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To cite this article: P. Kwasniak, F. Sun, S. Mantri, R. Banerjee & F. Prima (2022) Polymorphic nature of $\{332\}$ $\langle 113 \rangle$ twinning mode in BCC alloys, Materials Research Letters, 10:5, 334-342, DOI: [10.1080/21663831.2022.2049906](https://doi.org/10.1080/21663831.2022.2049906)

To link to this article: <https://doi.org/10.1080/21663831.2022.2049906>



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Polymorphic nature of $\{332\}\langle 113 \rangle$ twinning mode in BCC alloys

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ABSTRACT

Unprecedented mechanical properties of the novel TWIP/TRIP titanium alloys are controlled by $\{332\}\langle 113 \rangle$ twinning and stress-induced martensitic transformation, which can operate separately, simultaneously or even in synergy, following a still unclear atomic-scale mechanism. Using *ab initio* calculations and experimental observations, we show that $\{332\}\langle 113 \rangle$ twinning can be described as a polymorphic solid-state transformation able to produce either twinned or martensitic structures with a unified transformation path. The required lattice strains and atomic shuffles are provided by the shear-shuffle mechanism of twin operation, of which trajectory, due to accompanied atomic relaxation, is not linear and strongly influenced by β phase stability.

ARTICLE HISTORY

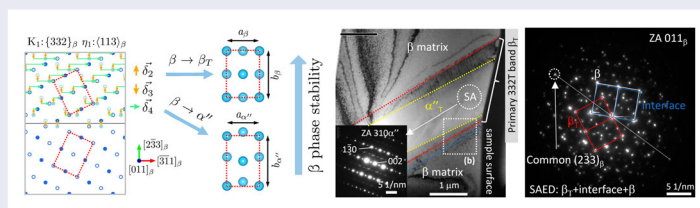
Received 17 December 2021

KEYWORDS

Titanium; BCC alloys; twinning; TWIP; TRIP

IMPACT STATEMENT

Plasticity of metastable alloys is extended by the concept of polymorphic deformation modes of which path is sensitive to the composition of the alloy, enabling stabilization of the intermediate transition states.



Introduction

Twinning- and transformation-induced plasticity (TWIP and TRIP, respectively) are the two phenomena enabling an outstanding development of modern body-centered cubic (bcc) β -Ti alloys [1,2]. The resulting mechanical properties of these systems, such as work hardening, tensile strength or ductility, are stellar across the group of lightweight structural materials [1,3]. Although TRIP and TWIP exhibit many similarities, i.e. both mechanisms utilize the low thermodynamic stability of β phase to provoke strain-induced rearrangement of atoms acting as efficient deformation modes [4,5], the latter effect remains poorly understood. While TRIP is realized through the $\beta \rightarrow \alpha''$ (orthorhombic martensite) transformation, TWIP is controlled by $\{332\}\langle 113 \rangle_\beta$ twinning [6].

The difficulties of rationalizing the mechanism of $\{332\}\langle 113 \rangle_\beta$ twinning are related to the necessary shuffling of atoms in the direction perpendicular to the $\{332\}_\beta$ plane that, together with simple crystal shearing, forms the twinned structure [7,8]. Such additional movement of atoms is absent in a most typical $\{112\}\langle 111 \rangle_\beta$ twinning mode [9,10], which, however, is less active in metastable TWIP Ti alloys. The above issue, i.e. the true atomic-scale mechanism of $\{332\}\langle 113 \rangle_\beta$ twinning was extensively explored in recent decades [7,8,11–15]. Kawabata et al. [11] and Rusakov et al. [12] suggested that $\{332\}\langle 113 \rangle_\beta$ twinning could be reached by the slip of $1/22\{113\}_\beta$ or $5/22\{113\}_\beta$ partial dislocations on $\{332\}_\beta$ planes complemented by eventual shuffling of atoms. Taking into account that $\{332\}_\beta$ plane and $\langle 113 \rangle_\beta$ direction are not close-packed, other dislocation-free

