Zr</th>
<th>O</th>
<th>e/a</th>
<th>Bo</th>
<th>Md</th>
<th>Grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.87O</td>
<td>Bal.</td>
<td>23.1</td>
<td>0.62</td>
<td>1.99</td>
<td>0.87</td>
<td>4.24</td>
<td>2.87</td>
<td>2.45 eV</td>
<td>~550</td>
</tr>
<tr>
<td>1.52O</td>
<td>Bal.</td>
<td>22.7</td>
<td>0.62</td>
<td>1.96</td>
<td>1.52</td>
<td>4.23</td>
<td>2.87</td>
<td>2.45 eV</td>
<td>~150</td>
</tr>
<tr>
<td>1.83O</td>
<td>Bal.</td>
<td>22.5</td>
<td>0.55</td>
<td>1.88</td>
<td>1.83</td>
<td>4.23</td>
<td>2.87</td>
<td>2.45 eV</td>
<td>~150</td>
</tr>
</tbody>
</table>

Dog-bone-shaped tensile bars with a gauge section length of 4 mm and a cross section of 2 mm by 1 mm were cut using EDM. Prior to deformation, one 4 × 2 mm² surface of the samples was painted with graphite speckle pattern for local strain field measurements or polished for post-mortem surface relief observations. Tensile tests were performed on a Kammrath and Weiss tensile stage with an initial strain rate of 2.5 × 10⁻³ s⁻¹, while images of the speckled surface were acquired with two cameras at a speed of 1 frame/s. Local strain field measurements were made using the DIC technique implemented in Aramis software (GOM GmbH, Germany), where image correlation were carried out on the graphite speckle patterns [53]. In order to examine the deformation microstructures in detail, cold rolling to 5% and 60% total thickness reduction,
respectively, was conducted. A part of the cold-rolled sheets was cut along the plane which is parallel to the rolling direction (RD) and perpendicular to the normal direction (ND) and, then, ground and polished for microstructure characterization.

SEM and TEM imaging as well as EBSD mapping were employed to observe and analyze the deformation-induced surface relief and microstructures. The phase constitutions were determined by SXRD and TEM. A Zeiss-Crossbeam XB 1540 FIB-SEM instrument (Carl Zeiss SMT AG, Germany) equipped with an EDAX/TSL system (Draper, UT, USA) operated at 15 kV was used for the SEM observations and EBSD mapping. SXRD experiments were carried out on beamline P02.1 at PETRA III (DESY Hamburg, Germany) using 60 keV X-rays with a wavelength of 0.20727 Å. The Fit2D software [83] was utilized to calibrate the raw diffraction patterns by the aid of a silicon calibration sample and to output the intensity/2θ spectra. For TEM analyses, discs with a diameter of 3 mm were punched from the cold rolled material and mechanically ground to a thickness of 70–100 μm. The discs were further thinned by twin-jet electropolishing (Struers Tenupol 5) at −30 °C and 28 V until perforation using an electrolyte of 10% perchloric acid in ethanol. In addition, some TEM lamellae with a thickness of ~50 nm were cut at the locations of surface deformation traces from the pre-polished tensile samples by a dual-beam FIB workstation (FEI Helios Nanolab 600). TEM observations were conducted on a JEOL JEM-2200FS microscope operated at 200 kV.

3.3 Results

3.3.1 Initial microstructures

Fig. 3.1 shows low and high magnification characterization of the microstructure of the produced alloys. The EBSD analysis reveals only equiaxed β grains (Fig. 3.1a). Nevertheless,
upon using higher diffraction intensity and resolution such as provided by SXRD and TEM, both $\beta$ and $\omega$ phases were detected in the as-homogenized 0.87O, 1.52O and 1.83O alloys. Fig. 3.1b displays the SXRD pattern of 0.87O alloy, where a distinct diffraction spot corresponding to (0001)$\omega$ is observed within the (110)$\beta$ diffraction ring. Due to the large grain size (Table 3.1), most of the $\beta$ diffraction rings are discontinuous. The [110]$\beta$ SAD pattern of 0.87O alloy clearly shows the existence of $\omega$ phase as well (Fig. 3.1c). Apart from the primary {110}$\beta$, {112}$\beta$ and {002}$\beta$ reflections of the bcc $\beta$ matrix, distinct secondary intensity maxima and reciprocal lattice streaking are visible at the 1/3 and 2/3 {112}$\beta$ positions, which results from the diffraction of the $\omega$ lattice. The orientation relationship of the $\beta$ matrix and the $\omega$ phase is $\{111\} \beta // \{0001\} \omega$ and $<110>\beta // <11\overline{2}0> \omega$, as usually reported for thermally induced $\beta \rightarrow \omega$ transformation [84].

Fig. 3.1d shows a dark field image recorded from one of the secondary intensity maxima (indicated by a white circle in Fig. 3.1c). It is seen that nanometer-sized ellipsoidal $\omega$ particles are homogeneously distributed throughout the $\beta$ matrix. The average lengths of the major and minor axes of the $\omega$ particle are 2.8 nm and 1.9 nm, respectively. Clearly, such small sizes are beyond the spatial resolution of EBSD. Neglecting particles with a size below 1 nm, 1131 particles can be counted in Fig. 3.1d. Considering that the four crystallographic variants of the $\omega$ phase precipitated with equal population during the cooling process [84], a total of 4524 particles are determined in the viewing area of Fig. 3.1d. By assuming that the observed $\omega$ particles are on the same plane, the average surface density $n_s$ of the $\omega$ phase is estimated as $3.7 \times 10^{-2}$ nm$^{-2}$ and the mean inter-particle spacing $D$ is calculated to be 2.6 nm by the relation $D = 0.5/\sqrt{n_s}$ [85]. Due to the assumption, the estimated $n_s$ and $D$ here correspond to their upper bound and lower bound, respectively. The average volume density $n_v$ of the $\omega$ phase can be deduced from the
Wigner-Seitz equation \( n_v = 3/4\pi D^3 \) [74], where an \( n_v \) value of \( 1.4 \times 10^{-2} \) nm\(^{-3} \) is obtained. This means that the volume fraction of the \( \omega \) phase is 7.2%.

Fig. 3.1. (a) EBSD phase map of the as-homogenized Ti–23Nb–0.7Ta–2Zr–1.52O alloy. The grain boundaries are indicated by blue (2°–15°) and black (>15°) lines. (b) SXRD pattern, (c) [110]β SAD pattern and (d) dark-field image of the as-homogenized Ti–23Nb–0.7Ta–2Zr–0.87O alloy. The dark-field image is taken from the diffraction spot indicated by a circle in (c). (e) Intensity \( 1/2 \theta \) spectra extracted from the SXRD patterns of the as-homogenized Ti–23Nb–0.7Ta–2Zr–(0.87, 1.52, 1.83)O alloys. The positions of the β and \( \omega \) peaks are labelled and indexed.

The \( \omega \) particles within the β matrix has been reported to form by collapse of the \( \{111\}\)β planes of the β lattice [84, 86]. The partial plane collapse, which usually occurs in the alloys rapidly cooled from the high temperature β phase field, produces the trigonal \( \omega \) lattice (space group: \( \text{P}\bar{3}m1 \)). For the complete collapse, the hexagonal \( \omega \) lattice (space group: \( \text{P}6/\text{mmm} \)) is
obtained. The relatively small size of the ω particles observed in the 0.87O alloy is a characteristic feature of the trigonal ω phase [86]. Nonetheless, it is not possible to unambiguously identify whether the present ω lattice is trigonal or hexagonal from the diffraction patterns in Fig. 3.1. In the next chapter, the energetic pathway of the β → ω transformation in Ti–Nb alloys will be presented, which shows that there is no energy minima (corresponding to trigonal ω) between the bcc β and hexagonal ω lattices except an energy barrier for the compositions with e/a close to 4.24. This means that the {111}β planes are prone to collapse completely when the energy barrier is overcome for these compositions. Thus, it is more probable that the ω phase formed in the current alloys is hexagonal, since there was enough time for the {111}β planes to collapse completely due to the slow cooling rate.

The intensity $^{1/2}/\theta$ spectra extracted from the SXRD patterns (Fig. 3.1e) illustrate that the phase constitution of the as-homogenized 1.52O and 1.83O alloys is identical to that of the 0.87O alloy. Peaks derived from the β and ω phases are evident for all three alloys in the spectra. The lattice parameter of the bcc β phase is determined to be 3.30 Å for all three oxygen concentrations, indicating a trivial dependence of bcc lattice parameter on constituent concentration. Similar situation has been found in binary Ti–Nb alloys, where Nb plays a minor role in affecting the bcc β lattice parameter [7].

### 3.3.2 Tensile behavior

Fig. 3.2 shows the representative tensile engineering stress–strain curve of the 1.52O alloy. A distinct yield drop from the sharply defined upper yield point (UYP) to the lower yield point (LYP) is observed. Similar yielding behavior is reported by Saito et al. in their pioneering paper for another composition of gum metal (see Fig. 1A of Ref. [24]), Ti–12Ta–9Nb–3V–6Zr–1.5O (at.%). The UYP (645 MPa), here, is also the ultimate tensile strength. Although the ultimate
tensile strength is reached relatively quickly, the alloy does not fail until much later, at an
engineering strain of 31%. A long plateau following the yield drop occurs in the engineering
stress–strain curve, resembling a Lüders plateau found in mild steel [87]. The left inset of Fig.
3.2 displays its normalized work hardening rate \( \Theta \) defined by

\[
\Theta = \frac{1}{\sigma_T} \left( \frac{\partial \sigma_T}{\partial \varepsilon_T} \right),
\]

where \( \sigma_T \) and \( \varepsilon_T \) are the true stress and true strain, respectively. The limited but positive \( \Theta \) is
responsible for the large elongation to fracture.

![Fig. 3.2. Representative tensile engineering stress–strain curve of the Ti–23Nb–0.7Ta–2Zr–1.52O alloy. The upper yield point (UYP) and lower yield point (LYP) are indicated by arrows, which clearly reveal a distinct yield drop. The left inset shows its work hardening rate, \( \Theta \) (normalized by true stress), against true strain. For comparison, the inset on the right hand side shows typical features of the tensile engineering stress–strain curves for all three oxygen concentrations.](image)

A long plateau with limited work hardening is also found in the tensile engineering stress–
strain curves of 0.87O and 1.83O alloys as shown in the right hand side inset of Fig. 3.2. The
elongation to fracture reaches 41% and 37%, respectively, for these two alloys. It should be noted that a yield drop occurs in the 1.52O and 1.83O alloys but is absent in the 0.87O alloy. Previous studies [40, 72] suggest that the absence of yield drop was observed in the gum metal with 1.2 at.% O as well, indicating an oxygen concentration dependence of this phenomenon. It is concluded that a yield drop occurs specifically in the gum metal compositions with higher oxygen concentration (1.5 at.% [24] and more).

3.3.3 Deformation-induced microstructure evolution

Fig. 3.3 reveals the typical deformation-induced surface traces which are characteristic of widely displaced deformation bands (DBs). Most of the DBs are straight, although some curved DBs were observed as well (e.g., Fig. 3.3b). The intersection of these DBs with the pre-polished surface yielded pronounced surface steps, which are analogous in morphology to the giant faults reported previously [24, 28, 30]. The density of the DBs increases with the global deformation strain (see Fig. 3.3a and b), implying their role as the governing plastic deformation mechanism. In the areas between the DBs, no apparent deformation traces were observed. However, at the intersections of two DBs, large shear displacements were produced, as indicated by arrows in Fig. 3.3a. These observations indicate that the majority of the accommodated plastic strain was localized in the DBs.

Most of the DBs were observed to originate from the grain boundaries and propagate into the grain interiors. Fig. 3.3c shows one of the DBs when encountering a grain boundary: the DBs propagate through the grain boundary and enter the adjacent grain interior. The EBSD inverse pole figure (IPF) and image quality (IQ) map, displayed in the inset of Fig. 3.3c, reveal that the transmission process produced a large offset (~1 μm) in the grain boundary. Similar offset
incidents have been observed resulting from the interaction of giant faults and grain boundaries as well [28].

**Fig. 3.3.** Deformation bands (DBs) with pronounced surface steps formed on free surfaces of the Ti–23Nb–0.7Ta–2Zr–1.52O alloy deformed under tension. (a) and (b) Representative distribution of DBs at different strain levels. The insets show the corresponding global strain values measured by digital image correlation and locations on the failed tensile samples. (c) Transmission of DBs through a grain boundary (GB). The inset shows an IPF+IQ (inverse pole figure + image quality) map of the region framed by a black dashed rectangle. The arrow in the map points to the shear induced offset in the grain boundary. (d) Blockage of a DB by a grain boundary. (e) Blockage of a DB with out-of-plane displacements along the grain boundary. The white dotted lines in (c)–(e) indicate the grain boundaries.

In addition to the cases of DBs transmitting through grain boundaries, the blockage of DBs by grain boundaries have been observed, including blockage of DBs and blockage of DBs with out-of-plane displacement along the grain boundary. Evidence of the two cases is revealed by SE and
BSE images as shown in Fig. 3.3d and e, respectively. The former case is characterized by a blocked DB inside one grain with no apparent transmission into the neighboring grain. The arrow in Fig. 3d points to surface reliefs in the adjacent grain close to the intersection site of the DB and the grain boundary, which may be due to the stress concentrations at the tip of the DB. Such surface reliefs are absent in Fig. 3.3e, but the blockage of DB in this case was accompanied by out-of-plane displacements along the grain boundary (arrow). It seems that the DB propagated along the grain boundary upon being first blocked by it.

In order to examine the internal microstructure of the DBs, TEM lamellae were cut using FIB at the locations of the surface steps. Fig. 3.4a displays a representative in-depth lamella, which was cut across a DB. The STEM bright field image of this lamella (Fig. 3.4b) reveals that the DB is planar in nature and its contrast is weak. There is no sharp boundary between the DB and the matrix, hence, excluding the possibility that the interface is bounded by a mechanical twin. In areas far away from the DB, few deformation features are found, consistent with the localized deformation character indicated by the SEM images provided in Fig. 3.3. The SAD pattern taken around the DB reveals reflections from the $\beta$ and the $\omega$ phase, where the two distinguishable $\omega$ variants ($\omega 1$ and $\omega 2$) are indicated by arrows. The diffraction spots from these two phases exhibit almost no difference with those of the as-homogenized samples (Fig. 3.1c). However, a striking difference is found in the dark field image (Fig. 3.4c) taken from the ($\bar{1}104)\omega 1$ diffraction spot (the same diffraction spot as that indicated by a circle in Fig. 3.1c): here the $\omega$ phase is significantly depleted within the DB. Two more features appear in the dark field image: (i) the initial density and spatial distribution of the $\omega$ phase (Fig. 3.1d) are sustained in areas far away from the DB; (ii) there is no $\omega$ particle pile-up near or along the edges of the DB. The same features are present for the dark field image taken from the ($\bar{1}100)\omega 2$ spot, as illustrated in the
inset of Fig. 3.4c. These observations suggest that the initiation and propagation of DBs consumed the encountered \(\omega\) particles and, thus, formed a channel depleted of \(\omega\) phase within the \(\beta+\omega\) microstructure (Fig. 3.4d). This means that each DB is actually a channel that is depleted of the \(\omega\) phase.

**Fig. 3.4.** (a) SEM image of an in-depth lamella cut from a deformation band (DB) of the Ti–23Nb–0.7Ta–2Zr–0.87O alloy deformed under tension. The lamella was then lifted out by a nano-manipulator and thinned to become electron-transparent. (b) STEM bright field image and [110]\(\beta\) SAD pattern of the lamella shown in (a). Weak contrast of the DB is revealed and the SAD pattern is taken around the DB. (c) Dark field image taken from (\(\bar{1}104\))\(\omega1\) diffraction spot. The inset framed by an orange rectangle is a portion (including the DB) of the dark field image taken from the (\(\bar{1}100\))\(\omega2\) diffraction spot. (d) Schematic representation of the formation of a DB within the initial \(\beta+\omega\) microstructure (Fig. 3.1d).
This process suggests that complete removal of the \( \omega \) phase should be expected when a sufficient amount of deformation is applied to the \( \beta+\omega \) microstructure and the entire material is penetrated by multiple such \( \omega \)-devoid channels.\(^3\) This is confirmed by the SXRD patterns of the 60% cold-rolled samples for all three oxygen concentrations, as illustrated in Fig. 3.5. Primary diffraction rings from the bcc \( \beta \) phase are apparent in all patterns, but no reflection from the \( \omega \) phase can be observed, indicating complete removal of the \( \omega \) phase during the deformation process. On the other hand, since no third phase has been detected by TEM in the vicinity of the channel (Fig. 3.4b), it can be concluded that the disappeared \( \omega \) phase within the channel has transformed into the \( \beta \) phase.

![SXRD patterns from the 60% cold-rolled alloys. Primary diffraction rings from the bcc \( \beta \) phase are labelled and indexed.](image)

**Fig. 3.5.** SXRD patterns from the 60% cold-rolled alloys. Primary diffraction rings from the bcc \( \beta \) phase are labelled and indexed.

