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A Review of In Situ Observations of Deformation-Induced \( \beta \leftrightarrow \alpha'' \) Martensite Transformations in Metastable \( \beta \) Ti Alloys

Frank Niessen and Elena Pereloma*

This review summarizes the current knowledge on the \( \alpha'' \) martensite transformation in metastable \( \beta \) Ti alloys under different stress state conditions gained using various in situ techniques that range from the meso- to the nanoscale. Compared to ex situ observations, in situ observation can be conducted on a single region while changing external stimuli, and are therefore capable of elucidating the interim microstructural evolution. The strengths and shortcomings of different techniques to give insight into the martensitic transformation are identified. Both the formation of \( \alpha'' \) martensite and its reversion on load removal are addressed. The phenomena of \( \alpha'' \) martensite formation including preferential nucleation sites, its growth, interactions, and variant selection are described. The review also discusses the details of the macro- and micro-level mechanical behavior caused by the phase transformation and highlights the research questions for further investigation.

1. Introduction

A class of metastable \( \beta \) Ti alloys accommodates plastic deformation not only by slip, but also by the activation of twinning and deformation-induced phase transformations.\(^{[1-4]} \) As a result of the latter two accommodation mechanisms, a dynamic Hall–Petch effect and hetero-deformation-induced hardening produce extensive strain hardening.\(^{[5-8]} \) These alloys also exhibit an excellent combination of strength and ductility, thus attracting significant interest both from scientists and product developers. The design of new alloys within this class is generally based on the “d-electron” approach depicted in the so-called Morinaga’s diagram and its extended version\(^{[9-11]} \) (Figure 1), in which the fields of operation of twinning, slip, and deformation-induced martensite formation are outlined. The initiation of one or another plastic deformation accommodation mechanism or their combination depends on the stability of the \( \beta \) phase, which is defined by several factors. These include composition, \( \beta \) grain size (or \( \beta \) domain size in where the microstructure consists of \( \beta \) and \( \alpha \)), orientation (or texture) of \( \beta \) grains, and the deformation conditions (mode of loading, strain rate, temperature, etc.).\(^{[1,12-18]} \) The molybdenum equivalent (\( \text{Mo}_{eq} \)) parameter can also be applied to predict the \( \beta \) phase stability.\(^{[19,20]} \) but this approach, which bears similarities to the Morinaga’s diagram, only accounts for the effect of the composition. Thus, both these approaches provide only a basic prediction for the operation of deformation mechanisms and do not take into account the previous processing history, presence of additional phases, solute interactions, or deformation conditions. According to Kolli et al.,\(^{[20]} \) the formation of deformation-induced \( \alpha'' \) martensite has been observed in alloys with \( \text{Mo}_{eq} \) in the range from 3% to 20%.

As a very complex sequence of deformation accommodation mechanisms can produce hierarchical microstructures in such alloys,\(^{[6,13,21,22]} \) the in situ characterization of these events is critical to obtaining a better understanding of each mechanism and their interactions. In situ observations enable tracking the microstructural evolution on a particular site of interest while external stimuli are applied, and can therefore reveal the interim microstructural evolution. Such indispensable data allows to further advance the development of these attractive alloys for a wide range of industrial applications. As this is a very wide topic, this review will mainly focus on deformation-induced \( \alpha'' \) martensite formation.

2. Fundamentals of the \( \beta \)-to-\( \alpha'' \) Martensitic Transformation

Compositions of all alloys in this review are given in wt\%, with exception of Ti–Nb-based alloys, which are given in at\%. Exceptions from this convention will be explicitly stated.
2.1. Crystallography and Morphology

In Ti-alloys with low to medium β phase stability, deformation-induced α″ martensite (orthorhombic crystal structure) forms from the β phase (body–centered cubic (bcc)) upon reaching the required triggering stress. This phase transformation follows the Burgers orientation relationship (OR)\(^{[23,24]}\)

\[
\frac{1}{2} [100]_{\alpha''} \parallel \frac{1}{2} [110]_{\beta} \parallel [011]_{\alpha''} \parallel [011]_{\beta}
\]

The lattice correspondence between β and α″ is shown in Figure 2.

The intrinsic structure of martensite plates typically depicts columnar domains perpendicular to the habit plane. Their formation was linked to the alternating directions of atomic shuffle taking place during β→α″ transformation.\(^{[27]}\) When athermal ω is present in the β matrix, then an additional atomic shuffle could be incorporated in these domains.\(^{[28]}\)

The phenomenological theory of martensite crystallography (PTMC) is commonly used to predict the habit planes of α″ plates based on invariant-line strain theory.\(^{[29,30]}\) Chai et al.\(^{[26]}\) predicted the habit planes for Ti–20at%Nb to be of \(\{755\}\) type and found consistent habit planes experimentally with single trace analysis in transmission electron microscope (TEM). This habit plane type was also found experimentally in Ti–27Nb,\(^{[31]}\) Ti–24Nb–4Zr–8Sn\(^{[32]}\) and Ti–12Mo alloys.\(^{[13]}\)