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Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2022.2049906>

models were developed [8,14]. The most notable achievement in this field was elaborated by Tobe et al. [8] who determined the favoured mechanism of $\{332\}\langle 113 \rangle_\beta$ twinning with a significantly reduced shuffling distance achieved by additional distortion of the bcc structure known as lattice modulation. The proposed modulation assumes an initial shuffle of $\{011\}_\beta$ planes towards $\langle 0\bar{1}1 \rangle_\beta$ direction, analogous to those occurring during the $\beta \rightarrow \alpha''$ transformation, thus leading to pseudo α'' (α''_p) configuration with $\{332\}\langle 113 \rangle_\beta \rightarrow \{130\}\langle 310 \rangle_{\alpha''_p}$ perfect lattice correspondence. Although many of the later experiments indeed identified the α'' at the $\{332\}_\beta$ twin interface [14,16,17], the first direct observation of the discussed twinning mechanism was reported by Castany et al. [18]. This *in situ* synchrotron investigation performed on the superelastic Ti-27Nb (at.%) alloy showed that the β phase, under applied load, first transforms into the α'' structure, which according to the proposed phenomenological model should undergo $\{130\}\langle 310 \rangle_{\alpha''}$ twinning at a high strain value and reverse back to β and twinned β when the load is removed. The superficial harmony of the theory and experiment was undermined by further studies describing the different sequence of the β and α'' twinning at increasing strains [19] or even lack of the α'' during the $\{332\}\langle 113 \rangle_\beta$ twins formation in various, non-superelastic Ti alloys [20–22]. These new findings demonstrate that knowledge of the TWIP phenomenon remains fragmented and raises the question of its fundamentals.

In this article, we present a crystallographic analysis supported by the density functional theory (DFT) [23–25] calculations and experimental observations of the shear-shuffle mechanism of $\{332\}\langle 113 \rangle_\beta$ twinning. The provided results clarify the available experiments and help revise the current view of this deformation mode.

Materials and methods

DFT total energy calculations of perfect, modulated and $\{332\}\langle 113 \rangle_\beta$ twinned β structures were performed with the VASP code [24–26]. Since the investigated effects depend on the relative stability of hexagonal closed packed (hcp or α) and bcc phases, the theoretical part of the study concerns two boundary systems, i.e. Ti for the highly metastable bcc phase boundary and V, the first transition metal forming a stable bcc structure. The experimental observations were conducted on a solution treated and deformed TWIP/TRIP Ti-10V-4Cr-1Sn (wt%). More details on the adopted methodology can be found in the Supplementary Material.

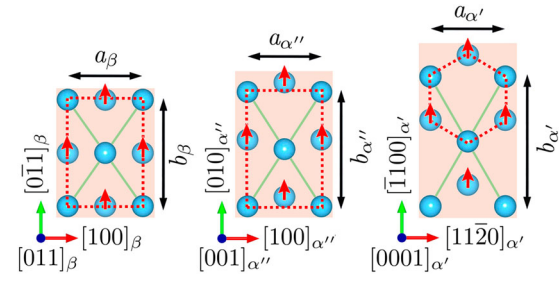


Figure 1. Atomic reconfiguration of $\beta \rightarrow \alpha'' \rightarrow \alpha'$ martensitic transformation. The $\langle 011 \rangle_\beta$ plane of $[0\bar{1}1]_\beta$ atomic shuffle indicated by red vectors is normal to the surface of the figure. The $\{112\}_\beta$ shear planes are marked by green colour. Crystallographic correspondences of particular structures are denoted by black arrows.

Results & discussion

The $\{332\}\langle 113 \rangle_\beta$ twinning and $\beta \rightarrow \alpha''$ transformation are similar in terms of the course of the reaction, i.e. both transitions include the shear and shuffling motion of atoms. In the martensitic transformation, the $\{112\}_\beta$ planes are sheared along the $\langle 111 \rangle_\beta$ direction and each second $\{110\}_\beta$ planes shuffle along $\langle 110 \rangle_\beta$ [27–29]. As noted in Figure 1, this transition produces three lattice strains related to the original $\langle 011 \rangle_\beta$, $\langle 100 \rangle_\beta$ and $\langle 0\bar{1}1 \rangle_\beta$ lattice parameters. It should be highlighted that the listed strains together with the shuffle distance of $\{110\}_\beta$ planes are closely associated with the composition of the alloy. Orthorhombic α'' is formed at a moderate concentration of β -stabilizers, not enough to maintain the bcc crystal symmetry, while further reduction of these elements stabilizes the hcp α' structure, reached for the maximum shuffling distance equal to $b_\beta/6$ [30].