Wider-area TEM observations were performed on the TEM foils prepared by conventional twin-jet electropolishing. Many DBs have been observed on the foils. A lower magnification

\(^3\) When considering such an experiment, much attention should be paid to second order effects as well, such as those due to the increase of temperature during deformation. If the temperature is above the \( \omega \) transition temperature, the \( \omega \) phase may precipitate again during the cooling process after deformation.
overview of the DBs is shown in Fig. 3.6, which displays the SEM backscattered electron image of a TEM foil extracted from the 5% cold-rolled 1.52O alloy. DBs with different widths (~10–120 nm) are clearly visible. The white arrows point to some of the DBs connecting two parallel DBs, which may have initiated at one DB and then propagated to the other one. The features indicated by surface traces (Fig. 3.3) such as localization of plastic deformation, curved DBs and intersecting DBs with associated shear displacements can be observed as well. The shear displacements at the intersections of individual DBs should result from the formation sequence of the DBs, i.e., those DBs formed at a later strain stage sheared the DBs formed at an earlier strain stage.

![Image of SEM backscattered electron image](image)

**Fig. 3.6.** SEM backscattered electron image of a TEM foil prepared from the 5% cold-rolled Ti–23Nb–0.7Ta–2Zr–1.52O alloy. The white arrows indicate some of the deformation bands (DBs) connecting two parallel DBs.

TEM analysis reveals that profuse dislocations are present in the DBs (ω-devoid channels), as shown in Fig. 3.7. This implies that the large plastic flow within the DBs as described above is
actually carried by dislocation slip. Similar phenomena have been observed in Ti–11Mo and Ti–14Mo (at.%) alloys, where densely distributed ω particles were introduced by aging at 350 °C or 400 °C [79]. In those alloys, the dislocation glide was localized in well-defined slip bands and the ω particles within the slip bands were removed. Apparently, the main difference compared to conventional dislocation plasticity is that this massive dislocation activity is here confined to the ω-devoid regions inside the channels. To be more specific, the aforementioned deformation band (DB) will be referred to as dislocation channel (DC) hereafter. Fig. 3.7a shows two representative dislocation channels (denoted by DC1 and DC2) intersecting each other. The dislocation density in the channel DC1 is too high to separate the individual dislocations and the dislocations are tangled significantly. Such dislocation configurations naturally impede further slip of dislocations within the channel, which may indicate that the channel DC1 is at a later stage of formation. By contrast the channel DC2 seems to be still developing (at an earlier stage of formation) as it contains only ~20 individual dislocations along a length of ~1.5 μm on the left hand side of DC1. Another important feature is that few dislocations are observed in the regions far away from the channels, which is in accord with the character of plastic flow localization indicated above.

Curved channels have been observed as well, as displayed in Fig. 3.7b. The white dashed line indicates the turning point of a curved channel, where it changes its propagation direction. This effect is assumed to be mediated by cross slip of the dislocations inside the channel. The red arrows point to some narrower channels which nucleated from wider channels or from intersecting sites of individual channels. Comparing the individual channel widths is not useful here, since the channel plane may be inclined to the viewing plane and only a portion of the channel plane projected to the viewing plane can be observed, as schematically illustrated in the
inset of Fig. 3.7b. It is also seen that limited individual dislocations between channels occur when multiple channels intersect in a rather small region.

Fig. 3.7. STEM bright field images of dislocation channels (aforementioned deformation bands) in the TEM foils of 5% cold-rolled Ti–23Nb–0.7Ta–2Zr–1.52O alloy. $g$ is diffraction vector. (a) Two dislocation channels (denoted by DC1 and DC2) containing different densities of dislocations. (b) A curved channel and some narrower channels (red arrows) nucleated from wider channels or from intersecting sites of individual channels. The inset schematically illustrates the possible relationship between the observed channel plane and the actual channel plane intersecting the foil. The blue arrow points to a thickness fringe.

The observation of the dislocation channels reveals that a considerable number of dislocations passed through the channels and produced steps on the surface (Fig. 3.8a). The slip plane can thus be determined by trace analysis of the surface steps [88]. As illustrated in Fig. 3.8b, nine traces from eight grains were randomly selected on the pre-polished tensile samples of 1.52O alloy and their normal planes, determined by means of EBSD, were plotted on a [001]$\beta$ standard stereographic projection. Each normal plane corresponds to a great circle, on which the pole of
its slip plane lies. It is found that all great circles contain a \{112\}\(\beta\) plane rather than a \{110\}\(\beta\) plane. Thus, the operative slip planes are determined to be \{112\}\(\beta\) planes.

![Diagram](image)

Fig. 3.8. (a) Schematic representation of the formation of a dislocation channel (DC, aforementioned deformation band) and a surface step. (b) Surface trace normal plotted on a [001]\(\beta\) standard stereographic projection. Each great circle (blue curve) represents the normal plane of a surface trace. Nine traces from eight grains of the pre-polished tensile samples of Ti–23Nb–0.7Ta–2Zr–1.52O alloy are displayed.

3.4 Discussion

The results reveal that the originally-reported special deformation features in gum metal, including plastic flow localization, pronounced surface steps, low work hardening, large elongation and even yield drop (occurred in Ti–12Ta–9Nb–3V–6Zr–1.5O, at.\%) \[24, 27, 28, 30\], have been observed in the present gum metal samples with confirmed existence of nanometer-sized \(\omega\) particles (~2.8 nm). Careful characterizations via TEM and SXRD illustrate that the
plastic deformation mechanism in the current gum metal is governed by dislocation channeling, where dislocation activity is exclusively confined in channels that are devoid of \( \omega \) particles.

Interestingly, similar dislocation channeling phenomenon have been reported in irradiated metals and alloys, where the corresponding nanometer-sized particles are irradiation-induced defect clusters, typically in the form of stacking-fault tetrahedra or self-interstitial atom clusters, and the dislocation channels are devoid of such defects [89-93]. In addition, the yield drop, plastic flow localization and pronounced surface steps have been observed in irradiated materials as well [90-94]. It seems that these features are intrinsically associated with the dislocation channeling process. Below the underlying mechanisms that are responsible for these features and for the limited work hardening in gum metal are discussed.

3.4.1 Yield drop

The yield drop observed at the onset of plastic deformation is usually due to the strain aging in mild steels [87], Cu-Zn alloys [95] and Al-Mg alloys [96]. The strain aging phenomenon arises from the diffusion of solute atoms (e.g., C, N, Zn and Mg) to temporarily arrested dislocations, which slightly increases the critical resolved shear stress (CRSS) for dislocation motion [97]. It is characterized by jerky dislocation motion and sudden strain softening, leading to an initial peak stress followed by a yield drop phenomenon or even to more extended and serrated instable stress–strain curve regimes as observed in the PLC effect [87, 96]. For irradiated metals and alloys, the yield drop has been attributed to the enrichment of nanometer-sized particles (irradiation-induced defect clusters) surrounding the grown-in dislocations [89, 90, 92].

In the as-homogenized gum metal studied here, both interstitial oxygen (fast-diffusion element in \( \beta \) titanium [98]) and nanometer-sized \( \omega \) particles are present. Normally, the thermal \( \omega \)
phase is found to precipitate homogeneously in β titanium alloys [84, 99]. Lasalmonie and Chaix [100] claimed that the precipitation behavior may be changed though by the addition of interstitial atoms, resulting in the heterogeneous precipitation of the ω phase on dislocations. This means that both the interstitial oxygen and the ω particles may act as potential dislocation decoration items, promoting a yield drop as described above. The latter possibility is, however, ruled out in the current case since (i) no decoration of omega particles at dislocations was found and (ii) the 0.87O alloy, containing a high density of omega particles (Fig. 3.1d), does not exhibit a yield drop (Fig. 3.2). Only at higher oxygen concentrations (above 1.2 at.%), a yield drop occurs. This situation is also present in another series of β titanium alloys, Ti–20Nb–4.5Ta–3Zr–(0.56, 1.31, 2.75)O (at.%), where a yield drop merely occurred in the alloy with 2.75 at.% O (without ω phase) [101]. This oxygen concentration dependence of the yield drop phenomenon, on the other hand, supports the strain aging effect, i.e., interstitial oxygen diffuses to the grown-in dislocations during the high-temperature homogenization process forming Cottrell-clouds around them. The observed yield drop is thus caused by releasing of the grown-in dislocations from their oxygen decoration.

3.4.2 Dislocation–ω phase interaction and plastic flow localization

Beyond the yield drop, the plastic deformation continues by motion of the generated dislocations in the β matrix containing a forest of nanometer-sized ω particles (~2.8 nm) (Fig. 3.1d). The deformation-induced microstructure evolution reveal three features: (i) the dislocation movements were confined to a few widely spaced channels; (ii) the ω particles within the dislocation channels have reversely transformed into the parent β phase (Fig. 3.4 and 3.5); (iii) the slip planes of the dislocation channels were indexed as {112}β (Fig. 3.8). This means that the ω particle is softer with respect to the slip systems on {112}β planes and the passage of
dislocations on these planes promotes the $\omega \rightarrow \beta$ transformation. Thus, it can be inferred that a special interaction mechanism between matrix dislocation and $\omega$ phase is present in the current gum metal. In the following this mechanism is addressed based on the orientation relationship between $\beta$ and $\omega$.

There are 48 potential slip systems in the bcc $\beta$ crystal, with 12 on the $\{110\}$-$\beta$ planes, 12 on the $\{112\}$-$\beta$ planes and 24 on the $\{123\}$-$\beta$ planes [102, 103]. The slip direction is $<111>$-$\beta$ on all slip planes. Figure 3.9 shows the orientation relationship between hexagonal $\omega$ and hexagonally illustrated bcc $\beta$ lattice, i.e., $(0001)_{\omega}//(111)_{\beta}$ and $[11\bar{2}0]_{\omega}//[\bar{1}10]_{\beta}$. It reveals that the prismatic slip plane $\{\bar{1}100\}_{\omega}$ of the $\omega$ phase is parallel to the $\{11\bar{2}\}$-$\beta$ slip plane of the $\beta$ matrix. Taking into account the relatively low misfit between the $\omega$ and the $\beta$ lattice and the coherent character of the $\omega/\beta$ interface [104], such a coherence of the slip planes in $\beta$ and $\omega$ facilitates the slip transfer of dislocations from the $\{11\bar{2}\}$-$\beta$ planes onto the $\{\bar{1}100\}$-$\omega$ planes. Nonetheless, the coherence of the slip planes is not given for slip on $\{110\}$-$\beta$ and $\{123\}$-$\beta$ glide planes, indicating higher CRSS for the dislocations on these planes to move through the $\omega$ particles.

Hsiung and Lassila [105, 106] proposed a dislocation dissociation model to account for the stress-induced $\beta \rightarrow \omega$ transformation: A perfect $1/2<111>\beta$ dislocation on the $\{11\bar{2}\}$-$\beta$ slip plane dissociates into two $1/12<111>\beta$ partials and one $1/3<111>\beta$ partial on three consecutive $\{11\bar{2}\}$-$\beta$ planes, whose motions leave behind the $\omega$ phase. In fact, this model can account for the $\omega \rightarrow \beta$ transformation as well when treating it the other way round, i.e., the passage of these partials through the $\omega$ phase on three consecutive $\{\bar{1}100\}$-$\omega$ planes (parallel to $\{11\bar{2}\}$-$\beta$ planes) leaves behind the $\beta$ phase. This process is schematically illustrated in Fig. 3.10, where the bcc $\beta$ matrix is displayed as the sequential stacking of $\{111\}$-$\beta$ planes, $A_0B_0C_0A_1B_1C_1A_2\ldots$, and the hexagonal $\omega$ phase within the $\beta$ matrix is displayed as the stacking of $\{0001\}$-$\omega$ planes with the sequence of
The motion of a 1/2<111>β dislocation \( \mathbf{b} \) on the \{1\overline{2}1\}β plane gets blocked by the ω phase and dissociates into three partials (Fig. 3.10a), \( \mathbf{b}_1 = 1/12<111>β \), \( \mathbf{b}_2 = 1/3<111>β \) and \( \mathbf{b}_3 = \mathbf{b}_1 \), on three consecutive \{1\overline{2}1\}β planes. The passage of these dislocation partials (Fig. 3.10b–d) renders the ω phase reversely transforming into the β phase. This process is energetically favorable as indicated in the next chapter. The β and ω crystal structures correspond to two local energy minima over the energy landscape with an energy barrier between them. Though the β phase is less stable than the ω phase for the specific slightly instable gum metal composition, it can remain metastable due to the energy barrier.

![Fig. 3.9. Orientation relationship between hexagonal ω and bcc β phase. For the β phase, a hexagonal lattice exacted from the bcc structure is presented and it is aligned to be consistent with the ω phase via the orientation relationship determined by TEM (Fig. 3.1), i.e., (0001)ω//(111)β and [11\overline{2}0]ω//[\overline{1}10]β. The hexagons below the hexagonal lattices consist of the prismatic planes projected to the viewing plane, which shows that the prismatic slip plane \{\overline{1}100\}ω of the ω phase is parallel to the \{1\overline{2}1\}β slip plane of the β phase.](image-url)
The \( \omega \rightarrow \beta \) transformation mechanism described above corresponds to a shearing mode for the dislocation moving though the coherent \( \omega \) phase. Gleiter and Hornbogen [107] studied the interaction forces between glissile dislocations and coherent particles and came up with a theoretical model to calculate the increase in CRSS when the dislocations shearing the ordered misfit-free particles. Gysler et al. [79] adjusted this theoretical model for the movement of single dislocations and proposed that the increase in CRSS for shearing the \( \omega \) particles is given by

\[
\Delta \tau_s = 1.02 \gamma^{3/2} G^{-1/2} b^{-2} r^{1/2} f^{1/2},
\]

where \( \gamma \) is the anti-phase boundary energy, \( G \) the shear modulus and \( b \) the Burgers vector of the \( \beta \) matrix. \( 2r \) and \( f \) are the length of the minor axis and the volume fraction of the ellipsoidal \( \omega \) particles, respectively. The \( G \) of gum metal has been claimed to be relatively low due to its low \( \beta \) phase stability (\( e/a \) close to 4.24) [24]. With the aid of in-situ SXRD, Talling et al. [78] have measured the single crystal elastic constants of gum metal, from which Poisson’s ratio \( \nu \) and \( G \) can be estimated to be 0.39 and 25 GPa, respectively, within the Voigt-Reuss-Hill averaging scheme [61]. Gysler et al. [79] plotted the yield stress \( \sigma_{0.1} \) \( \sim 2\Delta \tau_s \) versus \( r^{1/2} f^{1/2} \) for the Ti–11Mo (at.%) alloy (with \( e/a \) close to the gum metal) and estimated \( \gamma \) of the \( \omega \) particles to be 0.3 J/m\(^2\).

Assuming the same value for the current gum metal and with the parameters measured in the present study, the \( \Delta \tau_s \) of the 0.87O alloy is estimated as 110 MPa. This is a relatively small value compared to the measured yield stress (~480 MPa, Fig. 3.2), indicating that it is feasible for the dislocations on \{112\}\( \beta \) planes to shear the \( \omega \) particles.

It should also be noted that the dislocations may bypass the \( \omega \) particles. This process does not concern the coherence of slip planes between \( \beta \) and \( \omega \), i.e., all slip systems can be active. Nonetheless, the bypassing mechanism normally requires very high CRSS. Taking the 0.87O
alloy as an example, the estimated increase in CRSS, $\Delta \tau_b$, is around 700 MPa, according to the following equation proposed by Ashby [79, 108],

$$\Delta \tau_b = \frac{1}{1 - \nu} \frac{Gb}{2\pi D} \ln \frac{\sqrt{2/3}r}{b}. \quad (3.3)$$

This implies that $\omega$ phase is actually strong resistance against dislocation slip with respect to the bypassing mechanism. It is consistent with the observed channeling phenomenon, where the dislocation movements are confined to the $\omega$-devoid channels and there is little indication of dislocation motion in the areas between the channels.

Fig. 3.10. Schematic representation of the $\omega \rightarrow \beta$ phase transformation due to the dissociation and motion of a perfect dislocation, $b = 1/2<\overline{1}11>\beta$. The dislocation $b$ dissociates into three partials, $b_1 = 1/12<\overline{1}11>\beta$, $b_2 = 1/3<\overline{1}11>\beta$ and $b_3 = b_1$. The passage of these partials through the $\omega$ phase leaves behind the $\beta$ phase. Here, two layers of atoms from the $(10\overline{1})\beta$/$(\overline{2}110)\omega$ planes (the orange planes indicated in Fig. 3.9) are displayed.
The characters of dislocation–ω phase interaction suggest that mobile dislocations shear the ω particles along the \([1\bar{1}2]\beta/(\bar{1}100)\omega\) slip planes according to the mechanism described above, leaving behind channels that are almost completely devoid of ω particles. The resistance against further dislocation motion within these channels is thus significantly reduced, so the dislocation movements are localized in such channels. Therefore, it is the combination of strong dislocation obstacle and its removal along certain slip planes that results in the dislocation channeling phenomenon and the plastic flow localization.