In Ti–10V–2Fe–3Al the habit plane was determined as \(\{543\}\) from electron backscatter diffraction (EBSD) single trace analysis.\(^{[34]}\)

To accommodate the transformation strains, there is a tendency for martensite plates to form self-accommodating arrangements in the form of perpendicularly intersecting plates, zigzag (V-shaped), or triangular morphologies. During deformation of α″ martensite, the accommodation of

### Table 1. Lattice correspondence variants for the β and α″ crystals.

<table>
<thead>
<tr>
<th>Variant</th>
<th>([100]_{\alpha''})</th>
<th>([010]_{\alpha''})</th>
<th>([001]_{\alpha''})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>([100]_{\beta})</td>
<td>([011]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
</tr>
<tr>
<td>II</td>
<td>([100]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
</tr>
<tr>
<td>III</td>
<td>([010]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
</tr>
<tr>
<td>IV</td>
<td>([010]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
<td>([0\overline{1}T]_{\beta})</td>
</tr>
<tr>
<td>V</td>
<td>([001]_{\beta})</td>
<td>([1\overline{1}0]_{\beta})</td>
<td>([T\overline{1}0]_{\beta})</td>
</tr>
<tr>
<td>VI</td>
<td>([001]_{\beta})</td>
<td>([1\overline{1}0]_{\beta})</td>
<td>([T\overline{1}0]_{\beta})</td>
</tr>
</tbody>
</table>

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strain could be accomplished by the formation of \{110\}_{α''} \[31,33–37\] or \{110\}_{α''} \[38\] twins.

### 2.2. Variant Selection and Variant Pairing

Although six equivalent crystallographic variants could form during \(β → α''\) transformation (Table 1), the interaction of the stress field with the transformation strains during deformation-induced \(α''\) martensite selection leads to variant selection. It is generally accepted that the variants that can accommodate the most stress by their transformation strain will nucleate and grow.\[39\]

This stress accommodation is expressed by the available work \((U)\) done by the applied stress \((σ)\) on the martensitic transformation system with a shape strain \((P)\) \[36\]

\[
U = \text{tr}(Pσ)
\]

where \(\text{tr}(X)\) is the trace function. The transformation strain of a variant can be determined with PTMC theory or approximated with the Bain strain \((P_B)\)

\[
P_B^α = \begin{bmatrix}
λ_1 & 0 & 0 \\
0 & λ_2 & 0 \\
0 & 0 & λ_3
\end{bmatrix}
\]

and \(P_B^β = \begin{bmatrix}
λ_1 & 0 & 0 \\
0 & λ_2λ_α^{1/2} & λ_2λ_α^{1/2} \\
0 & λ_2λ_α^{1/2} & λ_2λ_α^{1/2}
\end{bmatrix}\)

(3)

with the principal lattice strains being

\[
λ_1 = \frac{a_{α''} - a_0}{a_0}, \quad λ_2 = \frac{b_{α''} - \sqrt{2}a_0}{\sqrt{2}a_0} \quad \text{and} \quad λ_3 = \frac{c_{α''} - \sqrt{2}a_0}{\sqrt{2}a_0}
\]

(4)

The transformation strain matrices in (3) are given for variant 1, and the matrices for the remaining variants are obtained by rotation according to the lattice correspondences in Table 1. A high magnitude of available work is associated with favorable conditions for the formation of a variant. The often-used Schmid factor analysis\[40,41\] is a simplified version of this analysis, in which the resolved stress on a transformation system is determined by the angle between the shearing direction and the habit plane normal of the transformation system with a uniaxial stress axis.

\(α''\) plates can form in \{011\}_{α''} compound twins,\[36,39\] in \{111\}_{α''} type I twins,\[26,36,39,42\] or in \{211\}_{α''} type II twin relationships.\[26,36,39,42\] Compound twins only occur between variants that share the same shear plane, which is the case for variant pairs \(V1\text{–}V2\), \(V3\text{–}V4\), and \(V5\text{–}V6\) in Table 1.\[39\] When compound-twin-related variants are favored, they have high available work, and can therefore be predicted confidently.\[34\] Type I and II twinning systems usually dominate when variants form in self-accommodation during athermal martensite formation\[26,35,42\] or when the formation of no single variant is particularly feasible during deformation-induced martensite formation.\[34\] The operation of variant selection during deformation-induced \(β → α''\) transformation dictates the \(α''\) martensite texture.

### 2.3. Effect of Alloy Composition on \(α''\) Martensite Characteristics

Lattice parameters of \(α''\) martensite depends on the presence of specific alloying elements, as well as its morphology (dislocation or twinned) and habit plane. A summary was provided by Pinilla Ducreux et al.\[43\] and selected examples for deformation-induced \(α''\) martensite are included in Table 2.