In the case of the $\{332\}\langle 113 \rangle_\beta$ twinning, the shear and shuffle components operate along the $\langle 113 \rangle_\beta$ and $\langle 2\bar{3}3 \rangle_\beta$ directions, respectively. As stated before, Tobe et al. [8], based on the theory of deformation twinning [31,32], determined the most favourable, in terms of the magnitude of twinning shear and the complexity of shuffle, atomic displacements, which are presented in Figure 2(d). It can also be seen that the proposed lattice modulation [8] (Figure 2(a)) shortens the critical shuffling distance (Figure 2(b)) and can be reversed (Figure 2(c)) to reach the twinned β configuration. Comparing Figures 1 and 2, it is easy to note that the modulated α''_p structure is close to α'' martensite, i.e. lattice modulation uses the same type of $\{110\}_\beta$ plane shuffling. The calculated $\vec{\delta}_1$, $\vec{\delta}_5$, $\vec{\delta}_6$ modulation, $\vec{\delta}_2$, $\vec{\delta}_3$ shuffle and δ_4 shearing displacement vectors shown in Figure 2 are as follows:

$$0 < \vec{\delta}_1 < \frac{b_\beta}{6}, \quad (1)$$

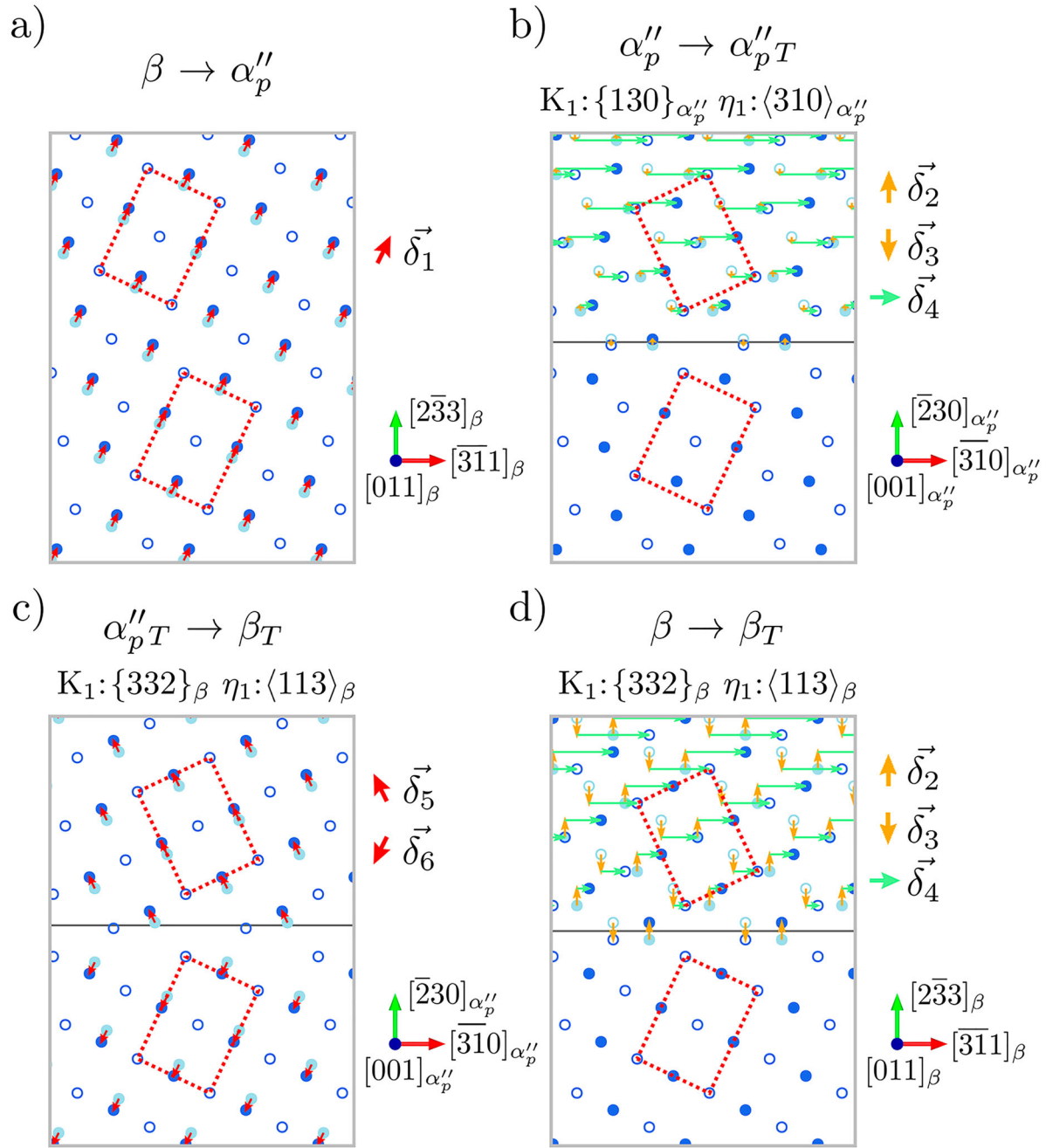


Figure 2. Atomic displacements during the $\{332\}\langle 113 \rangle_\beta$ twinning of the modulated $\beta \rightarrow \alpha''_p \rightarrow \alpha''_{pT} \rightarrow \beta_T$ (a-c) and direct $\beta \rightarrow \beta_T$ transitions (d). $\vec{\delta}_1$ used in this plot is equal to $b_\beta/9$. Twinning planes and directions are denoted by K_1 and η_1 , respectively. Subsequent original $(011)_\beta$ planes are indicated by empty and filled blue circles. Please note that arrows located next to $\vec{\delta}_{1-6}$, do not reflect the length of particular displacements but only indicate their directions. An exact formula of plotted $\vec{\delta}_{1-6}$ are given in Equations (1)–(6).

$$\vec{\delta}_2 = \frac{b_\beta a_\beta}{4v_\beta} \left(1 - \frac{6|\vec{\delta}_1|}{b_\beta} \right) \quad (2)$$

$$\vec{\delta}_3 = -\vec{\delta}_2, \quad (3)$$

$$\vec{\delta}_4 = \frac{(3a_\beta^2 - b_\beta^2)}{4v_\beta}, \quad (4)$$

$$\vec{\delta}_5 = \frac{|\vec{\delta}_1|}{b_\beta} b_{\beta_T}, \quad (5)$$

$$\vec{\delta}_6 = -\vec{\delta}_1, \quad (6)$$

where a_β , b_β and v_β are the bcc lattice parameters along $[100]_\beta$, $[011]_\beta$ and $[3\bar{1}1]_\beta$, respectively. Symbols marked with the “T” subscript indicate equivalent directions in the twinned structure. Since the twinning value q of $\{332\}\langle 113 \rangle_\beta$ twinning is $q = 2$, the magnitude of shear increases by $\vec{\delta}_4$ in each two $\{332\}_\beta$ atomic planes.

For more details see [8,9,31,32]. Analysing Equation (2), one can find that the shuffling of atoms vanishes when $\vec{\delta}_1 = b_\beta/6$ meaning that the twin operation is a pure shearing process. Such transition is, however, unlikely to occur since the given $\vec{\delta}_1$ value stabilizes the hcp structure with $\{332\}_\beta \rightarrow \{1010\}_{\alpha'}$ correspondence where the prismatic $\{1010\}_{\alpha'}$ planes are the planes of easy dislocation glide [33–35].