3.4.3 Initiation and propagation of the dislocation channels

Edwards et al. [94] studied the initiation of dislocation channels in neutron-irradiated copper and a copper alloy and suggested that the channels initiate at grain and twin boundaries, large inclusions, intersection sites of individual channels and even at previously formed channels. These internal interfaces are commonly the locations of stress concentrations, where dislocation sources are prone to be activated. Similar phenomena are present in the gum metal investigated here: the grain boundaries, pre-existing channels and intersecting sites of individual channels have been observed to act as the initiation sites for the formation of new dislocation channels. The leading dislocations generated from these stress concentration sites pass through the initial \(\beta+\omega\) microstructure on \(\{112\}\beta\) planes and remove the encountered ω particles, leaving behind ω-devoid channels. Fig. 3.7 reveals that densely tangled dislocations developed inside the channels as deformation proceeded. In ion irradiated stainless steels, Kacher et al. [109] suggested that residual dislocation debris from previous dislocation–irradiation defect interactions contributes to the development of dislocation tangles at the matrix/channel border. It is not yet clear whether such a contribution is also present in the current gum metal.
Most of the initiated dislocation channels propagate through the grain interiors before encountering another channel or grain boundary. The pre-existing channels may terminate the impinging channels or get sheared by them. In the latter case, considerable displacements are produced, as shown in Fig. 3.3a. This demonstrates that the dislocation channel, even with high density of tangled dislocations (e.g., Fig. 3.7a), does not necessarily prevent slip transmission. It is, however, unclear how such slip transmission occurs. Further research is required to clarify this as well as the formation mechanism of dislocation tangles within the channels. This channel–channel interaction mechanism might – together with the dislocation tangles inside the channels – be responsible for providing a certain strain hardening effect which is contrasted by the dislocation softening mechanism acting inside the channels after the removal of \(\alpha\) phase.

The dislocation channel–grain boundary interactions, as illustrated in Fig. 3.3, exhibit three interaction categories: (i) slip transmission, where a dislocation channel in one grain continues into a connected dislocation channel in the neighboring grain; (ii) a blocked dislocation channel with a stress concentration ahead of its tip; (iii) slip along the grain boundary with an associated out-of-plane displacement. Similar behaviors have been found in irradiated stainless steels [110, 111]. It is claimed that the slip transfer within the dislocation channels across grain boundary is identical to conventional slip transfer, but the importance of the local resolved shear stress increases due to the homogeneously distributed particles (irradiation-induced defect clusters) [110].

With the concept of the giant fault, Gutkin et al. [30] attributed the remarkable ductility of gum metal to the work hardening produced by the intersection of giant faults and grain boundaries. Nonetheless, this contradicts the fact that the tensile stress–strain curve of the \(<100>\) gum metal single crystal also shows a plateau after yielding [36]. In the present study, it has been
demonstrated that the grain boundaries play a minor role in the overall work hardening. As revealed in Fig. 3.2, little variability of the work hardening rate has been found for the 0.87O alloy compared to the other two alloys with much smaller grain size (Table 3.1). Thus, the positive work hardening rate of the current gum metal should be primarily contributed by the dislocation tangles developed in the channels and the channel–channel interactions.

### 3.5 Conclusion

Three gum metal ingots, Ti–23Nb–0.7Ta–2Zr–(0.87, 1.52, 1.83)O (at.%), were produced by arc melting and drop casting. They were subjected to homogenization followed by furnace cooling to yield equiaxed \( \beta \) microstructures with dense nanometer-sized \( \omega \) particles. The mechanical behavior of the \( \omega \)-enriched gum metal was investigated by tensile testing. To explore the deformation mechanism, microstructural analyses were performed by SEM, EBSD, TEM and SXRD before and after tensile testing and cold rolling. Based on the observations, the following conclusions can be drawn:

- For all three oxygen concentrations, a long plateau occurs after yielding in the engineering stress–strain curve with elongation to fracture exceeding 30%. When the oxygen concentration is higher than 1.2 at.%, a distinct yield drop occurs, which is due to the unpinning of dislocations from oxygen decoration.

- The deformation microstructure is characteristic of widely spaced deformation bands, which are actually channels that are significantly depleted of \( \omega \) particles. These channels produce shear steps when intersecting the surface and large shear displacements when intersecting other channels, indicating a considerable amount of plastic flow concentrated within the channels.
• The plastic deformation within the channels devoid of ω particles is carried by dislocation motion on the \( \{112\} \beta \) slip planes. A model is proposed that the dissociation and motion of the perfect \(<111>\beta\) dislocations on \( \{112\} \beta \) slip planes can render the encountered ω phase transforming into the β phase. The passage of these dislocations, thus, leaves behind a channel almost completely consisted of β phase.

• 60% cold rolling can remove all the ω particles existed in the as-homogenized alloys by creating enough dislocation channels that cover the entire material.
Chapter 4  Shear induced $\beta \rightarrow \omega$ transition

In this chapter, a \{211\}<111> twinning induced $\beta \rightarrow \omega$ transition in metastable $\beta$ Ti–Nb-based alloys is demonstrated by transmission electron microscopy and analyzed employing ab initio calculations and the linear elastic inclusion theory. The theoretical results reveal a distinct energy barrier for the $\beta \rightarrow \omega$ transition, where the contribution from lattice rearrangement, rather than the elastic contribution associated with lattice parameter mismatch, plays the major role. It is shown that this energy barrier can be overcome by \{211\}<111> shear, explaining why \{211\}<111> twinning or, alternatively, the $\beta \rightarrow \alpha''$ transition promotes local formation of the $\omega$ phase. This chapter is a modified version of a paper that has been published in the journal *Acta Materialia* [104].

4.1 Literature review

Improved understanding of the metastable $\omega$ phase in $\beta$-type Ti alloys and Zr alloys is of high relevance since its discovery, due to its roles in affecting mechanical and physical properties and its special formation mechanism [84]. Banerjee et al. [99] documented the various $\omega$ phase morphologies and underlying formation mechanisms: The $\beta \rightarrow \omega$ transformation can occur (i) thermally, i.e., via rapid cooling from the single bcc $\beta$ phase field or by subsequent isothermal aging, producing ellipsoidal or cuboidal $\omega$ particles homogeneously distributed throughout the $\beta$ matrix; or (ii) mechanically, i.e., via extremely high strain-rate compressive loading (shock loading), producing non-uniformly distributed $\omega$ plates (hereafter referred to as plate-like $\omega$) [112, 113].
Interestingly, recent studies on Ti–Nb-based alloys [9, 32] report about a similar plate-like \( \omega \) phase during quasi-static compression (in the vicinity of the \{211\}<111> twin boundary, see Fig. 3 in Ref. [32]) and even during quenching (at the \( \alpha''/\beta \) interface, see Fig. 2 in Ref. [9]) as listed in Table 4.1. Considering that, both twinning and \( \alpha'' \) transformation involve a shear process [114], it can be assumed that the formation of the plate-like \( \omega \) phase is due to the local atomic shear rather than to the macroscopic compressive stress state. This assumption, however, is so far not fully confirmed in the literature. Moreover, for the compositions listed in Table 4.1 (valence electron number \( e/a = 4.22–4.24 \)), previous ab initio investigations [115, 116] show that the \( \omega \) phase is energetically more stable compared to the \( \beta \) phase, anticipating a spontaneous transition from \( \beta \) to \( \omega \), in contrast to the experimentally observed requirement for shear-assistance. Taking into account that the formation of an \( \omega \) inclusion is associated with a lattice mismatch [117] and that the phase transformation is a kinetic process, it can be assumed that the atomic shear primarily follows one of the two principles, namely, decreasing the elastic strain energy associated with lattice mismatch between \( \beta \) and \( \omega \), or overcoming a kinetic barrier associated with the energetic pathway. This is another aspect that is not fully clarified yet.

The present study thus aims at providing an improved understanding on these two points. First, for addressing the former aspect, both cold rolling and uniaxial tension experiments were performed on a Ti–Nb-based alloy with a valence electron number value \( e/a \) in the same range to examine whether the \{211\}<111> twin introduced by the two different loading modes induces similar plate-like \( \omega \) phases along the twin boundary. For the latter aspect, a treatise based on ab initio calculations and the theory of elastic inclusion was carried out to clarify the full energetic context of the atomic shear.
Table 4.1. Composition, valence electron number e/a, processing state of Ti–Nb-based alloys that show a plate-like ω phase. The corresponding microstructural location of the ω phase is also listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>e/a</th>
<th>Processing state</th>
<th>Location of ω phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–23Nb–0.7Ta–2Zr–1.2O (at.%) [32]</td>
<td>4.24</td>
<td>Compression</td>
<td>{211}&lt;111&gt; twin boundary</td>
</tr>
<tr>
<td>Ti–22Nb (at.%) [9]</td>
<td>4.22</td>
<td>Quenching</td>
<td>α''/β interface</td>
</tr>
<tr>
<td>Ti–24Nb (at.%) [9]</td>
<td>4.24</td>
<td>Quenching</td>
<td>α''/β interface</td>
</tr>
</tbody>
</table>

4.2 Experimental procedure

For the experiments, a laboratory-cast Ti–36Nb–1.4Ta–2.8Zr–0.3O (wt.%, e/a = 4.23) ingot was used. It was melted in an arc-melting furnace under argon atmosphere and cast into a copper mold. The as-cast material was then homogenized at 1200 °C for 4 hours, under vacuum, followed by furnace cooling. Individual samples were cut from the ingot using electron discharge machining. The initial microstructure was characterized by BSE imaging and EBSD mapping using a Zeiss-Crossbeam XB 1540 FIB-SEM instrument (Carl Zeiss SMT AG, Germany) at an accelerating voltage of 15 kV. A plate with a thickness of 5 mm was subjected to 3.5% rolling at room temperature. To examine the situation of tensile loading, uniaxial tension was conducted to a sheet of 10 mm × 1 mm cross section until fracture. Disks of 3mm diameter were cut (close to the fracture surface in the case of uniaxial tension) and then mechanically thinned to less than 100 μm followed by twin-jet electro-polishing until perforation. The electro-polishing was performed at 6 °C and 20 V in an electrolyte of 60 ml perchloric acid, 350 ml butoxyethanol and 590 ml methanol. TEM observations were carried out on a JEOL JEM-2200FS microscope operated at 200 kV.
4.3 Simulation procedure

4.3.1 Elastic contribution to free energy

Generally, the $\omega$ phase forms by a \{111\} collapse mechanism or, equivalently, by atomic shuffling on a \{211\} plane along a $<1\overline{1}1>$ direction [84, 99] as shown in Fig. 4.1a and b, respectively: 2/3 of the atoms in the \{111\} layers (layer “1” and layer “2”) collapse to a middle plane between them with the third layer left unaltered. Fig. 4.1a shows that both the $\beta$ phase (with lattice parameter $a_\beta$) and $\omega$ phase (with lattice parameter $a_\omega$ and $c_\omega$) can be depicted by a hexagonal lattice with three atoms per unit cell, giving the lattice parameter correspondence between $a_\omega$, $c_\omega$ and $\sqrt{2}a_\beta$, $\sqrt{3}a_\beta / 2$, respectively. The atomic positions are (0, 0, 0), (2/3, 1/3, 2/3 $\pm Z_\omega$) and (1/3, 2/3, 1/3 + $Z_\omega$) with the latter two atoms belonging to the same sub-lattice, where $Z_\omega = 0$ defines the bcc $\beta$ crystal, $0 < Z_\omega < 1/6$ defines the non-ideal $\omega$ crystal and $Z_\omega = 1/6$ defines the ideal $\omega$ crystal.

![Fig. 4.1. Relationship between bcc $\beta$ and hexagonal $\omega$ structures. (a) Hexagonally illustrated $\beta$ and $\omega$ crystal lattices. (b) (011)$_\beta$//(1210)$_\omega$ atomic plane showing a shuffle transformation process from $\beta$ to $\omega$.](image)
The $\beta \rightarrow \omega$ transformation strain tensor can be expressed as

$$
\varepsilon^0_{ij} = \frac{1}{3} \begin{bmatrix}
2\eta_1 + \eta_2 & \eta_1 - \eta_2 & \eta_1 - \eta_2 \\
\eta_1 - \eta_2 & 2\eta_1 + \eta_2 & \eta_2 - \eta_1 \\
\eta_1 - \eta_2 & \eta_2 - \eta_1 & 2\eta_1 + \eta_2
\end{bmatrix},
$$

(4.1)

where $\eta_1 = a_2 / (\sqrt{2}a_p) - 1$ and $\eta_2 = 2a_2 / (\sqrt{3}a_p) - 1$. The corresponding elastic strain energy in a stress-free state was calculated using the Khachaturyan theory for an elastic inclusion [118, 119]:

$$
\Delta F^{\text{els}} = \frac{1}{2} \int \int \int B(e) \left| \Theta(k) \right|^2 \frac{d^3k}{(2\pi)^3},
$$

(4.2)

where $\Theta(k)$ is the Fourier transform of the shape function of the inclusion, and

$$
B(e) = \lambda_{ijkl} \varepsilon_{ij}^0 e_{kl}^0 - \varepsilon_i \sigma_0^{ij} \Omega(e) \sigma_0^{ij} e_m
$$

(4.3)

is a function of the direction $e = k/k$. $\lambda$ is the elastic constant tensor, which correlates the transformation stress with strain according to Hooke’s law, $\sigma_0^{ij} = \lambda_{ijkl} e_{kl}^0$, and $\Omega$ a Green’s tensor defined by its inverse $\Omega^{-1}(e) = \lambda_{ijkl} e_{kl}$. In this work, the difference between the moduli of $\beta$ and $\omega$ of the same composition was neglected. This approximation is justified due to the composition invariance and the crystallographic match of the $\beta$ and $\omega$ lattices.

### 4.3.2 Chemical contribution to free energy

The chemical contribution to the total free energy at a Wigner-Seitz radius $r$ and temperature $T$ can be approximated as $F^{\text{chem}}(r, T) = E(r) + F^{\text{vib}}(r, T) + F^{\text{elec}}(r, T)$, where $E$ is the 0 K total energy, $F^{\text{vib}}$ the phonon vibrational free energy calculated by the Debye-Grüneisen model [120, 121] and $F^{\text{elec}}$ the thermal electronic contribution to the free energy [122]. The vibrational free energy at a Wigner-Seitz radius $r$ and temperature $T$ is expressed as

$$
F^{\text{vib}}(r, T) = E_D(r, T) - TS_D(r, T),
$$

(4.4)
where $E_D$ and $S_D$ are the phonon energy and entropy, respectively. Within the Debye theory [120, 121], they take the following forms,

$$E_D = 9k_B T \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_0/T} \frac{x^3}{e^x - 1} dx + \frac{9k_B \Theta_D}{8}$$

(4.5)

and

$$S_D = 3k_B \left[ \frac{4}{3} \int_0^{\Theta_0/T} \frac{x^3}{e^x - 1} dx - \ln \left( 1 - e^{-\Theta_0/T} \right) \right],$$

(4.6)

where $k_B$ is Boltzmann constant and $\Theta_D$ Debye temperature. According to the Debye approximation, $\Theta_D$ is a function of the Poisson’s ratio $\nu$, Wigner-Seitz radius $r$, bulk modulus $B$ and atomic mass $M$. It is expressed as

$$\Theta_D = \frac{h}{k_B} \left( \frac{4\pi}{3} \right)^{1/6} f(\nu) \left( \frac{rB}{M} \right)^{1/2},$$

(4.7)

where $h$ is Planck constant. The full expression of $f(\nu)$ can be found in Ref. [121].

The Debye theory considers only the harmonic vibrations of the lattice, while the anharmonic effects in the vibrating lattice, which accounts for the thermal expansion, are usually described by means of the Grüneisen constant [121],

$$\gamma = -\frac{\partial \ln \Theta_D}{\partial \ln V}.$$  

(4.8)

Assuming a constant $\gamma$ for a given temperature, the above expression gives the volume dependence of Debye temperature as [120]

$$\Theta_D / \Theta_{D,0} = \left( \frac{r_0}{r} \right)^{3\gamma},$$

(4.9)

with $\Theta_{D,0}$ and $r_0$ being the 0 K Debye temperature and Wigner-Seitz radius, respectively. For room temperature, $\gamma$ is calculated via the Dugdale-MacDonald expression, which is claimed to yield Grüneisen constants in good agreement with low-temperature experimental values [120].
The thermal electronic contribution to the free energy is obtained from \( F_{\text{elec}} = E_{\text{elec}} - TS_{\text{elec}} \).