To study \(α''\) martensite formation in metastable \(β\) Ti-alloys during deformation, the athermal \(α''\) martensite start temperature should be below room temperature. For the Ti–Nb system, it was established that at Nb levels below 25.5 at% athermal \(α''\) martensite forms above room temperature.\[44\] Thus, for these alloys, the compositions should have either >25.5 at% Nb or other \(β\)-stabilizing elements (for example, Fd\[45\]) should be added.

### 2.4. Double-Yielding Phenomenon

In alloys with fully metastable \(β\), \(β + ω_{α''}\), or \(β + ω_{α''} + α(<30%)\) initial microstructures subjected to tensile or compressive loading, \(β → α''\) martensite transformation leads to a more or less distinctive double yielding behavior (Figure 3). The so-called triggering stress (defined in the inset of Figure 3b) was introduced as the characteristic for the start of \(α''\) martensite formation.\[2\] The triggering stress is composition-dependent and increases with an increase in \(β\) phase stability. A decrease in grain (or domain) size of the parent \(β\) phase also increases the triggering stress as the accommodation of the shape changes associated with martensite phase formation becomes more difficult and martensite start transformation temperature is decreased.\[44\] For example, with an increase in Nb content and a decrease in \(β\) domain size, the triggering stress was reported to increase from 180 to 309 MPa.\[13\] The conditions under which deformation is applied together with simultaneously operating deformation mechanisms have a pronounced effect on triggering stress. Prolific slip operation in addition to martensite formation will mask the appearance of a stress plateau on the stress–strain curve. An increase in strain rate leads to a significant increase in triggering stress: in Ti–10V–2Fe–3Al and Ti–10V–3Fe–3Al alloys, the triggering stress is more than doubled when the strain rate is increased by four orders of magnitude from \(10^{-3}\) to \(10^{-1}\) s\(^{-1}\).\[14,49\]
However, this trend is not followed at very high strain rates exceeding $10^3$ s$^{-1}$.\cite{50} The deformation path also affects both the triggering stress and the yield stress of metastable $\beta$ Ti-alloys due to the asymmetry of deformation-induced martensite formation.\cite{49,51} For example, the values of 268 MPa under tension and 203 MPa under compression were reported for an annealed Ti–10V–2Fe–3Al alloy consisting of $\beta$ phase only.\cite{49}

Martensite transformation starts in the elastoplastic transition region (Region II in Figure 3c,d) and dominates until the second yield point (Figure 3b). Prolific formation of martensite ($\approx$70\%) in the slow stress rising region (Region III in Figure 3c,d) corresponds to a significant increase in work hardening rate. This is typically explained by the dynamic Hall–Petch effect.\cite{5,53} After $\alpha''$ martensite formed, it is also subjected to deformation, which becomes the dominant process at later stages of deformation (Figure 3b).

3. X-Ray, Synchrotron and Neutron Diffraction Studies

In situ X-Ray diffraction (XRD), synchrotron X-Ray diffraction (SXRD), and neutron diffraction (ND) studies are commonly used to gain insight into deformation accommodation mechanisms in alloys exhibiting phase transformation during loading. A number of publications described the $\alpha''$ martensite formation in metastable $\beta$ Ti–Nb-based,\cite{45,52,54–59} Ti–Zr–Nb,\cite{60} Ti–Mo-based,\cite{61} Ti–2Al–4.8Mo–6.3V–7.7Cr,\cite{62} Ti–5Al–5V–3Mo–3Cr,\cite{63} and Ti–10V–2Fe–3Al alloys.\cite{43} The X-Ray sources used in laboratories have limitations compared to neutron and synchrotron X-Ray sources due to their relatively large wavelength, low intensity, and presence of both $K_{\alpha1}$ and $K_{\alpha2}$ wavelengths make it difficult to separate the major peaks of $\beta$ and $\alpha''$ martensite. Thus, the use of neutron or synchrotron sources provides a better avenue for

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**Figure 3.** a) Stress–strain curves for T–17Nb–1Fe, b) Ti–24Nb–0.5N, and c) Ti–10V–2Fe–3Al alloys subjected to uniaxial tensile loading. d) Evolution of volume fractions of phases with strain in Ti–10V–2Fe–3Al alloy. Inset in (a) is diffraction in the axial direction at $\approx$3% strain showing $\alpha''$ martensite reflections (arrowed). Inset in (c) demonstrated triggering stress determination. (a) adapted with permission.\cite{45} Copyright 2017, Elsevier; b) reproduced with permission.\cite{52} Copyright 2015, Elsevier.; c,d) reproduced with permission.\cite{43} Copyright 2021, Elsevier.
studies of $\alpha''$ martensite under applied load. Generally, such high-energy sources are required to conduct measurements in transmission geometry, which is necessary for determining the evolution of the bulk rather than the surface microstructure.