To reveal the influence of lattice modulation on the energy path of $\{332\}\langle 113 \rangle_\beta$ twinning, the *ab initio* calculations considering the linear shear-shuffle twinning transition of Ti and V were performed with the results shown in Figure 3. Although the simulation setup covers a full range of $\vec{\delta}_1$, reduction of the energy barrier is not observed and both metals exhibit single energy extrema occurring in the middle of the reaction coordinate ζ (ζ describing the progress of structural transition by counting the displacement of all atoms normalized to the total displacement at the end of reaction). The lattice configurations at $\zeta = 0.5$, irrespectively of the δ_1 value, exhibit deformed hcp symmetry, as presented in Figure 3(b). These structures are the low energy states for Ti, which favours hcp atomic arrangement but in the case of V such hexagonal embryos are the states corresponding to the energy barrier of the twinning process. Twinning transition alloys in a quenched state exhibit the β structure which as for V, is energetically preferred relative to α'' or α' [36–41]. The presented results show that the initial lattice modulation towards martensitic configuration does not reduce the energy barrier of $\{332\}\langle 113 \rangle_\beta$ twinning and thus is not required for this deformation mode, which is in line with the recent experiments [20,21,42]. Nevertheless, other observations [19] detected $\beta \rightarrow \alpha'' \rightarrow \alpha'_T \rightarrow \beta_T$ transition at an increasing strain in the Ti-12Mo alloy. This transition is different from the path observed by Castany et al. [18] where the α'_T occurs under a high load and β_T is formed after unloading. The sequence of formation the α'_T and β_T phase under increasing strain is thus the general difference of active $\{332\}\langle 113 \rangle_\beta$ twinning mechanism. The reversion of α'_T to β_T at unloading, was observed for superelastic alloys [18] where α'_T is formed at the maximum strain, meaning that full shear operation is achieved. Other sequences of transformation, i.e. $\beta \rightarrow \alpha'' \rightarrow \alpha'_T \rightarrow \beta_T$ disclosed for TWIP/TRIP alloy [19] indicates increase in shear deformation (since the strain is increasing) for the last step of transition: α'' twinned $\rightarrow \beta$ twinned. According to Figure 2(c), it is easy to note that the reversion of α'_{pT} to β_T does not provide additional $\langle 113 \rangle_\beta$ shearing, and since that is not expected to operate at a growing deformation. It could also be speculated that the formation of α'' is related to the beneficial (low energy) configuration of the α'' twin boundary, however