The energy \( E_{\text{elec}} \) due to electron excitations takes the form

\[
E_{\text{elec}}(r, T) = \int n(\varepsilon, r) f(\varepsilon) d\varepsilon - \int_0^{\varepsilon_F} n(\varepsilon, r) d\varepsilon ,
\]

where \( n(\varepsilon, r) \) is the electronic density of states and \( f(\varepsilon) \) the Fermi-Dirac distribution. The electronic entropy \( S_{\text{elec}} \) can be expressed as

\[
S_{\text{elec}}(r, T) = -k_B \int n(\varepsilon, r) [f(\varepsilon) \ln f(\varepsilon) + [1 - f(\varepsilon)] \ln [1 - f(\varepsilon)]] d\varepsilon .
\]

The 0 K total energy was calculated using the ab initio exact muffin-tin orbitals method [61, 123, 124], where the chemical disorder was treated by coherent potential approximation [125, 126]. The one-electron equations were solved within the scalar-relativistic and soft-core approximations. The EMTO self-consistent calculations were performed for a muffin-tin basis set including \( s, p, d, f \) orbitals, and the Green function for the valence states were calculated for 60 complex energy points exponentially distributed on a semicircular contour with 2.8–3.6 Ry diameter enclosing the occupied states. The elastic constants of the bcc structure (\( \beta \) phase) were calculated using the volume-conserving orthorhombic and monoclinic distortion method [61] for six distortions \( \varepsilon = 0.00, 0.01, \ldots, 0.05 \). The \( k \)-point meshes were carefully tested such that 3549–19683 uniformly distributed \( k \)-points were used to sample the irreducible wedge of the Brillouin zones depending on the crystal structures and distortions. The Perdew-Burke-Ernzerhof functional in generalized gradient approximation is used to describe the electronic exchange and correlation [127].
4.4 Results and discussion

4.4.1 Twinning induced $\beta \rightarrow \omega$ transformation

The typical microstructure of the as-homogenized Ti–36Nb–1.4Ta–2.8Zr–0.3O (wt.%) alloy is shown in Fig. 4.2. The alloy presents an equiaxed microstructure consisting of $\beta$ grains with about 80 $\mu$m size. Neither BSE nor EBSD detected any twins in the pre-deformed alloy. The absence of twins is also confirmed by TEM observations reported in a previous work [46]. It should be noted that small amounts of granular $\omega$ phases formed during the final cooling were observed by TEM. The relatively small size (less than 10 nm) and limited volume fraction of the $\omega$ particles render them invisible to the spatial resolution of BSE and EBSD.

Fig. 4.2. Microstructure of the as-homogenized Ti–36Nb–1.4Ta–2.8Zr–0.3O alloy: (a) BSE image; (b) EBSD inverse pole figure map; (c) EBSD phase map of the bcc $\beta$ phase, where the grain boundaries (>15°) are also shown.

After 3.5% cold rolling, twin lamellae with nano-scale width were found in the alloy as displayed in Fig. 4.3. The bright-field image in Fig. 4.3a shows two twin lamellae (referred to as T1 and T2) oriented along the [111] direction. The width of T1 and T2 is 12 nm and 27 nm, respectively, while their length extends over several microns. The [0T1]-zone selected area
diffraction pattern (Fig. 4.3b) and dark-field image (Fig. 4.3c) of these two lamellae indicate that they are \((2\bar{T}\bar{T})[111]\) twins.

**Fig. 4.3.** TEM images of the 3.5% cold rolled sample. (a) Bright field image displaying two twin lamellae (referred to as T1 and T2). (b) \([0\bar{1}1]_\beta\) selected area diffraction pattern of the circled area in (a). \((2\bar{T}\bar{T})_\beta[111]_\beta\) twin and two variants of \(\omega\) are illustrated. (c) Dark field image taken using the twin reflection \((011)_{\beta,T}\). (d) HRTEM image of T1, where the inset shows its FFT image corresponding to the electron diffraction pattern.
In addition to the twin reflections, ω diffraction spots located at 1/3 and 2/3 \{211\} positions can also be seen in Fig. 4.3b. There are four variants of the ω phase with \([\bar{2}110]_{\omega 1}, [\bar{1}014]_{\omega 2}, [01\bar{4}]_{\omega 3}\) and \([\bar{1}2\bar{1}0]_{\omega 4}\) parallel to \([0\bar{1}1]\), where the diffraction spots of ω2 and ω3 are completely overlapping with those of the β phase. Thus, only ω1 and ω4 are distinguishable in the SAD pattern. Since the four ω variants formed with equal probability during the cooling process following homogenization [46, 84], the populations of them are equal and, hence, it is reasonable to observe both ω1 and ω4 spots in Fig. 4.3b. Interestingly, a difference in diffraction intensity between these two variants is observed as well, where ω1 shows higher intensity, indicating that more ω1 formed during the cold rolling.

HRTEM images reveal that there is a layer of ω phase along the boundary between (2\{2\})\{111\} twin and β matrix. As an example, Fig. 4.3d displays the HRTEM image of T1, where the inset is its Fourier filtered transformation (FFT) image corresponding to the electron diffraction pattern. The plate-like ω phase located along the twin boundary is indexed as ω1 variant, whose diffraction intensity is much higher than that of the other variant ω4 as seen in the FFT image. The orientation relationship between the β matrix and the plate-like ω phase is \((\bar{2}11)\/(01\bar{1}0).\) Apparently, the additional formation of the plate-like ω phase interprets the higher diffraction intensity of the ω1 variant.

In the case of uniaxial tension, identical phenomenon concerning \{211\}<111> twinning and plate-like ω phase is observed, as shown in Fig. 4.4. Fig. 4.4a is a TEM bright field image showing a (211)[\{111\} twin lamella in the alloy deformed by uniaxial tension. The diffraction pattern and its key diagram, Fig. 4.4b, illustrate that the twinned β reflections overlap the matrix and the ω reflections, rendering corresponding ω diffraction spots brighter. The HRTEM image

---

4 In this chapter, the four-digit and three-digit indices are with respect to the hexagonal ω and bcc β phases, respectively.
in Fig. 4.4 reveals $\omega$ phase regions aligned along the twin boundary in the same manner as found for the cold rolling and compression cases [32]. This demonstrates that the formation of plate-like $\omega$ phase accompanying $\{211\}<111>$ twinning is not exclusive to the macroscopic compressive stress state. It depends on twinning itself, rather than on the specific loading mode.

![Fig. 4.4](image)

**Fig. 4.4.** (a) TEM bright field image showing a twin lamella in the sample deformed by uniaxial tension; (b) $[01\bar{1}]_\beta$ selected area diffraction pattern with corresponding key diagram and (c) high resolution TEM image of the twinned area revealed in (a).

Since small amounts of $\omega$ particles were already present in the as-homogenized microstructure, it is important to clarify if the plate-like $\omega$ phase is formed by a preferential growth of the pre-existed $\omega$ particle or by nucleation of a new twinning-induced $\omega$ phase. During deformation the local stress state may affect the equally-probable growth of the four $\omega$ variants, promoting selective growth of a specific variant and inhibiting the growth of others. This assumption is nonetheless excluded by taking into account the low temperature and the limited dwell time of the deformation processes. In general, the growth of $\omega$ phase in $\beta$ titanium alloys occurs at 150–500 °C and the process is known to be sluggish [5, 82, 86, 128]. For example, the
particles with an average size <10 nm in Ti–9 at.% Mo alloy require 48 hours at 475 °C to grow to an average size of ~40 nm [86]. Here, the plate-like \( \omega \) phase extends to several microns accompanying the \{211\}<111> twin, but the dwell time of the deformation processes is less than one minute, which is apparently not enough for the nano-sized particles to grow to a plate with a length of several microns. On the other hand, the formation of plate-like \( \omega \) phase along the \{211\}<111> twin boundary in the similar composition without pre-existed \( \omega \) phase [32] already proves that the \( \omega \) plate is newly nucleated, i.e., induced by twinning.

The \( \omega \) particles already present prior to deformation may act as barriers for dislocation slip [79, 80], but they seem to play a minor role in the propagation of twin. This situation is also true for the \{332\}<113> twin occurred in metastable \( \beta \) titanium alloys [14, 129].

4.4.2 Elastic and chemical contribution to the relative phase stability between \( \beta \) and \( \omega \)

The governing potential of the \( \beta \rightarrow \omega \) transformation for a specific composition is the total free energy difference, which concerns the elastic contribution associated with lattice parameter mismatch and the chemical contribution from lattice rearrangement (Fig. 4.1a). Previous studies [115, 116] considering only the chemical contribution at 0 K predict a spontaneous transformation from \( \beta \) to \( \omega \). Nonetheless, as shown in the previous subsection, the plate-like \( \omega \) phase formed inside the bulk \( \beta \) matrix and linked to the bcc \( \beta \) lattice coherently, may introduce elastic strain energy to the system if there is a lattice parameter mismatch between these two phases. On the other hand, temperature effects may also contribute to the relative stability of \( \beta \) and \( \omega \).

To the author’s knowledge, few studies exist on the measurement of the lattice parameter of the \( \omega \) phase in Ti–Nb-based alloys due to the difficulty associated with its relatively small size and limited volume fraction. In this work, ab initio simulations were used to assess the room-
temperature lattice parameters of $\beta$ and $\omega$ phases of Ti–Nb alloys with temperature effects approximated by the Debye-Grüneisen model [120, 121]. Fig. 4.5a and b present the lattice parameters of the $\beta$ and $\omega$ phases of Ti–Nb alloys ($e/a = 4.14–4.30$), respectively. Available experimental data [130-132] are also displayed for comparison. A good agreement between theory and experiment is shown and the experimentally observed slightly increasing trend in $a_\beta$ is well reproduced. For a specific composition, the volume per atom of the $\omega$ phase turns out to be larger than that of the $\beta$ phase (not shown here), similar to the volume expansion phenomena in Ti–V alloys observed via neutron diffraction [117]. When $\beta$ transforms to $\omega$, there is an enlargement in $a_{<110>}$ ($\sqrt{2}a_\beta$) and a decrease in $a_{<111>}$ ($\sqrt{3}a_\beta/2$), and, therefore, a homogeneous isotropic strain in the \{111\} planes and a change in the spacing between adjacent \{111\} planes are induced. Thus, these lattice parameter differences cause a lattice mismatch between $\omega$ and the surrounding $\beta$, hence introducing an elastic misfit strain into the system.

Fig. 4.5. Lattice parameters of the $\beta$ and $\omega$ phases of Ti–Nb alloys at room temperature. (a) Theoretically predicated lattice parameters of the $\beta$ phase compared with available experimental data [130-132]. (b) Theoretically predicted lattice parameters of the $\omega$ phase compared with those of the $\beta$ phase.
Fig. 4.6a displays the elastic strain energy $\Delta F^{\text{els}}$ of the plate-like $\omega$ inclusion formed inside the $\beta$ matrix which was calculated based on the experimentally determined habit plane $\{211\}$ [32] and theoretical structural parameters, assuming an infinitesimal thickness of the $\omega$ plate. For comparison, the $\Delta F^{\text{els}}_{\text{exp}}$ calculated with the lattice parameters and elastic constants of the $\beta$ phase interpolated and extrapolated from the available experimental data [131, 133, 134] are also shown. Both sets of elastic strain energies increase with $e/a$, which can be interpreted by the enhancing mismatch between the lattice parameters of $\beta$ and $\omega$ phases (Fig. 4.5b), i.e., larger lattice parameter mismatch results in larger elastic strain energy. It should be noted that all elastic strain energy values are positive, implying that the lattice parameter mismatch between $\beta$ and $\omega$ inhibits the $\beta \rightarrow \omega$ transformation for all compositions.

In order to clarify whether the elastic contribution to the total free energy suppresses a spontaneous transformation from $\beta$ to $\omega$, the chemical contribution at room temperature is calculated as $\Delta F^{\text{chem}} = F^\omega - F^\beta$ with $F^\omega$ and $F^\beta$ being the chemical free energies of the $\omega$ and $\beta$ phases, respectively. Figure 4.6b shows $\Delta F^{\text{chem}}$ as a function of $e/a$ (Nb concentration), revealing that $\Delta F^{\text{chem}}$ increases monotonically with increasing Nb concentration, reproducing the experimentally determined $\beta$-stabilizing effect of Nb. Similar to Ref. [115, 116], the $\omega$ phase appears to be thermodynamically more stable than the $\beta$ phase in the composition range of $e/a = 4.22 \pm 4.25$ even when the temperature effect is taken into account.

Although the elastic contribution favors the $\beta$ phase, for $e/a = 4.22 \pm 4.25$ it is too small to compete with the energy difference determined by the chemical contribution $\Delta F^{\text{chem}}$. As seen in Fig. 4.6b, the combination of elastic and chemical contributions still shows an energy gap between $\beta$ and $\omega$ for $e/a = 4.22 \pm 4.25$, indicating the existence of a thermodynamic driving force.
for a spontaneous transition from \( \beta \) to \( \omega \). This result contradicts current experimental observations of a shear assisted transformation [9, 32, 135].

**Fig. 4.6.** Elastic and chemical contributions to the free energy difference between the \( \beta \) and \( \omega \) phases as a function of \( e/a \) in the Ti–Nb alloys. (a) Elastic strain energy \( \Delta F_{\text{els}} \) determined by *ab initio* simulations. For comparison, the \( \Delta F_{\text{exp}}^{\text{els}} \) determined based on the experimental structural parameters of \( \beta \) phase [131, 133, 134] is also included. (b) Chemical free energy \( \Delta F_{\text{chem}} \) associated with lattice rearrangement from \( \beta \) to \( \omega \). The combination of elastic and chemical contributions is also shown.
4.4.3 **Energy barrier of the $\beta \rightarrow \omega$ transformation**

As discussed above, when only comparing the free energies of $\beta$ and $\omega$, the $\beta \rightarrow \omega$ transition is expected to occur spontaneously even when the elastic contribution and temperature effects are taken into account. In fact, such a comparison ignores the energy change of the intermediate transition states ($0 < Z_{\omega} < 1/6$) transiently formed during the transformation process. If the transformation (from $Z_{\omega} = 0$ to $Z_{\omega} = 1/6$) is spontaneous, the energy of these intermediate transition states should decrease monotonously with the increase of $Z_{\omega}$. In order to probe the energy landscape along the transformation path, ab initio calculations were performed to determine the chemical free energies of seven intermediate transition states with $Z_{\omega} = 1/48, 2/48, \ldots, 7/48$ between the $\beta$ and $\omega$ structures. During the calculations, the lattice parameters of each crystal structure were optimized to minimize the total energy. Taking Ti–24Nb alloy ($e/a = 4.24$) as an example, the change of the chemical energies $\Delta F_{\text{chem}}$ with respect to the $\beta$ structure for each intermediate structure is shown in Fig. 4.7, where the inset illustrates the (011) and (1210) atomic planes characteristic of the movement of the inner two atoms (i.e., transformation path). When the inner atoms move from the positions they occupy in the $\beta$ phase to their new positions in the $\omega$ phase, $\Delta F_{\text{chem}}$ increases first up to a maximum near $Z_{\omega} = 3/48$, and then decreases monotonously until the transition is finished. This result reveals an energy barrier of $\sim 6.04$ meV/atom for the transformation pathway. Based on the theoretically determined structural parameters, the elastic strain energy $\Delta F_{\text{els}}$ of each intermediate transition state was calculated as well. The elastic contribution slightly enlarges the energy barrier to $\sim 6.30$ meV/atom, but contributes only 4% to the total barrier value.

Theoretical results also demonstrate that the energy barrier is composition dependent and drops with the decrease of $e/a$. When the $e/a$ is 4.14, the energy barrier falls to $\sim 1.87$ meV/atom.
(including the elastic contribution). The existence of the energy barrier suggests that the $\beta \rightarrow \omega$ transformation in the above experimentally investigated composition range ($e/a = 4.22-4.24$) is not spontaneous and, hence, requires the contribution of external stimuli.

![Fig. 4.7. Change of free energy during the $\beta \rightarrow \omega$ transition process in Ti–24Nb alloy at room temperature. $\Delta F^{\text{chem}}$ and $\Delta F^{\text{els}}$ are the ab initio determined chemical and elastic contributions, respectively. The inset illustrates the start and end structures of the transition process characteristic of two inner atoms moving from $Z_\omega = 0$ to $Z_\omega = 1/6$.]

To this end, thermal fluctuations at around room temperature are not sufficient, although a simple comparison of the energy barrier and the mean kinetic energy (~26 meV/atom for room temperature) seems suggestive of a thermally driven transition. Such a scenario is, however, ruled out by taking into account the fact that the transition process requires a highly correlated atomic movement of a sufficiently large nucleus to form the first instance of the $\omega$ phase. The corresponding probability of this correlated movement to occur (i.e., the product of the individual probabilities of the atoms to perform a movement into the specific direction) is negligibly small when considering the weakly correlated thermal fluctuations. Instead, it is
required to extend the search to external stimuli that naturally inherit the type of correlated movement needed for the phase transformation.