All XRD, SXRD, and ND studies agree on the formation of $\alpha''$ martensite taking place upon reaching the first yield point for a particular alloy. The evolution of the volume fraction of $\alpha''$ martensite with increasing stress/strain is easily followed (Figure 3d). It is also reported that in many alloys the formation of martensite occurs simultaneously with $\beta$ grain reorientation, and $\alpha''$ martensite forms initially only in the $\beta$ grains that are favorably oriented. For example, $\beta$ grains oriented with {200} planes perpendicular to the compression axis exhibit such preferential phase transformation.\(^{[63]}\) Consistent with the orientation relationship, also the {200}$_\alpha$ planes have a strong preferential orientation perpendicular to the compression axis.

As mentioned in Section 2.2, during deformation the martensite variants with the highest transformation strain will form in favorably oriented grains. The maximum transformation strains depend on the lattice parameters of each phase (alloy composition) and can be calculated for various crystallographic directions using the lattice parameters determined from XRD, ND, or SXRD experiments. For example, corresponding to the three principal crystallographic directions of the bcc $\beta$ phase the maximum transformation strain values could be calculated using the following equations\(^{[44,46,64]}\)

$$
\varepsilon_{110} = \frac{b_\alpha - \sqrt{2}a_\beta}{2a_\beta} \tag{5}
$$

$$
\varepsilon_{001} = \frac{\sqrt{b_\alpha^2 + c_\alpha^2} - 2a_\beta}{a_\beta} \tag{6}
$$

$$
\varepsilon_{111} = \frac{\sqrt{a_\alpha^2 + b_\alpha^2} - 3a_\beta}{3a_\beta} \tag{7}
$$

where $a_\beta$ is the lattice parameter of $\beta$ and $a_\alpha$, $b_\alpha$, and $c_\alpha$ are the lattice parameters of $\alpha''$. The maximum transformation strain for any crystallographic direction is given by\(^{[46]}\)

$$
\varepsilon_{1[1d]} = \frac{|x(V)| - |x|}{|x|} \tag{8}
$$

where $x$ is any vector of the $\beta$ phase that transformed during $\alpha''$ martensite transformation to $x(V)$ by

$$
x(V) = T(V)x \tag{9}
$$

where $T(V)$ is the lattice distortion matrix expressed in the coordinates of the $\beta$ phase for each variant $V$. Based on these calculations, the inverse pole figure (IPF) distribution of maximum transformation strains was obtained for a variety of alloys, and the example of a Ti–24Nb–4Zr–8Sn alloy is shown in Figure 4. The reported data for Ti–10Nb, Ti–10Nb–20Zr and Ti–10Nb–20Ta\(^{[47]}\) as well as for Ti–20Zr–3Mo–3Sn and Ti–24Nb–4Zr–8Sn\(^{[46,65]}\) agree in that the maximum transformation strain is along the (011)$_\beta$ direction, which corresponds to the (010)$_{\alpha''}$ direction. The transformation strain decreases when directions are changed toward (001)$_\beta$ or (111)$_\beta$ directions, with minimum values obtained along (111)$_\beta$ directions.

Formation of strong a {041}$_{\alpha''}$ texture was observed in a Ti–17Nb–1Fe alloy, normal to [0 1.7 0.46], only $\approx 3^\circ$ from the (031)$_{\alpha''}$ (Figure 5a). A strong (210)$_\beta$ texture is present, which corresponds to (012)$_\beta$–(031)$_{\alpha''}$ according to the orientation relationship. Furthermore, this transition results in the largest transformation strain of $\approx 4\%$ for this alloy and the most effective accommodation of the axial deformation stress, which underpins this variant selection for (210)$_\beta$ grains.\(^{[45]}\) Similarly, in Ti–10V–2Fe–3Al alloy, strong (021)$_{\alpha''}$ texture forms from (210)$_\beta$ (Figure 5b), with (021)$_{\alpha''}$ being $\approx 5^\circ$ from (031)$_{\alpha''}$.\(^{[43]}\)

XRD, ND, and SXRD studies provide a useful insight into bulk material behavior during deformation including the initiation and extent of $\alpha''$ martensite formation, its preferred texture, and response to deformation. As Ti alloys generally exhibit very coarse $\beta$ grain sizes (>100 $\mu$m), there is a limitation on the number of grains detected depending on the analyzed volume. In this respect, ND has an advantage over XRD and SXRD. However, the precise information on martensite nucleation, growth and interactions, and its crystallographic characteristics is lacking in all these techniques. Therefore, in situ microstructure evolution observations by electron microscopy are essential and will be addressed in the following sections. Recent developments towards more powerful 3D X-Ray microscopy will likely make X-Ray-based methods suitable for local in situ observations on the microstructural level in the future.\(^{[66,67]}\)

4. EBSD Studies

Over the past two decades, EBSD has become the dominant characterization technique in the scanning electron microscope (SEM) for mapping orientations and phases of deformation and transformation microstructures.\(^{[48]}\) Only within recent years, EBSD matured into a more common technique for in situ experiments. In situ EBSD studies on deformation-induced $\alpha''$ formation in Ti-alloys in particular, were only published after 2019. An exception is a study by Mao et al.\(^{[49]}\) from 2008, in which a strip of TiNi shape-memory alloy was exposed to a constant bending...
strain by a clamping mechanism. The increased use of EBSD as an in situ technique is mainly due to the development of purpose-made in situ deformation stages optimized for use in scanning electron microscopes, improved electron beam optics, and a gradual increase in the acquisition rate of EBSD detectors.