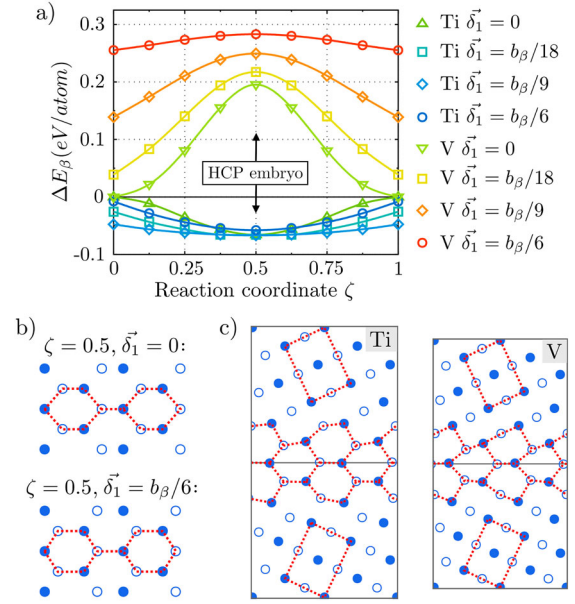


Figure 3. ΔE_β —energy variation relative to initial β phase determined for the linear shear-shuffle path of $\{332\}\langle 113 \rangle_\beta$ twinning and $0 < \vec{\delta}_1 < b_\beta/6$ initial lattice modulation (a). Examples of the intermediate deformed hcp structures at $\zeta = 0.5$ (b) and the $\{332\}\langle 113 \rangle_\beta$ twin boundaries of Ti and V (c). The size of the (c) subfigures reproduces different lattice parameters of Ti and V.

as already noted, the observed β twinning without α'' phase [20,21,42] eliminates such scenario. Additionally, the relaxed structures of $\{332\}\langle 113 \rangle_\beta$ Ti and V boundaries presented in Figure 3(c) display only small changes in the local relaxation of atoms and agree with the structure of this interface observed in the Ti-30Nb-3Pd alloy [16].

The discussed discrepancies clearly indicate the existence of an alternative to the previously reported [18] $\{332\}\langle 113 \rangle_\beta$ twinning transitions for which α'' is not mandatory but can be created depending on the alloy composition. Possibility of formation martensitic phase from $\{332\}\langle 113 \rangle_\beta$ twin was also recently proposed based on theoretical, broken symmetry method of twinning, nevertheless, an exact atomic-scale solution of transformation at progressive strain remains unknown [15,44]. To rationalize such lattice reconfiguration, the shear and shuffle twinning components are analysed in detail. The $\vec{\delta}_{2,3}$ and $\vec{\delta}_4$ create a mirror symmetry of the bcc structure relative to the $\{332\}_\beta$ planes. As shown in Figure 4(a), this operation can be presented as a $(21\bar{1})[\bar{3}\bar{1}1]_\beta$ shear ($\vec{\delta}_4$) supplemented by $(011)[2\bar{3}3]_\beta$ and $(011)[\bar{2}3\bar{3}]_\beta$ atomic shuffling ($\vec{\delta}_{2,3}$). The $\beta \rightarrow \alpha''$ martensitic transformation manipulates the same atomic planes but uses different directions, i.e. $(21\bar{1})[\bar{1}\bar{1}1]_\beta$ shear and $(011)[0\bar{1}\bar{1}]_\beta$ shuffle [27,28]. The difference in the listed

