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Origin of $\{112\}\langle 111\rangle$ antitwinning in a Ti-24Nb-4Zr-8Sn superelastic single crystal

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Abstract

$\{112\}\langle 111\rangle_{\beta}$ twins are observed in a superelastic β Ti-24Nb-4Zr-8Sn (wt.%) single crystal after tensile test. A careful Schmid factor analysis shows that these twins are formed in the antitwinning sense regarding the classical $\{112\}\langle 111\rangle_{\beta}$ twinning system of bcc structures. These are then $\{112\}\langle 111\rangle_{\beta}$ antitwins. Moreover, a full stress-induced martensitic (SIM) transformation of β phase into α'' martensite is evidenced from *in situ* synchrotron X-rays diffraction. This transformation is fully accomplished before the onset of plastic deformation and, in turn, the formation of twins. From crystallographic reconstruction, $\{112\}\langle 111\rangle_{\beta}$ antitwins are shown to be passively formed from the reversion, during the reverse SIM

transformation when the stress is released, of $\{110\}\langle 110 \rangle_{\alpha''}$ twins actually formed in α'' martensite. The martensitic transformation occurring before twinning plays a key role in the activation of antitwinning systems by reducing both shear and shuffle magnitudes of twinning. Variant selection of stress-induced martensite and Schmid factor analysis show that the classical $\{112\}\langle 111 \rangle_{\beta}$ twins can never be activated in β titanium alloys involving SIM transformation, while the non-classical $\{112\}\langle 111 \rangle_{\beta}$ twinning system in the antitwinning sense is always favored.

Keywords: Metastable β titanium alloys; Twinning; Antitwinning; Stress-induced martensitic transformation; Schmid factor analysis.

1. Introduction

Metastable β titanium alloys can be designed with highly-biocompatible elements such as Nb, Ta, Mo, Zr [1-5] and exhibit a low Young's modulus which makes these alloys particularly suitable for medical applications [6-11]. Numerous deformation mechanisms are known to operate in metastable β titanium alloys: stress-induced martensitic (SIM) transformation [12-16], mechanical twinning [17-22] and dislocation slip [23-26]. These deformation mechanisms lead to peculiar mechanical properties such as superelastic or shape memory effects [27,12,28-30,13,16,15,14] and transformation induced plasticity (TRIP) or twinning induced plasticity (TWIP) effects [31-35].

SIM transformation occurs from the β phase (bcc) to the α'' phase (C-centered orthorhombic). It has to be noticed that stress-induced α'' martensite is formed as single untwinned variant in β Ti-based alloys [14,4,18] contrarily to other superelastic alloys such as NiTi alloys wherein pairs of twinned variants are formed [36-39]. The crystallographic correspondence between these two phases is given by the modified Burgers Orientation Relationship (BOR):

$\{110\}_{\beta} // (001)_{\alpha''}$ and $\langle 111 \rangle_{\beta} // [110]_{\alpha''}$. Its reversibility generally depends on the metastability of the alloy [40]: a SIM transformation occurring during plastic deformation is no or few reversible and leads to TRIP effect [31-35], while a SIM transformation occurring before plastic deformation is generally highly (completely in the most favourable case) reversible and leads to superelasticity [12,13,41,28,29]. Superelasticity is generally evidenced by the occurrence of a stress plateau on tensile curves followed by a full recovery when the stress is removed. The presence of SIM phase in superelastic alloys can then only be detected under stress due to its reversibility when the stress is released. Residual α'' phase can be observed in highly deformed samples as plasticity impedes the reversion of martensite [42,43], but a full reversible SIM transformation can only be evidenced by *in situ* techniques [12-14,44,15,45].

Observed twinning systems generally have a low magnitude of shear and a low magnitude of shuffle [46]. In body centred cubic (bcc) metals, the operating twinning system is then $\{112\} \langle 111 \rangle$. Even if its magnitude of shear is high (0.707 from Tobe et al. [47]), the absence of shuffle makes $\{112\} \langle 111 \rangle$ twins more favorable in comparison to other theoretical twinning systems with lower magnitude of shear but involving shuffle [46]. It can also be noticed that there is another theoretically predicted twinning system with the same twinning plane and the same twinning direction than the classical $\{112\} \langle 111 \rangle$ twinning system, which involves a lower value of shear (0.354 from Tobe et al. [47]) but a high magnitude of shuffle [46]. This twinning system with shuffle will be referred as “non-classical” $\{112\} \langle 111 \rangle$ twinning in the present paper in contrast to the “classical” $\{112\} \langle 111 \rangle$ system without shuffle. This non-classical system is then unfavourable in comparison with the classical one that not involves any shuffle and is thus not experimentally observed. These two twinning systems share exactly the same twinning plane and shear plane, but share the same twinning direction with a different sense [46]. The classical one is in the twinning sense while the non-

classical one lies in the opposite sense, i.e. the antitwinning direction regarding the classical one. The secondary twinning elements are also different between these two systems. All the crystallographic features of these two $\{112\}\langle 111 \rangle$ twinning systems will be detailed in the section 3.4.