In situ EBSD studies are often combined with other imaging modes in an SEM. Even using the latest state-of-the-art EBSD detectors, the acquisition of EBSD maps takes several minutes to hours, so faster imaging modes such as forward-scatter electron imaging can be utilized to capture dynamic events during loading or unloading. In contrast to nano-scale samples in in situ transmission electron imaging can be utilized to capture dynamic events during loading or unloading. In comparison to X-Ray and neutron powder diffraction techniques, which acquire average bulk planar spacings of the phases, EBSD acquires spatially resolved orientation and phase maps of microstructures on the sample surface. The mechanical constraints for these techniques are, therefore, essentially different, which needs to be taken into consideration in the interpretation of in situ experimental data. In contrast to nano-scale samples in in situ transmission electron microscopy, the dimensions of samples for in situ EBSD are commonly several hundred μm, so that, depending on the β-grain size, the observed mechanisms are considered to be constrained in the in-plane direction by the bulk. In situ EBSD is an ideal technique to acquire spatial maps of the microstructural evolution during applied deformation, which may reveal the direct interaction of microstructural features with each other. Thus, EBSD can give important insights into nucleation sites for deformation-induced α” formation, interaction of α” with surrounding microstructural features and reverse α” to β transformation during unloading. The orientation data obtained from EBSD is also ideal to apply the Schmid factor or available work analysis, to predict the potency of different martensitic variants in β-grains as a function of stress. Here the local stress within the β grains is often assumed to be equal to the applied stress, which is only a suitable assumption at low magnitudes of applied uniaxial stress.

As stated in Section 2.2, α” variants may form in different twin relationships with each other. Deformation of α” may also be accommodated by \{130\}\langle30\rangle_α twinning within formed α” plates. In EBSD datasets, these twin boundaries can be detected by comparing the local boundary misorientation with the characteristic misorientations of these twins, as listed in Table 3.

To date, only few publications reported in situ EBSD observations of deformation-induced α” formation in Ti–10V–2Fe–3Al, Ti–50.8at%Ni and Ti–24Nb–4Zr–8Sn alloys and a combination of deformation-induced α” formation and deformation–twinning in β in Ti–12Mo, Ti–12Mo–xZr, Ti–10V–4Cr–1Al and Ti–10V–2Fe–3Al alloys. As this narrow selection of studies features different compositions, heat treatments, load cases, and map sizes, there is limited information to draw general conclusions from. It, however, appears that the general mechanisms of deformation-induced martensite formation observed in these

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Transformation product & Misorientation axis & Misorientation angle \\
\hline
\{011\}_α^- Compound twin & \{100\}_α^- & 87° \\
\{111\}_α^- Type I twin & \{011\}_α^- & 96° \\
\{211\}_α^- Type II twin & \{011\}_α^- & 84° \\
\{130\}\langle30\rangle_α depletion twin & \{001\}_α^- & 57° \\
\hline
\end{tabular}
\caption{Characteristic misorientations of the most common transformation products given by misorientation axis and angle.}
\end{table}
studies at similar β stability are independent of the exact alloy composition. We, therefore, chose to present the generally observed microstructural evolution during deformation-induced α″ formation.

Figure 6 features a typical sequence of α″ formation during tensile loading, specifically for a Ti–12Mo–3Zr alloy.[37] In initially pure β alloys, α″ plates nucleate at β grain boundaries and grow in length and width with further loading. In the case of initial β–α microstructures, the β–α interfaces appear to be the most favorable nucleation sites for α″.[34,73] In the absence of α, also β-twin boundaries were observed as preferred nucleation sites for α″.[37] Niessen et al.[34] showed that the first forming variants are generally compound twin-related variants that have particularly high available work for the martensitic transformation. When impinging upon other α″ plates or a β grain boundary, the growth only advances by widening of a plate.[34,72]

Impingement with β boundaries also triggers the formation of new α″ plates in the neighboring β grain, which is termed sympathetic nucleation.[34,72] Upon further loading, the transformation strain and the elastic incompatibility of the β grains with each other lead to inhomogeneous stress fields that trigger the formation of additional variants in each β grain. At this stage, also grains that were aligned unfavorably for martensite formation begin to transform via Type I and Type II twin-related variants in self-accommodating morphologies.[34] At this stage, the interaction of α″ plates with each other[34,41] and deformation twinning[31,34,41,72] become prominent features of the increasingly complex microstructure. An example of the formation of deformation twins is evident from the different coloring of α″ plates in the orientation maps for ε = 2% and ε = 4% in Figure 6. In some alloys, these deformation twins revert to their original martensitic variant upon unloading, as visible in Figure 6 and discussed in more depth in section 6. A combination of forward-scatter electron imaging and EBSD mapping revealed that {130}⟨3T0⟩α″ deformation twinning can also be activated by impingement of growing α″ plates (Figure 7).[34]

In this particular observation, the deformation twins did not revert during unloading.