4.4.4 **Role of atomic shear in overcoming the energy barrier**

As displayed in Fig. 4.7, if there is a local stress moving a pair of adjacent \{211\} atomic planes along the \(<1\overline{1}1>\) direction by a displacement of \(Z_\omega = \pm 3/48\), the energy barrier will be overcome and then the transition can occur spontaneously. Thus, the atomic shear along the \{211\}<1\overline{1}1> direction can act as an assisting factor. Indeed, this explains why the \{211\}<1\overline{1}1> twinning or \(\beta \rightarrow \alpha''\) transformation induces a plate-like \(\omega\) phase in Ti–Nb-based alloys with an e/a range of 4.22–4.24, as schematically illustrated in Fig. 4.8. The bcc structure of the \(\beta\) phase can be generated by a stacking of \{211\} planes. Crystallographically, the \{211\}<1\overline{1}1> twinning can be referred to as a consecutive shearing of \{211\} planes along the \(<1\overline{1}1>\) directions [106], while the \(\beta \rightarrow \alpha''\) transformation involves (i) shearing of atoms in the \(<1\overline{1}1>\) directions on the \{211\} planes and (ii) shuffling of atoms in every other \{01\overline{1}\} atomic plane [114, 136]. Both processes impose a \{211\}<1\overline{1}1> shear stress on the surrounding \(\beta\) matrix, which assists in overcoming the energy barrier on the \(\beta \rightarrow \omega\) transition pathway and, therefore, induces the formation of a sequence of \(\omega\) phases aligned along the \{211\}<1\overline{1}1> twin boundary or \(\alpha''/\beta\) interface.

It should be noted that the energy barrier can be overcome by thermal activation as well if the alloy is subjected to higher temperatures. Normally, the \(\omega\) transformation start temperature in \(\beta\) titanium alloys is 150–500 °C [5, 82, 86, 128]. For the Ti–35.7Nb–2.01Ta–2.98Zr (wt.%) alloy, a similar composition as that investigated in this work, in-situ synchrotron X-ray diffraction analyses indicate that the \(\omega\) phase starts to form at around 200 °C [135]. This explains the
existence of dispersed $\omega$ phase precipitates in the $\beta$ matrix prior to deformation (Section 4.4.1), considering the long exposure to high temperatures during gradual furnace cooling.

![Diagram](image)

**Fig. 4.8.** Schematic representation of the formation of the plate-like $\omega$ phase induced by $\{211\}<1\bar{1}\bar{T}>$ twining and $\beta \rightarrow \alpha''$ phase transformation. The $\omega$ phases are located along the boundary between the $\beta$ matrix ($\beta_M$) and $\beta$ twin ($\beta_T$) or $\alpha''$.

### 4.5 Conclusion

The present study explains for the first time the critical role that the $\{211\}<111>$ atomic shear plays for the formation of the plate-like $\omega$ phase precipitates in Ti–Nb-based alloys and reveals the theoretical background and underlying mechanisms. The following conclusions can be drawn:

- The formation of plate-like $\omega$ phase along the $\{211\}<111>$ twin boundary in Ti–Nb-based alloys with $e/a = 4.22–4.24$ is independent of the macroscopic stress state. It is induced by the $\{211\}<111>$ twinning.
• At room temperature, the $\omega$ phase is thermodynamically more stable than the $\beta$ phase for the composition range of $e/a = 4.22\pm4.25$. The elastic strain energy introduced by the lattice parameter mismatch between $\beta$ and $\omega$ favors the $\beta$ phase, but it is too small to change the relative stability.

• There is an energy barrier on the energetic pathway of the $\beta \rightarrow \omega$ transition, preventing a spontaneous transformation, and the $\{211\}<111>$ shear associated with $\{211\}<111>$ twinning and $\alpha''$ transformation is critical in overcoming this barrier, interpreting why twin or $\alpha''$ induces plate-like $\omega$ phase along their boundary.
Chapter 5  Martensite-assisted \{332\} twinning

In this chapter, the mechanism of \{332\} twinning was studied in a metastable \(\beta\) Ti–36Nb–2Ta–3Zr (wt.%) alloy. Tensile tests were performed to induce the formation of \{332\} twins. By using EBSD, TEM and in situ SEM, the surface-to-bulk microstructures and the initiation and propagation of \{332\} twins were investigated. In addition to the previously reported high densities of straight dislocations within the twin, an \(\alpha''\) martensite band has been found to be present near the surface adjacent to the twin. During annealing at 900 °C, the \(\alpha''\) martensite band transforms into the adjacent twin rather than into the matrix, indicating that \{332\} twin nucleates within \(\alpha''\) martensite. Further evidence for this is the constitution of the twin in the initial stage of its formation, where the first portion formed consists of \(\alpha''\) martensite. During propagation, the twins propagating to the opposite directions can merge together when their lateral boundaries impinge on each other. Based on the experimental observations, an \(\alpha''\)-assisted twinning mechanism is proposed and the origin of the dislocations within the \{332\} twin is discussed accordingly. This chapter is a modified version of a paper that has been published in the journal \textit{Acta Materialia} [137].

5.1  Literature review

In addition to dislocation slip, deformation twinning is another fundamental plastic deformation mode in crystalline solids [138]. In materials with low crystal symmetry such as hexagonal close-packed (hcp) metals and some nanoscale metals, twinning even dominates the plastic deformation [138-140]. 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 [141-143]. This means that deformation twinning provides a substantial work hardening mechanism (twinning-induced plasticity (TWIP) effect) for these materials. Thus, the introduction of deformation twinning, e.g., by tailoring the stacking fault energy in fcc TWIP steels [144], has become an important approach for enhancing both strength and ductility.

Recently, the deformation mechanisms in bcc β titanium alloys have been studied in more detail, especially in so-called multifunctional β titanium alloys (e.g., gum metal), primarily due to their considerable potential for biomedical applications and their unusual gum-like deformation behavior [24, 66]. It was found that dislocation slip dominates the plastic deformation in stable β titanium alloys, while reduced bcc β phase stability results in the activation of additional deformation mechanisms including {112}<111> twinning, {332}<113> twinning and stress-induced α” martensitic transformation [33, 35, 39, 65, 104, 145]. Thus, like the stacking fault energy in fcc alloys, the β phase stability can serve as a criterion for the introduction of deformation twinning in bcc β titanium alloys. Hanada and Izumi [17] investigated the correlation of tensile properties, deformation mechanisms and phase stability in a series of β titanium alloys and found that the {332}<113> twinning associated with low β phase stability produced a high work hardening rate and thus significantly improved the poor ductility involved in slip-dominated β titanium alloys. Min et al. [18, 19] suggested that a combination of dislocation slip and {332}<113> twinning was effective for achieving high yield strength and large uniform elongation. These improvements in mechanical properties linked with TWIP effect, resembling those in TWIP steels [144], have attracted much attention recently in the design of metastable β titanium alloys with high strength and good ductility [21-23].
In bcc metals and alloys, \{112\}<111> is the most common twinning mode and is believed to form by the collective glide of partial dislocations (twinning dislocations) with the same Burgers vector 1/6<111> on successive \{112\} crystallographic planes [138, 140]. By contrast, \{332\}<113> twinning is much less common and had long been known as a unique twinning mode for metastable \(\beta\) titanium alloys since its first identification in a Ti–11.5Mo–6Zr–4.5Sn (wt.\%) alloy in 1971 [146]. Recently, this twinning mode has been observed in shock-loaded bcc \(\alpha\)-Fe and \(\alpha\)-Fe alloys [147, 148]. A common characteristic of materials where \{332\}<113> twinning occurs is that all of them are subjected to diffusionless phase transformations during water quenching or deformation, such as the \(\beta \rightarrow \omega\) (bcc \(\rightarrow\) hexagonal or trigonal) or \(\beta \rightarrow \alpha''\) (bcc \(\rightarrow\) orthorhombic) transitions in metastable Ti–Mo-based alloys [15, 17, 21-23, 129, 146, 149], Ti–Nb-based alloys [14, 15, 129], Ti–V-based alloys [15, 17, 129, 145, 150], Ti–Cr alloys [151] and Ti–Fe alloys [129] and the \(\alpha \rightarrow \varepsilon\) (bcc \(\rightarrow\) hcp) transition in shock-loaded \(\alpha\)-Fe and \(\alpha\)-Fe alloys [147, 148]. Both twinning and diffusionless phase transformations involve shear processes, but their interrelationship is not yet clear.

Earlier reports [15, 17, 129, 146, 149, 150] suggest that the internal microstructure of \{332\}<113> twins is characteristic of either a high density of dislocations or stress-induced \(\omega\) plates depending on \(\beta\) phase stability. In alloys with higher \(\beta\) phase stability, high densities of parallel straight dislocations have been observed traversing the \{332\}<113> twins [15, 17, 129, 146, 149, 150]. These straight dislocations in some circumstances seem to penetrate through the twin/matrix interface, extending into the \(\beta\)-matrix [17, 149, 150]. Furuhara et al. [150] speculated that the dislocations on the \(\beta\)-matrix side extending from \{332\}<113> twins might be expelled from the twin/matrix interface during the shrinkage of twins upon unloading. In alloys with lower \(\beta\) phase stability, it was reported that one particular \(\omega\) variant within the \{332\}<113> twins
was preferentially induced, producing a series of parallel $\omega$ plates of the same variant, which even evolved to occupy the whole twinned domain and caused the twinned region to become a single-variant $\omega$ plate with further decreasing $\beta$ phase stability [15, 129, 150]. These internal dislocations or $\omega$ plates should render twinned regions harder than the matrix and should, therefore, contribute to the high work hardening rate associated with $\{332\}<113>$ twinning [15, 17-19].

Crocker [152] proposed the first crystallographic model for the mechanism of $\{332\}<113>$ twinning. He illustrated that simple shears on successive twinning planes along the twinning direction such as that in $\{112\}<111>$ twinning could only move one half of the atoms from the untwinned lattice sites to their correct twinned lattice sites, so that additional shuffles were necessary for the other half of the atoms to reach their twinned positions. This shear mechanism involves large shuffles on planes with a small interplanar spacing [152], which may be energetically difficult. Therefore, several attempts have been made to overcome this problem, including the proposal of partial dislocation mechanisms [153-156] and a modification of Crocker’s shear mechanism [157]. Kawabata et al. [153] suggested that $\{332\}<113>$ twinning could be accomplished by successive slip of $1/22<113>$ partial dislocations on pairs of neighboring $\{332\}$ planes and subsequent shuffle of these paired planes towards each other along the $\pm<332>$ directions. A similar partial dislocation mechanism was also present in the work by Litvinov and Rusakov [154], where they proposed an additional partial dislocation mechanism characterized by the glide of $5/22<113>$ partial dislocations on a stack of $\{332\}$ planes without any additional atomic shuffle. Since neither the $\{332\}$ plane nor the $<113>$ direction is close-packed, the question whether such partial dislocation mechanisms are energetically favorable remains open. Recently, Tobe et al. [157] modified Crocker’s shear mechanism by considering
the instable bcc β lattice (characterized by the shuffling of adjacent \{0\overline{1}1\} planes to \langle011\rangle directions) as a modulated structure with base-centered tetragonal symmetry, producing a new shear mechanism with a smaller shuffling magnitude compared to Crocker’s mechanism. It should be noted that both the partial dislocation mechanisms and the shear mechanisms can generate an ideal \{332\}<113> twin lattice, but none of them has reasonably accounted for the characteristic internal microstructures (i.e., straight dislocations or \omega plates) of \{332\}<113> twins.

The present study has the aim of improving the understanding of the mechanism of \{332\} twinning. A metastable \beta Ti–36Nb–2Ta–3Zr (wt.%) alloy was produced by arc melting and drop casting. The formation of \{332\} twins was induced by tensile tests. The surface-to-bulk microstructures of these twins were characterized using SEM, EBSD, TEM and SXRD. Their evolution during high-temperature annealing was also examined. In addition, in situ SEM experiments were conducted to study their initiation and propagation.

5.2 Experimental procedure

The metastable β titanium alloy used in this study was produced by arc-melting mixed elemental materials with a target composition of Ti–36Nb–2Ta–3Zr (wt.%) under argon atmosphere and drop casting into a copper mold with an internal dimension of 10 × 60 mm². In order to promote chemical homogeneity, the as-cast ingot was homogenized at 1200 °C for 4 h, under vacuum, followed by furnace cooling. After that, it was sealed in a vacuum quartz tube, annealed at 1000 °C for 1 h and water quenched. The microstructure of the as-quenched alloy consists of large equiaxed grains with an average size of ~1000 µm and its measured chemical composition is Ti–35.7Nb–2.01Ta–2.98Zr–0.07O (wt.%). In order to maintain the large grain size for better observation of the evolution of deformation microstructures, the as-quenched alloy
was not subjected to any hot- or cold-working before the following tailored deformation experiments.

Flat dog-bone-shaped tensile samples with a gauge section length of 4 mm and a cross section of \(2 \times 1 \text{ mm}^2\) were cut using EDM. Prior to tensile deformation, one of their two \(4 \times 2 \text{ mm}^2\) surfaces was polished for microstructural characterization and the other one was painted with a graphite speckle pattern for digital image correlation analysis [53]. These samples were then deformed to an engineering strain of \(\sim 6.5\%\) on a Kammrath and Weiss (Dortmund, Germany) tensile stage with an initial strain rate of \(5 \times 10^{-4} \text{ s}^{-1}\). BSE imaging and EBSD mapping were performed to characterize the deformation microstructures on the pre-polished surface, after which the deformed samples were held at 900 °C for 30 min under vacuum followed by fast cooling. The cooling rate was estimated to be \(\sim 200 \text{ °C/s}\). These heat treatments were carried out using a Baehr Dil805 dilatometer. The heat-treated samples were subjected to EBSD mapping again on the same surface without any additional grinding or polishing.

For investigating the evolution of the deformation microstructure with accumulating strain, additional dog-bone-shaped tensile samples with gauge section dimension of \(4 \times 1 \times 0.5 \text{ mm}^2\) were cut using EDM. One \(4 \times 1 \text{ mm}^2\) surface of these samples was polished prior to deformation. They were then deformed on an in situ tensile stage mounted in a scanning electron microscope. The tensile tests were conducted at a constant cross head speed 2 \(\mu\text{m/s}\) (corresponding to an initial strain rate of \(5 \times 10^{-4} \text{ s}^{-1}\)) and were interrupted at various strain levels for microstructural observation on the pre-polished surface.

The experimental route for characterizing the deformation-induced microstructures is schematically shown in Fig. 5.1a. All SEM observations and EBSD mapping were performed in a Zeiss-Crossbeam XB 1540 FIB-SEM instrument (Carl Zeiss SMT AG, Germany) operated at
15 kV. The EBSD data were collected by an EDAX/TSL data acquisition system (Draper, UT, USA) and automatically indexed by the standard vote-rank algorithm [158]. SXRD experiments were carried out on beam-line P02.1 at PETRA III (DESY Hamburg, Germany) using 60 keV X-rays with a wavelength of 0.20727 Å. The Fit2D software [51] was used to calibrate the raw two-dimensional diffraction patterns and to output the intensity/2θ spectra. TEM lamellae were cut from the pre-polished surface by using a dual-beam FIB workstation (FEI Helios Nanolab 600). The intersection of deformation-induced microstructure features such as slip bands and twins with the pre-polished surface resulted in surface roughness, which enabled the identification and site-specific FIB cutting of specific microstructure features from locations of interest. An example is shown in Fig. 5.1b, where the in-depth TEM lamella contains a portion of the bulk of the deformation band. This lamella was then lifted out by a manipulator, welded to a copper grid and milled to become electron-transparent. Before FIB cutting, a Pt layer with a thickness of ~4 μm was deposited on the surface to protect the lamella. TEM observations were conducted in a JEOL JEM-2200FS microscope operated at 200 kV.

![Fig. 5.1.](image).

(a) Experimental route for characterization. (b) Example of an in-depth TEM lamella cut from a deformation band (DB).
5.3 Results

5.3.1 Surface-to-bulk characterization of \{332\} twins

Prior to deformation, the as-quenched Ti–36Nb–2Ta–3Zr alloy consisted of large \( \beta \) grains with an average grain size of \( \sim 1000 \mu \text{m} \), as shown by the EBSD inverse pole figure map in Fig. 5.2a. The colors on the IPF map represent the crystallographic orientation normal to the observed plane as indicated by the color bar on the right hand side of Fig. 5.2a. Neither twins nor secondary phases have been detected by EBSD. Nonetheless, weak and elongated diffraction spots from hexagonal \( \omega \) phase have been observed by using TEM, similar to the situation in other as-quenched metastable \( \beta \) titanium alloys [86, 129]. Representative deformation microstructures on the pre-polished surface of the tensile samples are shown in Fig. 5.2b, which are characteristic of nearly straight deformation bands with width ranging from \(<1 \mu \text{m}\) to tens of micrometers. Closer observation (Fig. 5.2c) reveals that the deformation band is composed of two parts along its length, which exhibit different contrasts in the BSE image.