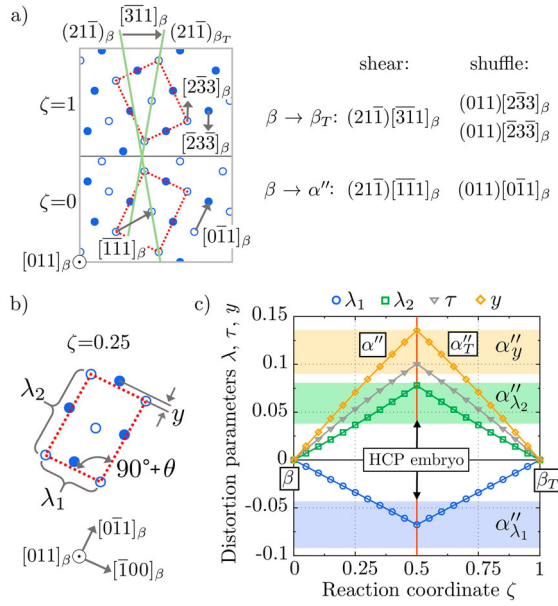


Figure 4. Perfect configuration of the $\{332\}\langle 113 \rangle_\beta$ twin with marked shear and shuffle displacement vectors of $\beta \rightarrow \beta_T$ and $\beta \rightarrow \alpha''$ transformations (a). Distortion parameters of linear twin operation are indicated in (b) and compared with their α''_{λ_1} , α''_{λ_2} and α''_{λ_2} equivalents (colored background) designated for α'' phase formed in Ti-Nb alloys [43] in (c).

directions results in the formation of the deformed α'' structure at $0 < \zeta < 0.5$ and $0.5 < \zeta < 1$ reaction coordinates, with $\zeta = 0.25$ example shown in Figure 4(b). These intermediate structures exhibit the same distortion parameters i.e. $\lambda_1 = (a_{\alpha''} - a_\beta)/a_\beta$, $\lambda_2 = (b_{\alpha''} - b_\beta)/b_\beta$ lattice strains and $y = (011)[0\bar{1}1]_\beta$ shuffling as those operating in $\beta \rightarrow \alpha''$ martensitic transformation (see Figure 1) [43,45]. An additional deformation component related exclusively to $\{332\}\langle 113 \rangle_\beta$ twinning is the $(100)[0\bar{1}1]_\beta$ shear strain $\tau = \tan(\theta)$. The distortion parameters calculated for the linear twinning transition are compared to available experimental values [43,45] obtained for the Ti-Nb alloys, which undergo $\beta \rightarrow \alpha''$ transformation in Figure 4(c). It can be seen that the deformation of the bcc structure during $\{332\}\langle 113 \rangle_\beta$ twinning widely overlaps the lattice distortion of the martensitic transformation, revealing that the distortion parameters required for the stabilization of the α'' structure are provided by twinning itself. The disclosed correlation shows that α'' can be created during the twinning process in alloys prone to $\beta \rightarrow \alpha''$ transformation; however, other compositions with a larger concentration of β -stabilizers will undergo twinning using the same set of shear-shuffle δ_{2-4} displacements without the intermediate martensitic phase.

The remaining questions associated with the investigated deformation mechanism concern the signature of

the τ strain and the favoured atomic-scale trajectory of shear and shuffle displacements at increasing ζ . Although the large elastic deformation capacity of β and α'' in TWIP/TRIP alloys was already reported [46–49], available experiments were not focused on measuring the shear strains of the investigated materials. To clarify this issue, transmission electron microscopy (TEM) observations of a solution treated and deformed Ti-10V-4Cr-1Sn (wt%) alloy were performed. Experimental observations presented in Figure 5(a–d) are complemented by *ab initio* simulations of the minimum energy path (MEP) of Ti and V $\{332\}\langle 113 \rangle_\beta$ twinning performed at stress/strain free conditions, the results of which are given in Figure 5(e) and S1 movie. Deformation band shown in Figure 5(a,b) comprises four structural elements, β , α'' , β_T and the interface region. According to the selected area electron diffraction (SAED) patterns (Figure 5(c,d)), the observed interface possesses the searched, tilted β configuration with the following distortion parameters: $\lambda_1 = 0.022$, $\lambda_2 = -0.025$, $\tau = 0.059$ ($\theta = 3.4^\circ$) and $y \sim 0$ as the diffraction pattern does not show the features of the modulated superlattice. It should be emphasized that the signs of λ_1 and λ_2 are opposite for conventional $\beta \rightarrow \alpha''$ transition (negative λ_1 and positive λ_2 , see Figure 1) and thus, the deformed structure of the interface cannot be interpreted as the initial stage of martensitic transformation. The stress-induced α'' (SIM) is also identified in the centre portion of the twin band (Figure 5(a)) with a habit plane different than the twin boundary. Formation of the α'' in the $\{332\}\langle 112 \rangle_\beta$ twins has been reported in various TRIP/TWIP Ti alloys as one of the secondary transformations able to accommodate extra strain [20,42,50,51]. Comparison of experimental data with the results of MEP calculations (Figure 5(e)) shows that, although the model systems are considered at 0 K temperature and not subjected to internal stresses and structural constraints occurring in the deformed alloy (e.g. elastic field generated by host crystal and opposing twinning operation), the predicted deformation trends are correct. Positive/negative values of λ_1/λ_2 tend to be reached at the beginning of $\beta \rightarrow \beta_T$ reconfiguration while shear and shuffle displacements described by τ and y parameters strongly depend on chemical composition. In general, high stability of the bcc structure (as for V) promotes $(100)[0\bar{1}1]_\beta$ shearing (increase of the τ) at the onset of the twinning transition with negligible $(011)[0\bar{1}1]_\beta$ atomic shuffling (y close to zero). For materials preferring the hcp configuration (like Ti), the favourable twin path is inverse, leading to pronounced y shuffle and low τ . In TWIP alloys, the relative structural stability of α'' and β are similar and the formation of these phases is closely linked to alloy stoichiometry. According to the results of the *ab initio* calculations (Figure 5(e))