Regarding the prediction of martensitic variants with applied load, Niessen et al.[34] Qian et al.[41] and Mao et al.[40] all found reasonable agreement between the variants predicted by a Schmid law/available work approach and the experimentally observed variants. Poor agreement was however found for variants that formed by sympathetic α″ nucleation across several β-grain boundaries and, in the case of Niessen et al.[34] and Qian et al.[41] for a complex interaction of the transformation products.

Regarding the effect of β stability on the transformation behavior, Qian et al.[37] studied the effect of adding 3, 6, and 10 wt% Zr to a metastable β Ti-12Mo alloy on the prevalent transformation modes. The Zr addition was associated with an increase in yield strength from 540 MPa at 3 wt% Zr to 740 MPa at 10 wt% Zr and similar ductility. While the Ti–12Mo–3Zr alloy revealed similar transformations characteristics to the Ti–12Mo alloy,[41] the addition of 6 wt% Zr led to {332}⟨113⟩β twinning, a reduced amount of deformation-induced martensite formation and no {130}⟨3T0⟩α″ deformation twinning, and addition of 10 wt% Zr suppressed deformation-induced martensite formation entirely. Combined deformation twinning and deformation-induced martensite were also investigated by Lilensten et al.[27] by in situ EBSD tensile testing on a Ti-10V-4Cr-1Al alloy. The tendency of β-grains to transform by deformation twinning or martensite formation was found to be linked to their orientation, manifesting in...
largely separated regions for both transformations. Martensite formation was generally most prominent at lower strain (≈5–12%) and was mostly saturated at higher strain (≈12–35%).

Regarding the role of the stress state, the in situ bending tests by Mao et al. [40] and Niessen et al. [34] indicated that the α00 morphology was not affected by either dominating tensile or compressive stress and that the variant selection could be predicted with similar confidence for either of these stress states.

In overall, in situ EBSD mapping of deformation-induced martensite formation has led to a more complete understanding of the microstructural evolution during loading (and unloading). While the initial stage of nucleation and growth gives a consistent picture that can readily be interpreted with computational modeling tools, the interaction of transformation products at higher deformation levels and the interaction of stress states in adjacent β grains still provide a complex picture that demands a more substantial computational modeling effort. It also remains to be clarified how far the missing mechanical constraint of the bulk in surface characterization techniques such as EBSD is responsible for the low predictability of the deformation and transformation behavior at increased levels of deformation. Here, 3D X-Ray microscopy techniques could provide a pathway to gain further insights in the future. [66, 67]

A limitation of EBSD as a characterization technique is its spatial resolution limit of ≈10 nm, which only enables the confident mapping of grains that are larger than 50 nm in their smallest dimension. [68] Therefore, detailed observation of the events at the atomic scale cannot be characterized using EBSD. The recent advent of transmission Kikuchi diffraction (TKD), which is a transmission-based technique and which shares many similarities with EBSD in its hardware and processing routines, could help to provide orientation maps at higher resolution. [74, 75] The trade-off when choosing TKD over EBSD would be a reduced area amenable to mapping and the loss of the in-plane mechanical constraint of a bulk material when working on electron-transparent foils. In terms of its spatial resolution, transmission electron microscopy is the dominant in situ technique for investigating the microstructural changes induced during martensite formation at the atomic scale.

5. Transmission Electron Microscopy Studies

A very limited number of researchers attempted the difficult task of observing β→α” transformation in a TEM. In situ testing at the nanoscale was predominantly achieved via single crystal pillar compression testing, [31, 76–78] but also by tensile testing. [12, 79] Formation of α” martensite in a single β crystal was observed in Ti–10V–2Fe–3Al alloy at ≈10% strain under compression in 011p direction following slip and reversion of one α variant within the slip band (Figure 8). The delay of the onset of martensite formation to higher strain compared with bulk observations was attributed to the orientation-sensitivity of martensite