Fig. 5.3 shows the EBSD analysis of the area highlighted in Fig. 5.2c. The entire deformation band has been indexed as bcc \( \beta \) phase by EBSD with an average confidence index value above 90%. The two portions of the deformation band along its length exhibit two slightly different colors on the IPF map (Fig. 5.3a), corresponding to different crystallographic orientations. This means that the deformation band shown in Fig. 5.2c is indeed composed of two bands which are closely adjacent to each other. Hereafter, the bands on the left and right hand sides will be referred to as band_1 and band_2, respectively, as indicated in Fig. 5.3b. Fig. 5.3d displays the point-to-point and point-to-origin misorientation profiles along the arrow in Fig. 5.3a. The two bands form two plateaus in the point-to-origin misorientation profile. The point-to-point misorientation angle across the matrix/band_1 boundary is \( 51.1^\circ \), corresponding to the
{332}<113> twinning system, while that across the band_1/band_2 boundary is $59.7^\circ$, corresponding to the {112}<111> twinning system [159]. An abrupt change occurs in the point-to-origin misorientation profile when crossing these two boundaries. Such an abrupt change is, however, absent for the band_2/matrix boundary. The point-to-origin misorientation angle across this boundary gradually decreases along the distance between 4.3 $\mu$m and 4.9 $\mu$m instead.

**Fig. 5.2.** Pre- and post-deformation microstructures on the polished surface of the tensile samples. (a) Inverse pole figure map of the pre-deformation microstructure. The color bar is shown as a stereographic triangle on the right hand side. (b) Backscattered electron image of the post-deformation microstructure. The yellow dashed line indicates a grain boundary (GB). (c) An image of the boxed region in (b) taken at a higher magnification. The small rectangle indicates the location for preparing in-depth TEM lamella by FIB.

The image quality map (Fig. 5.3b) superimposed with these boundaries shows that there is a layer on the matrix side adjacent to the matrix/band_1 boundary, which also generates a plateau with a relatively small misorientation angle ($\sim 1^\circ$) in the point-to-origin misorientation profile.
All of the boundaries are clearly visualized on the kernel average misorientation (KAM) map (Fig. 5.3c), where the KAM value represents the density of geometrically necessary dislocation (GND). The band_2/matrix boundary is visualized as a layer with a width of about 0.6 μm. The higher KAM value of this layer than that of the matrix suggests that high densities of GNDs are stored within it, interpreting the above mentioned gradual change of point-to-origin misorientation angle.

The deformation bands were characterized in greater detail by using TEM analysis, where the bulk microstructures of the deformation bands were revealed. Fig. 5.4 displays the TEM analysis of a FIB lift-out lamella prepared from the location indicated in Fig. 5.2c. Fig. 5.4a is a STEM bright-field image, illustrating a lower magnification overview of the deformation band. It is shown that band_1 penetrates considerably deep into the bulk, while band_2 is located near the...
surface with its largest depth reaching down to ~450 nm. The twinning relationship between matrix and band_1 was confirmed by selected area diffraction patterns (Fig. 5.4c, d and f). Following the usual notation for deformation twinning, a twin can be described by four elements: twinning plane $K_1$, twinning direction $\eta_1$, conjugate twinning plane $K_2$ and conjugate twinning direction $\eta_2$ [160]. The SAD pattern (Fig. 5.4f) taken from the band_1/ matrix boundary and its key diagram (Fig. 5.4i) imply that the twinning plane $K_1$ is $\{233\}$. Zhang et al. [160] proposed a theoretical method to calculate the other twinning elements with $K_1$ as input. By applying this method to the present twin (band_1), the $\eta_1$, $K_2$ and $\eta_2$ are determined to be $[311]$, $[211]$ and $\{\bar{1}11\}$, respectively.

The SAD pattern in Fig. 5.4e demonstrates that band_2 consists of an orthorhombic $\alpha''$ martensite phase rather than a bcc $\beta$ phase, in contrast to the EBSD indexing (Fig. 5.3). The cross section of the $\alpha''$ band is nearly triangle-shaped and locates on the $\beta$-twin side (Fig. 5.4a and b). The $\alpha''/\beta$-matrix boundary is characterized by a series of wrinkles emitted from the triple point of $\beta$-twin, $\alpha''$ martensite and $\beta$-matrix (Fig. 5.4b), which align along the straight extension of the $\beta$-twin/ $\beta$-matrix boundary. These wrinkles may be created by stress concentrations along the boundary, consistent with the high densities of GNDs indicated by the KAM map (Fig. 5.3c).

Elongated $\omega$ reflections are present in the SAD patterns of both $\beta$-matrix (Fig. 5.4c) and $\beta$-twin (Fig. 5.4d). In the $\beta$-matrix, the four $\omega$ variants (referred to as $\omega1$, $\omega2$, $\omega3$ and $\omega4$), with $[2\bar{1}10]_{\omega1}$, $[\bar{1}0\bar{1}4]_{\omega2}$, $[0\bar{1}4\bar{4}]_{\omega3}$ and $[\bar{1}2\bar{1}0]_{\omega4}$ parallel to $[0\bar{1}1]$, precipitated with equal probability during quenching, so the diffraction intensities of the two distinguishable $\omega$ variants ($\omega1$ and $\omega4$) are identical (see Chapter 4). Within the $\beta$-twin, however, the intensity of $\omega4$ is stronger than that of $\omega1$, indicating that more $\omega4$ formed during twinning. The orientation relationship between $\beta$-twin and $\omega4$ is $[0\bar{1}\bar{1}]_T/[\bar{1}\bar{2}\bar{1}\bar{0}]_{\omega4}$, $[\bar{1}\bar{1}\bar{1}]_T/[0001]_{\omega4}$ and $(211)_T/[(\bar{1}001)_{\omega4}$, where the subscript “T”
Fig. 5.4g illustrates that the reflections of $\omega_4$ further intensify near the $\beta$-twin/$\alpha''$ boundary. In the previous chapter, it has been demonstrated that $\{211\}<111>$ shear in $\beta$ phase can induce $\beta \rightarrow \omega$ transformation. This means that $(211)_T[\bar{1}11]_T$ shear was involved within the $\beta$-twin, especially near the $\beta$-twin/$\alpha''$ boundary, during the formation of $\beta$-twin.

![Fig. 5.4. TEM analysis of a FIB lift-out lamella prepared from the location indicated in Fig. 5.2c. (a) STEM bright-field image of the deformation band viewed along $[0\bar{1}1]$. (b) An image of the boxed region in (a) taken at a higher magnification. (c–h) SAD patterns taken from the regions indicated by circles in (b). (i–k) Key diagrams corresponding to the SAD patterns in (f), (g) and (h), respectively. The subscripts “T” and “O” denote bcc $\beta$-twin and orthorhombic $\alpha''$, respectively.](image)

The orientation relationship between $\beta$-twin and $\alpha''$ martensite, as determined from the SAD pattern in Fig. 5.4g and its key diagram in Fig. 5.4j, is $[01\bar{1}]_T//[001]_O$, $[1\bar{1}\bar{1}]_T//[\bar{1}10]_O$ and $(211)_T//(110)_O$, where the subscript “O” represents the orthorhombic $\alpha''$ martensite. The indices without any subscript are with respect to the $\beta$-matrix in this chapter.

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5 The indices without any subscript are with respect to the $\beta$-matrix in this chapter.
[001]_O//[011] SAD pattern taken from the wrinkled boundary between the α'' martensite and the β-matrix shows circular streaks between the two set of reflections (Fig. 5.4h and k), where the α'' reflections seem to be dragged to their current sites from locations close to the β-matrix reflections with a tail formed following each α'' reflection. It is illustrated that (110)_O is about 14.3° deviated from (211).

Like previous studies [15, 17, 129, 146, 149, 150], high densities of straightly elongated dislocations are present within the (233) twin (Fig. 5.4a and b). The dislocation lines are nearly parallel to the (211)_T and (110)_O planes. The angle between the dislocation lines and the [311] direction (β-twin boundary) is about 75.5° (Fig. 5.4b). These dislocations seem to penetrate through the β-twin/β-matrix interface on the left hand side of Fig. 5.4a and extend into the β-matrix, producing a layer along the interface which corresponds to the layer adjacent to the red boundary (45°–55°) on the IQ map (Fig. 5.3b) and the plateau of ~1° in Fig. 5.3d. Such dislocation-decorated layers in the vicinity of {332} twins were previously reported in other metastable β titanium alloys as well, e.g., in Ti–Mo-based and Ti–V-based alloys [17, 149, 150].

In order to characterize the Burgers vector of the dislocations within the {332} twins, TEM lamellae with orientations close to <111>_T were prepared and tilting experiments and contrast analyses were performed, as shown in Fig. 5.5. A β-twin with width 6.69 μm is indicated in Fig. 5.5a, where a triangle-shaped α'' region is also present on the β-twin side near the surface (inset). The straightly elongated dislocations in this twin seem to penetrate through the β-twin/β-matrix interface and extend into the β-matrix as well.

Fig. 5.5b, c and d present three typical STEM bright-field images of the same area surrounding the β-twin/β-matrix interface taken at \( \mathbf{g} = (101)_T, \mathbf{g} = (110)_T \) and \( \mathbf{g} = (01\overline{1})_T \), respectively. It is seen that the dislocations are visible under the former two two-beam diffraction
conditions but invisible under the last one. This means that the straight dislocations within the twin are of the same Burgers vector $b$. Using $\mathbf{g} \cdot \mathbf{b} = 0$ as the criterion for invisibility, the Burgers vector $b$ is determined to be $1/2[111]_\tau$, which is nearly parallel ($\sim 4.5^\circ$ deviation) to the dislocation lines. Thus, these straight dislocations have a very strong screw character.

**Fig. 5.5.** Contrast analysis of the dislocations within the {332} twin. (a) STEM bright-field image of a $\beta$-twin captured in a FIB lift-out TEM lamella. The inset shows the $\alpha''$ region near the surface at a higher magnification. (b–d) STEM bright-field images of the same area surrounding the $\beta$-twin/$\beta$-matrix interface taken under different two-beam diffraction conditions. $\mathbf{g}$ is diffraction vector.
The atomic configurations of the $\beta$-matrix/$\beta$-twin interface have been examined by using HRTEM. Fig. 5.6a is the HRTEM image of a (233) twin, which shows that the lattice fringes of $\beta$-matrix and $\beta$-twin are symmetrical with respect to the $\beta$-matrix/$\beta$-twin interface (or twinning plane), where the interface is parallel to the incident electron beam. The fast Fourier transform image in Fig. 5.6b reveals how the lattices of the $\beta$-matrix (yellow) and the $\beta$-twin (origin) are rotated about the $[0\bar{1}1]/[0\bar{1}1]_T$ crystallographic axis.

**Fig. 5.6.** Atomic scale characterization of the $\beta$-matrix/$\beta$-twin interface. (a) HRTEM image of the $\beta$-matrix/$\beta$-twin interface viewed along $[0\bar{1}1]/[0\bar{1}1]_T$. (b) Fast Fourier transform pattern of (a). (c) Magnified image of the boxed region in (a). The blue line indicates the $\beta$-matrix/$\beta$-twin interface, while the black open circles indicate two \{233\}$/\{2\bar{3}3\}_T$ atomic planes close to the interface.
The angle between (011) and (011)\textsubscript{T} lattice fringes is about 50.5°, as indicated in Fig. 5.6a. Thus, the β-twin lattice can be derived from the β-matrix lattice by a 50.5° rotation around [0\overline{1}1], consistent with the misorientation determined by EBSD (Fig. 5.3d). Within the coincidence site lattice (CSL) description, such an interface forms a Σ11 boundary. The magnified HRTEM micrograph of the β-matrix/β-twin interface is illustrated in Fig. 5.6c, where the Σ11 boundary is indicated by a blue line and two \{\overline{2}3\overline{3}\}/\{2\overline{3}3\}\textsubscript{T} atomic planes close to the boundary are marked by open circles. A nearly coherent interface is revealed. It should be noted that the interface is not flat at the atomic scale and the (011) and (011)\textsubscript{T} lattice fringes close to the interface are not straight, implying crystal distortions near the interface.

The lattice parameters of the β and α" phases were determined by SXRD experiments, where SXRD patterns were taken from the deformed regions of the tensile samples and intensity^{1/2}/2θ spectra were extracted from these patterns. Fig. 5.7 displays such an intensity^{1/2}/2θ spectrum, which shows distinct peaks derived from both bcc β phase (Space group: Im\overline{3}m) and orthorhombic α" martensite (space group: Cmcm). The fitted lattice parameter of the β phase is $a_{\beta} = 3.2949$ Å, while that of the α" martensite is $a_{o} = 3.2196$ Å, $b_{o} = 4.7676$ Å and $c_{o} = 4.6417$ Å.

The α" crystal lattice can be derived from the β crystal lattice by \{0\overline{1}1\}<01\overline{1}> shuffles with a relatively small shuffle amplitude δ [12, 161], as schematically illustrated in Fig. 5.8a. The lattice parameters of the α" martensite, $a_{o}$, $b_{o}$ and $c_{o}$, correspond to $a_{\beta}$, $\sqrt{2}a_{\beta}$ and $\sqrt{2}a_{\beta}$, respectively. The shuffling process is normally accompanied by a shape change which can be described by three principal transformation strains:

\begin{align}
\varepsilon_{1} &= (a_{o} - a_{\beta})/a_{\beta}, \quad (5.1a) \\
\varepsilon_{2} &= (b_{o} - \sqrt{2}a_{\beta})/\sqrt{2}a_{\beta}, \quad (5.1b) \\
\varepsilon_{3} &= (c_{o} - \sqrt{2}a_{\beta})/\sqrt{2}a_{\beta}. \quad (5.1c)
\end{align}
The substitution of the lattice parameters measured by SXRD into the above equations gives \( \varepsilon_1 = -2.29\% \), \( \varepsilon_2 = 2.32\% \) and \( \varepsilon_3 = -0.39\% \) for the current Ti–36Nb–2Ta–3Zr alloy.

![Intensity spectrum from the SXRD pattern](image)

Fig. 5.7. Intensity^{1/2}/2θ spectrum extracted from the SXRD pattern taken from the deformed region of a tensile sample. The positions of the \( \beta \) and \( \alpha'' \) peaks are labelled and indexed.

The small principal transformation strain values correspond to a very small shape change, i.e., the \( \alpha'' \) crystal lattice is close to the \( \beta \) crystal lattice, resulting in that the EBSD Kikuchi patterns of \( \alpha'' \) exhibit a pseudo-cubic symmetry. Therefore, the \( \beta \) and \( \alpha'' \) phases cannot be unambiguously discriminated by EBSD indexing with the standard vote-rank algorithm [158]. An example is illustrated in Fig. 5.8b, which shows that an EBSD Kikuchi pattern taken from the \( \alpha'' \) martensite can be indexed as both bcc \( \beta \) and orthorhombic \( \alpha'' \) with almost the same number of votes. This explains why the entire deformation band could be indexed as \( \beta \) phase with a high confidence index value in Fig. 5.3. It should be noted that the \{332\} twin and the \( \alpha'' \) martensite can still be
distinguished by examining misorientations, although they were indexed as the same phase by EBSD.

Fig. 5.8. (a) Lattice correspondence between bcc β phase and orthorhombic α″ martensite. (b) EBSD Kikuchi pattern taken from the α″ martensite on the pre-polished surface of a tensile sample, which can be indexed as both β and α″.

5.3.2 Initiation and propagation of {332} twins

The occurrence of α″ martensite bands adjacent to the {332} twins near the free surface indicates an intimate relationship between {332} twinning and β → α″ transformation. In order to clarify this relationship, the initiation and propagation of {332} twins have been investigated. In most cases, {332} twin nucleates at grain boundary. Fig. 5.9 shows such a case, where a deformation band has nucleated at one grain boundary and has then propagated into the grain
interior with a length of 48 μm. The width of this band decreases gradually from its initiation site to its tip, tapering to a point in the end (Fig. 5.9a).

![Fig. 5.9. Initiation of \{332\} twin at grain boundary. (a) Backscattered electron image, (b) inverse pole figure map, (c) image quality map overlaid with rotation angle boundaries (blue, red and green lines) and (d) kernel average misorientation map of the same region. The color bar of (b) is the same as that of Fig. 5.2a.](image)

The IPF map in Fig. 5.9b illustrates that the color of this band is not homogeneous along its length, indicating varied crystallographic orientations. By examining misorientations and plotting the rotation angle boundaries onto the IQ map (Fig. 5.9c), it is revealed that this band is not purely composed of \{332\} twin. In Fig. 5.9c, as revealed in the previous subsection, the blue
line (5–20°), red line (45–55°) and green line (55–65°) correspond to β-matrix/α'' boundary, β-matrix/β-twin boundary and α''/β-twin boundary, respectively. Thus, starting from its initiation site at the grain boundary, this band along its length is composed of α''/β-twin/α''/β-twin in sequence, which seems to imply that α'' band formed first and β-twin initiated within the α'' band. The intermittent α'' and β-twin sections along the band length can also be visualized on the KAM map (Fig. 5.9d), with β-matrix/α'' boundaries exhibiting higher KAM values (consistent with that revealed in Fig. 5.3c). It should be noted that {332} twin nucleates in the grain interior as well, forming a lenticular shape, as displayed in Fig. 5.2b.