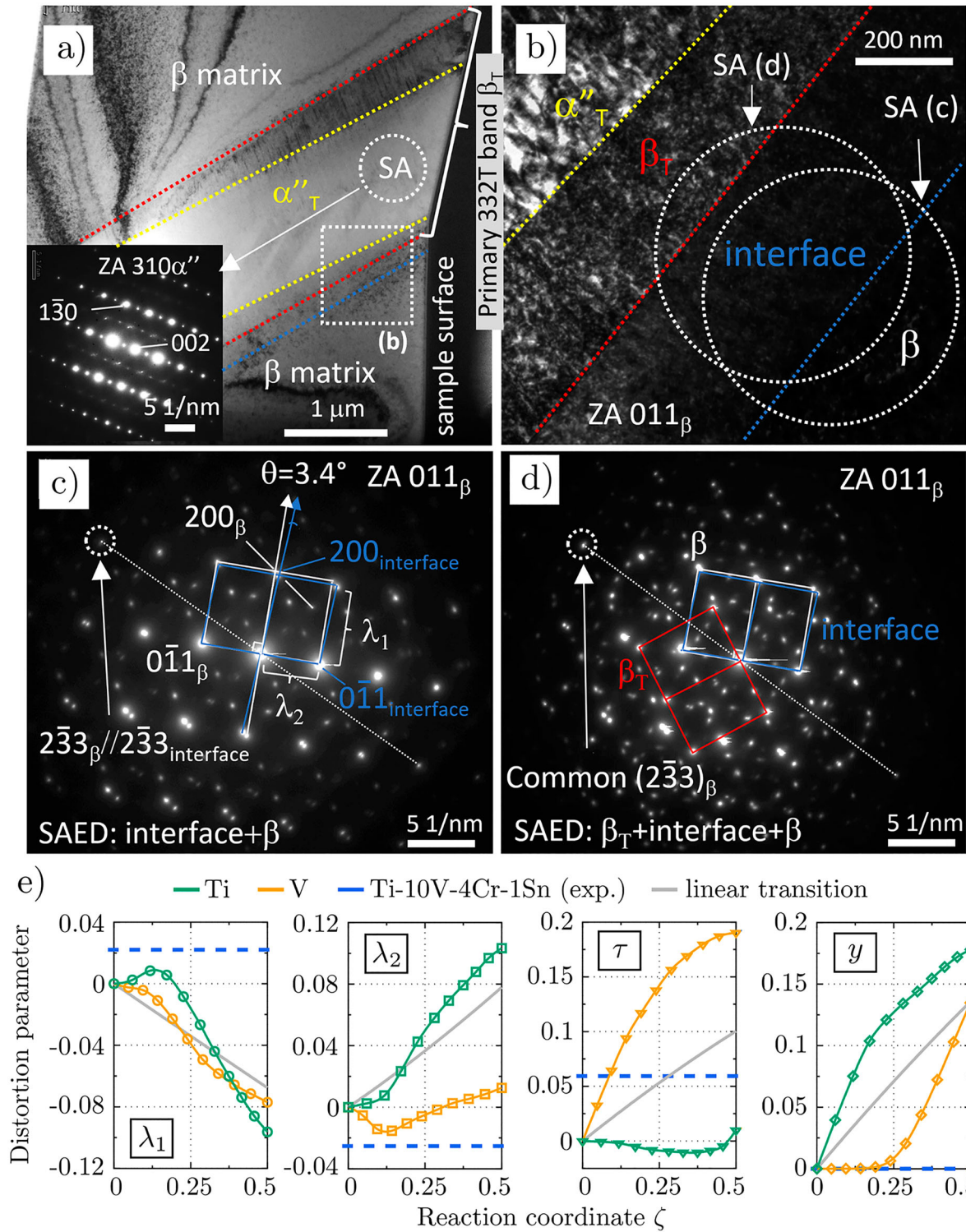


Figure 5. TEM observation of a deformed Ti-10V-4Cr-1Sn alloy together with the calculated MEP of $\{332\}\langle 113 \rangle_{\beta}$ twinning mode for Ti and V. (a) the bright field image of the deformation band profile with denoted (colour dashed line) boundaries between individual structural elements and the SAED pattern at the selected area (SA) indicating α'' near $[310]_{\alpha''}$ zone axis (ZA). (b) the magnified zone marked in (a), in which four layers are observed and identified to be α''_{T} , β_{T} , interface and β . (c) the SAED pattern obtained at the boundary of interface/ β , in which a distortion of the 'interface' phase from perfect bcc lattice (β) is identified with $\theta = 3.4^\circ$. (d) the SAED pattern of the β_{T} , interface and the β , which demonstrates the $(2\bar{3}3)[311]_{\beta}$ twinning relationship between β and β_{T} . It can be noticed that all three layers have parallel $(2\bar{3}3)_{\beta}$ planes in common. (e) the experimentally measured distortion parameters compared to the linear path and MEP of $\{332\}\langle 113 \rangle_{\beta}$ twinning for Ti and V.

and S1 movie) the τ deformation of α'' (exhibiting visible γ shuffle) is expected to be marginal, which is in line with previous observations where shearing distortion was not reported [2,3,14,19]. On the other hand, the tilted β should be formed in more stable bcc alloys or exist in the complex structures of TWIP/TRIP systems, as shown in this study. It should also be noted that the presented mechanism predicts the formation of α'' and α''_T at an increasing deformation level, but the terminating structure of the disclosed transition is β_T , which clarifies the recent *in situ* observations of the $\{332\}\langle 113 \rangle_\beta$ twinning path in the Ti-12Mo alloy [19]. Finally, the polymorphic $\{332\}\langle 113 \rangle_\beta$ twinning mode can proceed with two reaction sequences at increasing load: $\beta \rightarrow \alpha'' \rightarrow \alpha''_T \rightarrow \beta_T$ or $\beta \rightarrow \beta$ distorted $\rightarrow \beta_T$ in low and more stable β phase, respectively, in agreement with available experiments [19–22]. The disclosed, large and composition dependent deviation of the twinning path with respect to its linear transition is an essential feature of the $\{332\}\langle 113 \rangle_\beta$ twinning, allowing $\beta \rightarrow \beta_T$ transformation to proceed with or without α'' as an intermediate state of plastic deformation.