Figure 7. a–d) Forward-scatter electron image series showing an example of {130}@{370},, deformation twinning with increasing bending load. 
(a) Formation of first vertical variant (dark plate); b) Formation of second vertical variant and two horizontally nucleated or impinged variants; c) Local deformation of the vertical variants by predominant thickening of the impinged variants; d) Heavily deformed vertical variants show contrast change at impingement points with the horizontal variants. e) Crystal orientations of α” superimposed to the band contrast map from electron backscatter diffraction (EBSD). The dashed box marks the image region in panel (d) and the inset shows two deformation twins T1 and T2 that formed in the α” matrix (M). f) Stereographic projection of the orientations in the inset in panel (e) proving the {130}@{370},, twinning relationship. Adopted with permission. [34] Copyright 2021, Elsevier.
formation and a pillar size effect (max 3 μm diameter vs 100–200 μm β grain size in a polycrystalline alloy) on the triggering stress. Furthermore, as for martensite transformation, a certain strain level is required, and the availability of a large dislocation sink at pillar surfaces will also contribute to the delay in the initiation of transformation compared to the condition within the bulk samples. It is also worth noting that different orientation relationships were determined

\[(\overline{200})_\alpha \ || (002)_\beta, (002)_\alpha || (110)_\beta \text{ and } (010)_\alpha || (1\overline{1}0)_\beta\]

(10)

An in situ TEM study\[31\] of variously oriented pillars of Ti–27Nb alloy showed that α\" martensite formation occurred with strong variant selection; depending on the grain orientation of the pillar, between 1 and 3 variants were realized. Subsequent deformation of martensite proceeded by dislocation slip along \([110]_\alpha\), dislocation slip along \([101]_\alpha\), \{130\}<1\overline{1}0\>_\alpha\ twinning, and \{103\}[\overline{3}01]_\alpha\ twinning.

In situ tensile testing of a Ti–24Nb–4Zr–8Sn (wt%) (Ti2448) alloy,\[32,79\] revealed the formation of a single martensite variant within deformation bands at lower strains, whereas two variants along different directions formed in deformation bands at higher strain (Figure 9). In the region closest to the crack tip, a set of kinked laths was formed (Figure 10). These two variants of α\" laths displayed \{111\}\{110\}_\alpha\ twin relationships with \(\frac{1}{2}[01\overline{1}]\) dislocations located at \(\approx 12.2 \text{ nm distance}\) from each other along the interfaces. As the ratio of the Burgers vector magnitude to the dislocation distance agreed well with the kink angle per unit length, it was suggested that these arrays of dislocations are responsible for the observed kinks, which partially release high local strains in the near crack tip region. Further from the crack tip in the stress concentration area, the parallel \(\approx 400 \text{ nm wide } \alpha\"\) plates formed under \(\approx 47^\circ\) to the crack propagation direction. These plates also displayed the same twin relationships with \(\approx (755)_\beta\) and \(\approx (557)_\beta\) habit planes and one variant being favored over the other based on the intensity of diffraction spots.

Qian et al.\[33\] reported the formation of α\" martensite in Ti–12Mo (wt%) alloy at 3% strain from a pre-existing boundary under tensile loading. On subsequent straining to 5%, further growth of a primary α\" martensite plate together with \{110\}<1\overline{1}0\>_α\ twinning was recorded (Figure 11). The habit plane of primary α\" martensite was determined to be \((755)_\beta\). Twinning was deemed to be favorable for providing additional shear strain for the accommodation of the local deformation.

Despite limitations of very local observations in TEM and the surface effect, the information with respect to the martensite nucleation and growth, as well as the sequence of deformation accommodation mechanisms can be elucidated by such experiments. The role of dislocations and relationships between dislocation slip and martensite formation could be uncovered, which is not possible by using the in situ experimental techniques discussed previously.
6. Reversion of α'' Martensite


The reduction in volume fraction of α'' martensite on unloading was recorded in SXRD and ND experiments. In Ti–24Nb–4Zr–8Sn alloy, the reversion of α'' martensite started on unloading from 10% tensile strain and was completed on reaching ≈3% strain with no α'' phase peaks any longer present. Partial reversion of α'' martensite (≈18%) in Ti–5Al–5Mo–5V–3Cr alloy on unloading from 4.1% compression strain was detected by in situ high-resolution SXRD. Castany et al. observed a fully α'' martensite microstructure in Ti–27Nb alloy on cyclic straining beyond 3%, whereas EBSD study of unloaded after 5% strain showed only the presence of β phase with {332}<113>β twins, indicating a full

Figure 9. Time-resolved BF TEM images recorded at 0, 43, 159, and 220 s during the in situ TEM observations under tensile loading of Ti–24Nb–4Zr–8Sn alloy. Reprinted with permission. Copyright Elsevier, 2017.