Fig. 5.10 shows the results of an in situ SEM tensile test conducted on a pre-polished tensile sample, where the propagation of {332} twins with accumulating strain is illustrated. The engineering tensile stress curve is presented in Fig. 5.10a as a function of the ratio of the cross head displacement ΔL over the initial gauge length L₀. The applied strain levels at which BSE images (Fig. 5.10b–f) were taken are marked in this curve. Fig. 5.10b shows two twins propagating to the opposite directions. With the increase of applied strain, jerky formation of new twins accompanied by drops in the engineering stress was observed, as presented in the BSE images of Fig. 5.10c–f. These images also reveal that the growth of initiated twins is characterized by expanding in the longitudinal direction and thickening in the transverse direction, identical to the growth of conventional {112}<111> twins in bcc metals [140]. Another interesting feature revealed by these images is that the twins propagating to the opposite directions can merge when their lateral boundaries impinge on each other. This feature has been studied in more detail by correlating higher-magnification BSE images (Fig. 5.10g–i) and EBSD maps (Fig. 5.11) below.
**Fig. 5.10.** Propagation of \{332\} twins with accumulating strain. (a) Engineering stress against the ratio of the cross head displacement $\Delta L$ over the initial gauge length $L_0$. (b–f) Sequential backscattered electron images showing the propagation of \{332\} twins at the strain levels indicated in (a). The tensile direction is horizontal with respect to the image. (g–i) Images of the boxed regions in (b), (e) and (f), respectively, taken at a higher magnification. The red, green and blue dashed lines denote $\beta$-twin/$\beta$-matrix boundary, $\beta$-twin/$\alpha''$ boundary and $\alpha''$/β-matrix boundary, respectively.

**Fig. 5.11** displays the IPF map and IQ map of the twins shown in Fig. 5.10f. By examining misorientations (Fig. 5.11b), it can be determined that the purple, pink and blue colors on the IPF map (Fig. 5.11a) correspond to $\beta$-matrix, $\beta$-twin and $\alpha''$ martensite, respectively. It is shown that each twin is accompanied by an $\alpha''$ martensite band on its left hand side. The TEM analyses (Fig. 5.4 and Fig. 5.5) in the previous subsection have revealed that the $\alpha''$ martensite locates near the free surface (beneath the $\alpha''$ martensite is the $\beta$-twin) and the $\alpha''$/β-matrix boundary is oriented...
along the straight extension of the $\beta$-twin/$\beta$-matrix boundary, i.e., the $\beta$-twin width in the bulk is the sum of the $\alpha''$ martensite width and the $\beta$-twin width on the surface.

Fig. 5.11. EBSD analysis of the twins shown in Fig. 5.10f: (a) inverse pole figure map and (b) image quality map superimposed with rotation angle boundaries (blue, red and green lines). The color bar of (a) is the same as that of Fig. 5.2a. The areas of poor indexing in the center of the two maps, represented as black pixels, result from electron beam-induced contamination yielded by continuous high-magnification imaging.

By correlating the EBSD analysis to the BSE images, the merging process of adjacent twins is shown in more detail in Fig. 5.10g–i. Two twins are labelled in Fig. 5.10g as $\beta$-twin_1 and $\beta$-twin_2, respectively, where the former is a pure twin and the latter is accompanied by an $\alpha''$ martensite band along its length. With increasing the applied strain, these two twins grew by consuming adjacent $\beta$-matrix and eventually merged when their lateral boundaries impinged on
each other (Fig. 5.10h). During this process, an $\alpha''$ martensite band accompanying $\beta$-twin_1 formed on its left hand side. Also shown in Fig. 5.10h is the propagation of another twin (labelled $\beta$-twin_3) into the field of view. With further increasing the applied strain, Fig. 5.10i illustrates that the $\beta$-matrix in the field of view was completely consumed and $\beta$-twin_3 merged with $\beta$-twin_1, i.e., the three twins in the field of view coalesced into a single twin in this stage. Interestingly, the $\alpha''$ martensite bands remained unchanged during the merging of twins.

5.3.3 Evolution of $\alpha''$ martensite and $\{332\}$ twins during annealing

It is well known that $\alpha''$ martensite will transform into the $\beta$ phase when holding the sample at high temperatures, depending of course on the specific alloy composition [7]. In the present work, the $\alpha''$ martensite bands occurring near the surface are in contact with both the $\beta$-matrix and the $\{332\}$ $\beta$-twins. The question that arises is what the $\alpha''$ martensite band will transform to during high-temperature annealing, $\beta$-matrix or $\beta$-twin. It is of importance to clarify this question for determining the relationship between $\alpha''$ martensitic transformation and $\{332\}$ twinning.

Fig. 5.12a and b show the IPF map and IQ map of a $\{332\}$ $\beta$-twin with an $\alpha''$ martensite band adjacent to it, as confirmed by the rotation angles of the boundaries overlaid in Fig. 5.12b. Viewed on the surface, the width of the $\alpha''$ martensite is about three times that of the $\beta$-twin. The same region was mapped again by EBSD after annealing at 900 °C for 30 min, without any grinding or polishing on the surface. It is revealed that the $\alpha''$ martensite band has completely transformed into the $\beta$-twin rather than into the $\beta$-matrix (Fig. 5.12c and d). This suggests that $\alpha''$ martensite acts as initiation site of the $\beta$-twin.

Another interesting phenomenon is that detwinning of $\{332\}$ twins occurred during annealing, as shown in Fig. 5.13. The IQ map in Fig. 5.13a displays the traces of four twins existed before
annealing, which are marked as T1, T2, T3 and T4, respectively. T1, T2 and T3 are parallel, indicating that they belong to the same twinning variant [159]. T4 which belongs to another twinning variant intersected with them.

Fig. 5.12. EBSD analysis of a (332) twin before (a, b) and after (c, d) annealing at 900 °C for 30 min. (a, c) Inverse pole figure map. The color bar is the same as that of Fig. 5.2a. (b, d) Image quality map superimposed with rotation angle boundaries (blue, red and green lines).

The widths of T1 and T2 taper when they approaching T4, indicating that they initiated elsewhere and propagated to T4. In contrast, T3 seems to nucleate from T4. The line features inside T4 may result from merging processes of twins as revealed in the previous subsection. The IPF map in Fig. 5.13b and the rotation angle boundaries overlaid in Fig. 5.13a illustrate that T1 fully detwinned, while T2 and T4 partially detwinned. The detwinning process starts from the twin tip rather than the initiation site or lateral boundaries of the twin, as manifested by T2 and
T3. This is different from the reversion of martensite band which starts from its lateral boundaries [162].

**Fig. 5.13.** Detwinning of \{332\} twins after annealing at 900 C for 30 min. (a) Image quality map superimposed with rotation angle boundaries (blue, red and green lines). (b) Inverse pole figure map. The color bar is the same as that of Fig. 5.2a.

### 5.4 Discussion

Experimental observations of the present study illustrate the three-dimensional microstructure of \{332\} twin in a metastable $\beta$ Ti–36Nb–2Ta–3Zr alloy. In addition to the parallel straight dislocations inside the twin which have been reported previously [15, 17, 129, 146, 149, 150], it
was found that an $\alpha''$ martensite band with triangle-shaped cross section was embedded in the
\{332\} twin near the surface. Combine the surface EBSD analysis in Fig. 5.3 with the through-
thickness TEM analysis in Fig. 5.4, the three-dimensional microstructure of the (233) twin
shown in Fig. 5.2c can be schematically rebuilt, as displayed in Fig. 5.14a. The (233) twin
viewed on the (0\{11\}) plane was inclined to the horizontal at an angle of $\theta_1 = 48.74\pm0.18^\circ$ and
produced an inclined plane at an angle of $\theta_2 = 7.66\pm0.16^\circ$ when it intersected the surface as
measured in Fig. 5.4a. With these two inclination angles, the shear strain $s'$ generated by the twin
can be calculated as

$$s' = \frac{\sin \theta_2}{\sin \theta_1 \sin(\theta_1 - \theta_2)} = 0.2697.$$  \hfill (5.2)

Fig. 5.14b schematically shows a projection of twinned crystal structures onto the (0\{11\}) plane
as observed via HRTEM studies (Fig. 5.6). The $K_1$ and $K_2$ planes and $\eta_1$ and $\eta_2$ directions are
illustrated with respect to the $\beta$-matrix. The plane perpendicular to $K_1$ and $K_2$, i.e., the (0\{11\})
plane, is called the plane of shear. According to the theory of the crystallography of deformation
twinning [163], the inclination angle $\theta_2$ (Fig. 5.14a) produced by twinning shear reaches its
maximum when the twin is viewed on the plane of shear. This explains why the angle $\theta_2$ in Fig.
5.5a is fairly small ($\sim0^\circ$), where the twin was not viewed on the plane of shear.

The shear mechanisms [152, 157] and partial dislocation mechanisms [153-156] proposed for
\{332\} twinning are generally characterized by two activities, i.e., (i) collective movement of
atoms on successive \{332\} planes along \(<113>\) directions and (ii) additional atomic shuffles,
with the macroscopic shear strain merely contributed by the former activity. All of these
mechanisms can produce the ideal twinned crystal structures shown in Fig. 5.14b. Regardless of
the energetic difficulties associated with the collective movement of atoms on non-close-packed
planes along non-close-packed directions, these mechanisms give a shear strain (magnitude of twinning shear) \( s = 0.3536 \) [152, 153, 157], which is larger than the experimentally measured shear strain \( s' = 0.2697 \).

**Fig. 5.14.** Schematic illustrations of the \((\overline{2}33)\) twin. (a) Three-dimensional illustration the \((\overline{2}33)\) twin shown in Fig. 5.2c rebuilt by the EBSD analysis in Fig. 5.3 and TEM analysis in Fig. 5.4. (b) Atomic model of the twinned crystal structures. The solid circles indicate the atoms on plane of figure, while the open circles the atoms below plane of figure.

Indeed, the shear strain produced by deformation twinning is strongly dependent on the twinning mechanism. For instance, recent studies [164, 165] suggest that some special twinning mechanisms even result in zero net shear strain for the conventional fcc \{111\} twinning mode. Here, the discrepancy between \( s \) and \( s' \) implies that \{332\} twinning may not involve the
movement of atoms on successive \{332\} planes along \langle113\rangle directions as claimed in the shear mechanisms [152, 157] and partial dislocation mechanisms [153-156]. The enrichment of one \omega variant within the twin (\omega4, Fig. 5.4d and g), on the other hand, suggests that \{332\} twinning involves the shear of \{211\} planes along \langle111\rangle \text{T} directions.

Based on the fact that the \alpha'' martensite band near the surface transformed into the adjacent \beta-twin rather than into the \beta-matrix during annealing (Fig. 5.12), the following mechanism is proposed: the \{332\} twin nucleates within the progressively formed \alpha'' martensite during deformation, i.e., the stress-induced \alpha'' martensite forms first and then transforms to the \{332\} twin. This scenario is supported by Fig. 5.9, which clearly shows that the \alpha'' martensite first initiated from a grain boundary and the \{332\} twin formed within the \alpha'' martensite. Such an \alpha''-assisted twinning mechanism also explains why the \alpha''/\beta-matrix and \beta-twin/\beta-matrix boundaries are almost aligned along the same line (Fig. 5.4a and Fig. 5.5a). In order to better understand this mechanism, the nature of the \beta \rightarrow \alpha'' martensitic transformation in the metastable \beta Ti–36Nb–2Ta–3Zr alloy is firstly considered by employing the phenomenological theory of martensitic transformations (PTMT) as outlined by Lieberman et al. [54].

By applying the infinitesimal deformation approach by Liang et al. [166] to the \beta \rightarrow \alpha'' transformation, Inamura et al. [8] proposed that the twinning relationship amongst the \alpha'' variants is dependent on the sign of \varepsilon_3, where \varepsilon_3 > 0 corresponds to type I or type II twinning and \varepsilon_3 < 0 corresponds to compound twinning. For the present Ti–36Nb–2Ta–3Zr alloy, the \varepsilon_3 component as determined by SXRD is \epsilon -0.39\%, implying a compound twinning relationship.

When applying PTMT to the present \beta \rightarrow \alpha'' transformation, the two \alpha'' variants, V1 and V2, shown in Fig. 2.4 are considered and the lattice parameters measured by SXRD are used. Table 5.1 lists the calculated crystallographic characteristics of the transformation, where \alpha is the
relative amount of V2, \( n \) the normal of the habit plane, \( s \) the direction of shear, \( t \) the transformation twinning plane (between V1 and V2), \( m \) the magnitude of shear and \( \theta \) the angle of shear. The table shows that the indices of both habit plane and transformation twinning plane are irrational with respect to the coordinate system of the \( \beta \)-matrix, implying that these interfaces may be semi-coherent or incoherent. Such interfaces are normally characteristic of terraces and steps and are stabilized by the presence of dislocations, as revealed by Chai et al. [9] in a series of metastable \( \beta \)-Ti–Nb alloys with Nb content ranging from 20 to 24 at.%. When viewed edge-on along the \([001]_{\alpha'}\)|\(\beta\)/\([0\overline{1}0]_{\alpha'}\)|\(\alpha\) direction, they showed that the V2/V1 interface relaxed into a series of \((110)_{\alpha}\) terraces and steps.

**Table 5.1.** Crystallographic characteristics of the \( \beta \rightarrow \alpha'' \) transformation in the Ti–36Nb–2Ta–3Zr alloy calculated by the phenomenological theory of martensitic transformations [54]. All of the vectors are with respect to the coordinate system of the \( \beta \)-matrix.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( n )</th>
<th>( s )</th>
<th>( t )</th>
<th>( m )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8554</td>
<td>((-0.4828, 0.7336, 0.4783))</td>
<td>((-0.5163, 0.6796, 0.5211))</td>
<td>((-0.0205, -0.6907, 0.6909))</td>
<td>0.0463</td>
<td>2.4069°</td>
</tr>
</tbody>
</table>

The rotation matrices \( \Theta \) and \( \Omega \) defining the orientation relationships between the \( \beta \)-matrix and the martensite variants V1 and V2, respectively, are calculated to be

\[
\Theta = \begin{pmatrix}
0.9998 & -0.0149 & 0.0148 \\
0.0006 & 0.7231 & 0.6907 \\
-0.0210 & -0.6906 & 0.7230
\end{pmatrix}
\]  

(5.3a)

and

\[
\Omega = \begin{pmatrix}
-0.9998 & 0.0149 & -0.0148 \\
-0.0210 & -0.7097 & 0.7042 \\
0.0000 & 0.7044 & 0.7098
\end{pmatrix}
\]  

(5.3b)
With these two rotation matrices, any vector expressed with respect to the coordinate system of the \( \beta \)-matrix can be transformed into the same vector expressed with respect to the coordinate systems of the martensite variants. Table 5.2 lists the orientation relationships between important crystallographic planes predicated by PTMT. The angles between these planes are fairly small, indicating relatively small differences in the \( \langle 0\overline{1}1 \rangle /\langle 001 \rangle_o \) SAD patterns, i.e., the reflections of the \( \alpha'' \) martensite are close to those of the \( \beta \)-matrix at the onset of the formation of \( \alpha'' \) martensite. Both reduction in temperature and application of stress can act as driving force for the \( \beta \rightarrow \alpha'' \) martensitic transformation. For the former case, it has been revealed that the SAD pattern of the \( \alpha'' \) martensite is close to that of the \( \beta \)-matrix when taken along \([001]_o/\langle 0\overline{1}1 \rangle\) in water quenched Ti–Nb alloys [9], analogous to the prediction. Nonetheless, few studies have been conducted to examine the orientation relationship between the initially formed \( \alpha'' \) martensite and the \( \beta \)-matrix for the latter case, which may be due to the difficulty in retaining such martensite.

Under an external biasing stress, the initially formed twinned martensite during deformation will reorient and detwin [167], resulting in a single-variant martensite structure with a new orientation relationship relative to the \( \beta \)-matrix. This may explain the single-variant character and special orientation of the \( \alpha'' \) martensite band observed in the present study, which was retained after tensile deformation (Fig. 5.4). The possible scenario is that twin-related \( \alpha'' \) martensite variants formed first and then detwinned into one single variant and reoriented with respect to the \( \beta \)-matrix. The wrinkled microstructures which were observed to form along the \( \alpha''/\beta \)-matrix boundary in Fig. 5.4b (corresponding to high KAM values, Fig. 5.3c) and the circular diffraction streaks (or tails following the \( \alpha'' \) reflections) in Fig. 5.4h may thus result from the reorientation of the \( \alpha'' \) martensite. These circular streaks starting from the locations close to the \( \beta \)-matrix reflections seem to indicate that the \( \langle 001 \rangle_o \) SAD patterns of the initially formed \( \alpha'' \)
martensite variants during deformation are close to the [0\bar{1}1] SAD pattern of the β-matrix as predicted by the PTMT. After the detwinning and reorientation, the (110)\textsubscript{O} plane of the resultant single-variant α” martensite is nearly parallel to the (211)\textsubscript{T} plane of the β-twin (Fig. 5.4g).

**Table 5.2.** Orientation relationships between β-matrix and two α” martensite variants, V1 and V2, calculated by the phenomenological theory of martensitic transformations [54].