Summary and conclusions

In summary, the shear-shuffle mechanism of $\{332\}\langle 113 \rangle_\beta$ twinning is explored in detail with a particular focus on transformation trajectory on an atomic scale. We found that initial modulation of the β structure towards α'' does not reduce the energy barrier of twinning transition and thus is not required as a separate, initial stage of plastic deformation, as proposed previously [8,18]. Instead, the lattice strains and atomic shuffling needed to form α'' are provided by $\{332\}\langle 113 \rangle_\beta$ twinning itself. This dual nature of twin transformation arises from the fact that both $\beta \rightarrow \beta_T$ and $\beta \rightarrow \alpha''$ reconfigurations operate over the same set of atomic planes but use different displacement directions. As a result, a linear path of twinning transition produces the distorted α'' structure. However, since the shear-shuffle mechanism involves the displacement of atoms along and perpendicular to the shearing direction, the accompanying relaxation of the structure is pronounced and strongly related to the chemical composition of the deformed alloy. Because of that, the minimum energy path of $\{332\}\langle 113 \rangle_\beta$ twinning is far from rigid linear transformation, allowing to stabilize the α'' or promoting a direct $\beta \rightarrow \beta_T$ transition, depending on the β phase stability. The presented results provide extended knowledge about $\{332\}\langle 113 \rangle_\beta$ twinning from a previously reported mechanism occurring in superelastic alloys to a broad group of

Ti-based TWIP materials and uncover the unique, polymorphic nature of the studied twin mode also acting as a new mechanism of $\beta \rightarrow \alpha''$ martensitic transformation.

Acknowledgments

The authors acknowledge the PL-GRID infrastructure, which provided the computational resources—the Prometheus and Tryton supercomputers.

Data availability

All data needed to evaluate the conclusions of the paper are present in the paper and/or the Supplementary Materials. Any additional details are available from the corresponding author upon reasonable request.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was financially supported by the Polish National Science Centre [grant number 2019/35/D/ST5/02379 (UMO-2019/35/D/ST5/02379)].

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