Figure 10. a) SAED pattern and b) BF TEM image obtained from the region near the crack tip along the [010]β axis in a Ti–24Nb–4Zr–8Sn alloy. c–d) DF TEM images obtained with (022)α'' and (200)α reflections from α'' variants 1 and 2, respectively. Reprinted with permission. Copyright Elsevier, 2017.
reversion of α″ martensite with previously existing \{130\}<310> α′ twins reverting to \{332\}<113> β twins according to their crystallographic relationships. Full reversion of α″ martensite to the parent β phase on load removal in a 3% tensile-strained Ti–10V–4Cr–1Al alloy was visible in situ EBSD mapping.[72] On unloading of a Ti–12Mo alloy, which was also strained to 5%, Qian et al.[41] observed unchanged arrangements of α″ martensite plates in the β matrix with an only partial reversion of \{130\}<310> α″ twins to parent α″ martensite (Figure 12). In Ti–12Mo–(3–6)Zr alloys, partial reversion of α″ martensite and \{130\}<310> α″ de-twinning was recorded upon unloading after 4% straining.[17] Qian et al.[33] also suggested that de-twinning processes on unloading could take place by \{130\}<310> α″ twins → \{110\}<T10 > α″ twins → α″ martensite. In contrast, when Ti alloys were strained to a higher level (for example, 15% in Ti–12Mo), no reversion of α″ martensite on unloading

Figure 11. In situ tensile TEM investigations of deformation-induced α″ in Ti–12Mo: a,b) bright-field image: at (a) ε = 3%, b) ε = 5%; c,d) SAED pattern taken from the region indicated by a circle in (b), and corresponding dark-field images of: e) primary α″martensite and f) 110_α″ deformation twin, respectively. SIM here indicates stress-induced martensite. Adopted from Figure 4 in ref. [33] © 2022 The Author. Published by Taylor & Francis Group.

Figure 12. a) IPF maps of Ti–12Mo alloy in 5% tensile strained condition and b) after unloading. Reprinted with permission.[41] Copyright Elsevier, 2021.
was reported in Ti-1023\textsuperscript{[34]} and Ti-12Mo\textsuperscript{[80]} alloys. It could be speculated that in alloys with superelastic behavior and a less stable \( \beta \) phase, the reversion process occurs with ease even when the fully \( \alpha'' \) martensite microstructure is formed, but the limit of strain accumulation is not reached. In the alloys with a more stable \( \beta \) phase, the extent of \( \beta \rightarrow \alpha'' \) transformation is less, and martensite is more stable. In these alloys, depending on the level of strain reached, partial or no reversion of primary \( \alpha'' \) martensite plates could take place at lower strains (up to 5\%) together with de-twinnin, whereas no reversion occurs at higher strains. The latter might be associated with the loss of \( \beta/\alpha'' \) interface coherency. However, this phenomenon requires further investigation using in situ techniques for a wider range of alloy compositions with different \( \beta \) phase stability and loading conditions.

7. Concluding Remarks

This review attempts to summarize the currently available data from in situ experiments on the \( \alpha'' \) martensite formation in a wide range of metastable \( \beta \) Ti alloys. The recent advances in these in situ techniques and in data analysis enable a more complete picture of the evolution of \( \alpha'' \) martensite structure as a function of stress and strain to be obtained. However, due to the \( \beta \) grain size being very coarse in a large number of alloys, often just examples of \( \alpha'' \) formation without sufficient statistical data have been obtained. In some cases, this is the reason for some reported controversial results. Another important factor may be that the oxygen content of alloys is rarely reported in the literature, and that already slight deviations could affect the materials’ transformation behavior. All characterization techniques that can spatially resolve the microstructure, rely on surface observations, which affect the stress state and may change the evolving microstructure compared to the bulk behavior. This deficiency could be overcome by further development of 3D-XRD and other in situ techniques that can spatially resolve phase transformations within the bulk. Obtaining better statistics in data acquisition and correlating in situ characterization with advanced modeling techniques should shine more light on the peculiarities of \( \beta \rightarrow \alpha'' \) transformations in this important class of structural materials. In addition, only a handful of alloys have been investigated using in situ techniques at different microstructural scales. Better coverage of a wider range of materials with in situ techniques across the scales would be desirable for an improved understanding of the microstructural evolution.

In-depth knowledge of this \( \alpha'' \) martensite formation phenomenon is very important for the design of new metastable \( \beta \) Ti alloys for a wide range of both structural and biomedical applications, thus fueling the research efforts in this area. Currently, several questions remain unanswered with respect to how the transformation strain during nucleation and thickening of \( \alpha'' \) plates is accommodated in the matrix, the effect of an inhomogeneous stress state on variant selection, and the role of the local stress during impingement of two \( \alpha'' \) plates on subsequent complex microstructure development, to name but a few. To uncover the answers to these questions, better integration of experimental techniques with computational methods is required. This will lead to a better understanding of how to fine-tune the transformation-induced plasticity (TRIP) effect in Ti alloys and its combination with twinning-induced plasticity phenomenon. As the operation of TRIP in Ti alloys leads to relatively low-yield-strength values, efforts should continue to better understand how to use multiphase microstructures (parent \( \beta + \alpha \) phases) or how to trigger deformation-induced \( \omega \) plate formation in order to increase the yield strength in this class of alloys.

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Conflict of Interest

The authors declare no conflict of interest.

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