<table>
<thead>
<tr>
<th>β and V1</th>
<th>β and V2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) 1.2015° from (100)\textsubscript{V1}</td>
<td>(100) 1.2015° from (100)\textsubscript{V2}</td>
</tr>
<tr>
<td>(011) 1.3116° from (010)\textsubscript{V1}</td>
<td>(0\bar{1}1) 1.2218° from (010)\textsubscript{V2}</td>
</tr>
<tr>
<td>(0\bar{1}1) 1.7786° from (001)\textsubscript{V1}</td>
<td>(011) 0.2217° from (001)\textsubscript{V2}</td>
</tr>
<tr>
<td>(211) 1.2493° from (110)\textsubscript{V1}</td>
<td>(2\bar{1}1) 0.1369° from (110)\textsubscript{V2}</td>
</tr>
<tr>
<td>(\bar{2}11) 2.1566° from (\bar{1}10)\textsubscript{V1}</td>
<td>(2\bar{1}1) 2.4571° from (\bar{1}10)\textsubscript{V2}</td>
</tr>
</tbody>
</table>

As revealed in Fig. 5.12, the detwinned and reoriented α” martensite transformed back into bcc β phase during high-temperature annealing, but the resultant β domain was of a \{332\} twinning relationship relative to the β-matrix. Here, it is assumed that the α” → β transformation can be induced by the application of external stress as well, resulting in the formation of β-twins within the detwinned and reoriented α” martensite as shown in Fig. 5.9. This transformation should have involved atomic shears parallel to the \(<0001>_{\omega}\) direction of one of the four \(\omega\) variants (\{211\}\textsubscript{T}<\bar{1}11>\textsubscript{T} shears), similar to the β → α” transformation [104], thus leading to the preferential growth (or enrichment) of this specific \(\omega\) variant within the β-twin (Fig. 5.4d and g). It should be noted that the β-twin may initiate from different positions of the same α” martensite band (Fig. 5.9c) and these initiated β-twins can merge together when they propagate to each other as revealed in Fig. 5.10. Theoretical studies [168, 169] suggested that the presence of free
surface stabilizes the martensite. In the present study, the retained \( \alpha'' \) martensite near the surface has only been observed on the specific side of the \( \beta \)-twin where the angle between the \( \beta \)-twin/\( \beta \)-matrix interface (parallel to the \( \alpha''/\beta \)-matrix interface) and surface is acute. Such a geometrical feature may resist the \( \alpha'' \rightarrow \beta \) transformation and thus stabilizes the \( \alpha'' \) martensite.

The dislocations contributing to the (110) terraces and steps of the V2/V1 interface in the initially formed twinned martensite structure may be retained after the detwinning of martensite. These dislocations, lying on the \{110\}_O planes of the resultant single-variant martensite, would then become parallel to the \{211\}_T planes after the reorientation of martensite and may be left behind in the \( \beta \)-twin after the \( \alpha'' \rightarrow \beta \) transformation (reverse martensitic transformation). This provides a possible explanation for the origin of the straight parallel dislocations within the \{332\} twins, which were found to be almost parallel to the (110)_O and (211)_T planes (Fig. 5.4b). Similar phenomena have been reported by Kajiwara and Kikuchi [162, 170], where dislocation structures produced in parent phase by reverse martensitic transformation were observed in Cu–Zn and Fe–Ni–C alloys and they suggested that such dislocations originated from the twinning dislocations at the interfaces of martensite twins. For the dislocations on the matrix side which seem to be extended from the dislocations inside the \( \beta \)-twin (Fig. 5.4 and Fig. 5.5), Furuhara et al. [150] suggested that they originated from the reverse motion of \( \beta \)-matrix/\( \beta \)-twin interface during detwinning. However, the detwinning of \{332\} twins is found to start from their twin tips rather than from their lateral coherent twin boundaries (Fig. 5.13). In fact, the coherent twin boundaries have been considered to be very stable against migration due to their fairly low excess energy [171]. Thus, the dislocations on the matrix side are suggested to originate from the reverse transformation of the \( \alpha'' \) martensite which was not yet subjected to reorientation. Such martensite transformed to the \( \beta \) domain with the same orientation as the \( \beta \)-matrix during
unloading, while the dislocations lying on the \{110\}_O planes were left behind after the transformation.

### 5.5 Conclusion

The present study reveals the critical relationship between the stress-induced $\beta \rightarrow \alpha''$ martensitic transformation and the formation of \{332\} $\beta$-twins in a metastable $\beta$ Ti–36Nb–2Ta–3Zr alloy. The following conclusions can be drawn:

- Near the surface, an $\alpha''$ martensite band with triangle-shaped cross section is embedded in the $\beta$-twin. The $\beta$-twin/$\beta$-matrix boundary and the $\alpha''/\beta$-matrix boundary are oriented almost along the same line. The orientation relationship between $\beta$-twin and $\alpha''$ is $[01\bar{1}]_T//[001]_O$, $[\bar{1}\bar{1}1]_T//[\bar{1}\bar{1}10]_O$ and $(211)_T//((110))_O$ (the subscripts “T” and “O” represent $\beta$-twin and $\alpha''$, respectively), while a regular orientation relationship is absent between $\beta$-matrix and $\alpha''$.

- High densities of straight parallel dislocations are present within the $\beta$-twin. These dislocations are of a very strong screw character and all have the same Burgers vector, $1/2<\bar{1}11>_T$. One $\omega$ variant is enriched within the $\beta$-twin. The macroscopic shear strain produced by the $\beta$-twin is smaller than that predicted by the classic theory of the crystallography of deformation twinning.

- The $\beta$-twin/$\beta$-matrix interface is nearly coherent. The shape changes in crystal structures associated with the $\beta \rightarrow \alpha''$ transformation are relatively small, but the $\alpha''$ martensite, $\beta$-twin and $\beta$-matrix on the surface can be distinguished by examining misorientations in EBSD analysis.
• The β-twins initiate both at the grain boundaries and in the grain interiors. The first initiated band consists of α” martensite and the β-twin forms within the α” martensite. The β-twins propagating to the opposite directions can merge when their lateral boundaries impinge on each other, but the α” martensite bands near the surface remain unchanged during the merging processes.

• The α” → β transformation and detwinning of β-twins occur during annealing at 900 °C. The α” martensite band near the surface transforms into the adjacent β-twin rather than into the β-matrix, while the detwinning of β-twin starts from the twin tip rather than from the lateral twin boundaries.

• An α”-assisted twinning mechanism is proposed, in which {332} twins nucleate within progressively formed α” martensite during deformation. Explanations for the enrichment of one ω variant and the occurrence of straight dislocations within the β-twin are given based on this mechanism.
Chapter 6  Summary and future work

6.1  Dissertation summary

In this dissertation, the studies were dedicated to improving the understanding of the deformation mechanisms associated with the instability of $\beta$ phase in metastable $\beta$ titanium alloys. Three groups of metastable $\beta$ Ti–Nb–Ta–Zr–O alloys with varied $\beta$-phase stability were produced. The most stable group is gum metal, Ti–23Nb–0.7Ta–2Zr–($0.87, 1.52, 1.83$)O (at.%), in which neither deformation twinning nor stress-induced phase transformation are expected to occur during deformation. The intermediate stable group is Ti–36Nb–1.4Ta–2.8Zr–0.3O (wt.%), in which $\{211\}<111>$ twinning is expected to occur. The least stable group is Ti–36Nb–2Ta–3Zr (wt.%), in which $\{332\}$ twinning and stress-induced $\alpha''$ martensitic transformation are expected to occur.

Firstly, the effect of $\omega$ phase on the deformation mechanism of gum metal was investigated. A large number of nanometer-sized $\omega$ particles were introduced into the gum metal samples by furnace cooling following high-temperature homogenization. Tensile tests and SEM analyses reveal all the special deformation features (e.g., rather low work hardening, large elongation to fracture, plastic flow localization and pronounced surface steps) which were attributed to an unconventional dislocation-free deformation mechanism in the original reports. TEM analyses illustrate that the main deformation induced microstructures, i.e., the deformation bands (similar to the originally-reported giant faults) where plastic flow is localized, are dislocation channels that are devoid of $\omega$ phase. The removal of $\omega$ phase by deformation is also confirmed in cold rolling and SXRD experiments, which show that 60% cold rolling can remove all the $\omega$ particles.
in the as-homogenized gum metal. EBSD plane trace analysis demonstrates that the channel planes are \{112\}. Based on the experimental observations, a \{112\}<111> dislocation dissociation mechanism is proposed to account for the $\omega \rightarrow \beta$ transformation and the dislocation–$\omega$ phase interaction is discussed accordingly. It is demonstrated that although the $\omega$ particles can be removed by the glide of a series of partial dislocations on \{112\} slip planes, they act as dislocation obstacles on other slip planes (\{110\} and \{123\} planes). Thus, the dislocation channeling phenomenon is attributed to the combinatorial effects of dislocation obstacles and their removal on certain slip planes.

In Ti–36Nb–1.4Ta–2.8Zr–0.3O alloy (valence electron number $e/a = 4.23$), TEM analyses demonstrate that \{211\}<111> twinning can induce the $\beta \rightarrow \omega$ transformation, leading to the formation of plate-like $\omega$ phase along the twin boundaries. Considering that similar plate-like $\omega$ phase can also be induced by the $\beta \rightarrow \alpha''$ transformation in the $\beta$ Ti–Nb-based alloys with $e/a = 4.22–4.24$, it is deduced that the $\beta \rightarrow \omega$ transformation is induced by the \{211\}<111> atomic shear associated with \{211\}<111> twinning or with $\beta \rightarrow \alpha''$ transformation. Ab initio exact muffin-tin orbitals method and the linear elastic conclusion theory were employed to calculate the energetic pathway of the $\beta \rightarrow \omega$ transformation. The theoretical results illustrate that the $\omega$ phase is thermodynamically more stable than the $\beta$ phase for these alloys. Nevertheless, a distinct energy barrier is present along the energetic pathway, which prevents a spontaneous transformation from $\beta$ to $\omega$. The energy barrier is mainly contributed by the lattice rearrangement, while the elastic contribution associated with lattice parameter misfit is negligible. It is revealed that the \{211\}<111> atomic shear can act as an external stimulus in overcoming the energy barrier, clarifying why plate-like $\omega$ phase forms along the \{211\}<111> twin boundary or $\beta/\alpha''$ interface.
Lastly, the mechanism of \{332\} twinning was investigated in Ti–36Nb–2Ta–3Zr alloy. Tensile tests were conducted to induce the formation of \{332\} \(\beta\)-twins. The three-dimensional microstructures of these \(\beta\)-twins were characterized by using SEM, EBSD and TEM. Apart from the straightly aligned parallel dislocations within the \(\beta\)-twin, it was observed that an \(\alpha''\) martensite band is embedded inside the \(\beta\)-twin near the surface, implying a strong correlation between \(\beta \rightarrow \alpha''\) martensitic transformation and \{332\} twinning. HRTEM observations show that the \(\beta\)-twin/\(\beta\)-matrix interface is nearly coherent, but it is not straight at the atomic scale. The lattice parameters measured by SXRD reveal a relatively small shape change in crystal structures from \(\beta\) to \(\alpha''\). In situ SEM experiments illustrate that the twins initiate both at grain boundaries and within grain interiors and the twins propagating to the opposite directions can merge when their lateral twin boundaries impinge on each other. EBSD analyses before and after annealing at 900 °C demonstrate that the \(\alpha''\) martensite band transforms into the adjacent \(\beta\)-twin rather than into the \(\beta\)-matrix during annealing, indicating that \(\alpha''\) martensite acts as the initiation site of \{332\} twin. This is consistent with the constitution of the \(\beta\)-twin in the initial stage of its formation, where the first portion formed consists of \(\alpha''\) martensite. During annealing, detwinning of the \(\beta\)-twins occurs as well, which starts from the twin tip rather than from the lateral twin boundary. Based on the experimental observations, an \(\alpha''\)-assisted twinning mechanism is proposed, i.e., \{332\} twin initiates within progressively formed stress-induced \(\alpha''\) martensite. The nature of the \(\beta \rightarrow \alpha''\) transformation was explored by employing the phenomenological theory of martensitic transformation and the parallel dislocations within the \(\beta\)-twins are considered as being inherited from the interface dislocations at the \(\alpha''\) martensite twin boundaries.
6.2 Suggestions for future work

The experimental and theoretical results of this dissertation have provided some new insights into the deformation mechanisms of metastable β titanium alloys, especially the effects of metastable phases (ω and α”) on the conventional deformation modes (dislocation slip and deformation twinning). These results also point to the requirement of further studies on the following issues.

(1) In metastable β titanium alloys the hardening effect of ω phase has been put aside for long time, since this phase has long been considered to result in embrittlement. The present work illustrates that embrittlement is absent for rather small ω particles (~2.8 nm), i.e., this deleterious effect may be dependent on the size of the ω phase. It is required to determine the critical size above which embrittlement is induced, facilitating the use of the hardening effect of ω phase.

(2) The good ductility of ω-enriched gum metal (with elongation to fracture more than 30%) is to a large extent due to the formation of tangled dislocation configurations within the ω-devoid channels. Theoretical simulations or in situ TEM experiments should be performed to clarify how such dislocation configurations are developed.

(3) Normally the population of {211}<111> twin in metastable β titanium alloys is relatively small, leading to limited TWIP effects. A detailed analysis of the critical resolved shear stress for this twinning mode and for other deformation modes, such as <111> dislocation slip and {332} twinning, would help in clarifying why the {211}<111> twining cannot serve as the predominant deformation mode.

(4) For the {332} twinning mode, the atomic movements involved in the α”-assisted twinning process, i.e., the β-matrix → α” → β-twin process, are not yet clear. Such atomic details are
critical in illustrating (i) how the detwinning and reorientation of the twinned \(\alpha''\) martensite structure result in the \{332\} twinning relationship and (ii) why the \(\alpha'' \rightarrow \beta\) transformation promotes the formation or the preferential growth of one specific \(\omega\) variant.

(5) The present work demonstrates that the parallel \{332\} twins propagating into the opposite directions can merge together when they impinge on each other. Nonetheless, no attempt has been made to study the interaction of non-parallel \{332\} twins. Such interactions are expected to play an important role in affecting the mechanical properties.

(6) It has been recognized that there is a general trend in the transition of deformation mechanism with the decrease of \(\beta\) phase stability, i.e., \(<111>\) dislocation slip \(\rightarrow\) \{211\}<111> twinning \(\rightarrow\) \{332\} twinning. The present work reveals that some new features accompanying these mechanisms occur due to the existence of metastable phases (\(\omega\) and \(\alpha''\)). Thus, determining the composition ranges for the occurrence of these deformation mechanisms and of the metastable phases will be valuable when designing metastable \(\beta\) titanium alloys for improved mechanical properties.
Bibliography


I. Gutierrez-Urrutia, D. Raabe. Dislocation and twin substructure evolution during strain hardening of an Fe–22 wt.% Mn–0.6 wt.% C TWIP steel observed by electron channeling contrast imaging, Acta Materialia 59 (2011) 6449-6462.


## Glossary

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>bcc</td>
<td>body-centered cubic</td>
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<tr>
<td>BF</td>
<td>bright-field</td>
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<tr>
<td>BSE</td>
<td>backscattered electron</td>
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<tr>
<td>CRSS</td>
<td>critical resolved shear stress</td>
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<tr>
<td>DB</td>
<td>deformation band</td>
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<tr>
<td>DC</td>
<td>dislocation channeling</td>
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<tr>
<td>DF</td>
<td>dark-field</td>
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<tr>
<td>DIC</td>
<td>digital image correlation</td>
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<tr>
<td>EBSD</td>
<td>electron backscatter diffraction</td>
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<tr>
<td>ECCI</td>
<td>electron channeling contrast imaging</td>
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<tr>
<td>EDM</td>
<td>electron discharge machining</td>
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<tr>
<td>EMTO</td>
<td>exact muffin-tin orbitals</td>
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<tr>
<td>fcc</td>
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<tr>
<td>FFT</td>
<td>Fourier filtered transformation</td>
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<td>FIB</td>
<td>focused ion beam</td>
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<tr>
<td>GB</td>
<td>grain boundary</td>
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<tr>
<td>GND</td>
<td>geometrically necessary dislocation</td>
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<tr>
<td>hcp</td>
<td>hexagonal close-packed</td>
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<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
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<tr>
<td>IPF</td>
<td>inverse pole figure</td>
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<tr>
<td>IQ</td>
<td>image quality</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>KAM</td>
<td>kernel average misorientation</td>
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<td>OM</td>
<td>optical microscopy</td>
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<tr>
<td>PLC</td>
<td>Portevin-Le Chatelier</td>
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<tr>
<td>PTMT</td>
<td>phenomenological theory of martensitic transformation</td>
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<tr>
<td>SAD</td>
<td>selected area diffraction</td>
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<tr>
<td>SE</td>
<td>secondary electron</td>
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<tr>
<td>SEM</td>
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<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
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<tr>
<td>SXRD</td>
<td>synchrotron X-ray diffraction</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>TWIP</td>
<td>twinning-induced plasticity</td>
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