The classical $\{112\}\langle 111 \rangle$ twinning system is sometimes observed in metastable β titanium alloys, including TRIP/TWIP [33,34] and superelastic compositions [17], but a peculiar $\{332\}\langle 113 \rangle$ twinning mode is mainly observed in these alloys [17,40,4,20,33,34,19,21,18,22,35]. Classical $\{112\}\langle 111 \rangle$ twins, when observed, are then a secondary and minor twinning mode occurring in addition to preponderant $\{332\}\langle 113 \rangle$ twins [17,33,34]. $\{332\}\langle 113 \rangle$ twinning exhibits a much lower magnitude of shear (0.354 from Tobe et al. [47]) than classical $\{112\}\langle 111 \rangle$ twinning but is not observed in other bcc structures due to its high magnitude of shuffle. Occurrence of this peculiar twinning system can be attributed to a low shear modulus in $\{011\}$ planes along $\langle 011 \rangle$ directions leading to a lattice instability of the bcc structure [47]. This model is consistent with the observation of $\{332\}\langle 113 \rangle$ twins in TWIP and TRIP/TWIP metastable β Ti alloys where no SIM occurs before twinning [33,34,19,48]. However, this explanation cannot be applied to twins in β Ti-based superelastic alloys because a full transformation into SIM α'' phase occurs before twinning. Then, $\{332\}\langle 113 \rangle$ twins clearly result from twinning operations in α'' phase in these alloys. Recent *in situ* characterization of $\{332\}\langle 113 \rangle$ twins in a Ti-27Nb (at.%) showed that superelastic alloys undergo a complex deformation sequence: (1) A full stress-induced martensitic transformation into α'' occurs followed by (2) mechanical twinning of α'' phase and then (3) the reversion into β phase when the stress is released leading to formation of $\{332\}\langle 113 \rangle$ twins [49]. $\{332\}\langle 113 \rangle$ twins in β phase are then passively formed from the reversion of twins formerly produced into stress induced α'' martensite. Further observations

of transitional structures exhibiting residual α'' martensite along $\{332\}\langle 113 \rangle$ twin boundaries also support this mechanism of twin reversion [50,51].

As twins in β phase can be linked to twins in SIM α'' phase, twinning of α'' phase has to be considered. Twinning systems of α'' martensite are usually observed in titanium alloys with initial α'' microstructures. $\{111\}_{\alpha''}$ type I and $\langle 211 \rangle_{\alpha''}$ type II twinning modes preserve the orientation of the corresponding β phase by application of the BOR and are then considered as reorientation twinning systems rather than mechanical ones [27,52,53]. Plastic twinning systems are also observed in α'' microstructures. The $\{130\}\langle 310 \rangle_{\alpha''}$ system is identified in some α'' microstructures and its reversion into β phase leads to $\{332\}\langle 113 \rangle_{\beta}$ twins [27,54]. $\{103\}\langle 301 \rangle_{\alpha''}$ twins are similarly observed with the same relationship with $\{332\}\langle 113 \rangle_{\beta}$ twins [54]. $\{110\}\langle 110 \rangle_{\alpha''}$ twins are also evidenced at the surface of superelastic specimens [55]. Contrarily to the previous ones, this later twinning system corresponds to the classical $\{112\}\langle 111 \rangle_{\beta}$ twinning system of β phase [56]. Among these twinning systems of α'' phase, $\{130\}\langle 310 \rangle_{\alpha''}$ is the most observed one and was also recently evidenced in TRIP/TWIP alloys [48]. But clear criteria to explain the activation of twinning systems in α'' are still not elucidated.

This paper focuses on the deformation behavior of a Ti-24Nb-4Zr-8Sn (Ti2448) superelastic single crystal during a tensile test. $\{112\}\langle 111 \rangle$ mechanical twins are observed in this alloy after 4.5% of applied strain. Schmid factor analysis will show that these twins correspond to the non-classical $\{112\}\langle 111 \rangle$ twinning system operating in the antitwinning direction. Moreover, these antitwins in β phase will be shown to be due to the reversion of twins occurring in α'' phase. The role of SIM transformation on the observation of $\{112\}\langle 111 \rangle$ antitwins in β phase will be then investigated in terms of twinning shear and shuffle as well as variant selection of martensite.

2. Materials and methods

2.1. Experimental methods

A Ti-24Nb-4Zr-8Sn (wt.%) single crystal orientated along a $\langle 110 \rangle$ direction is used for this study. Experimental details are given in [56]. X-ray diffraction (XRD) Laue back reflection confirmed that the $\langle 110 \rangle_{\beta}$ direction is obtained within a 1° range and the absence of metastable α'' and ω phases. Flat tensile specimens with $3 \times 15 \times 0.5 \text{ mm}^3$ gauge dimensions were machined from the single crystal. An inverse pole figure (IPF) was taken from the single crystal using Electron backscattering diffraction on a Scanning Electron Microscope (SEM-EBSD) and showed that the surface plane of these specimens is $\{353\}$. A Jeol JSM 7100F SEM machine working with an accelerating voltage of 20 kV and equipped with a TSL-EBSD system (HKL-Channel 5 analysis software) was used. Specimen was previously prepared with the same procedure than for metallographic observation detailed below. Cyclic tensile tests were conducted at room temperature by strain increments of 0.5% followed by stress release up to an elongation of 5.5% using an INSTRON 3369 tensile machine with a strain rate of 10^{-4} s^{-1} . An extensometer was used to ensure the accuracy of strain measurement. Tensile direction (TD) was chosen along the $\langle 110 \rangle_{\beta}$ direction of the single crystal in order to maximize the transformation strain [57]. A specimen deformed up to 4.5% of applied strain is used for twin characterization. Samples were prepared for metallographic observation by mechanical polishing with increasing grades of SiC abrasive papers, final polishing with colloidal silica suspension and final etching in a solution composed of 8% HF, 15% HNO_3 and 77% H_2O (vol%). TEM specimens were also cut from tensile specimens and were twin-jet electropolished at 253-263 K in a solution of 6% perchloric acid and 94% methanol (vol. %). Electropolishing was stopped before perforation and final steps of thinning were performed by two-steps ion milling using successively 5 keV

and 1 keV Ar ions with a Fischione 1010 Model. Observations were conducted on a JEOL 2100 microscope operating at 200 kV.

In situ synchrotron X-ray diffraction (SXR) during cyclic tensile test was conducted on beam line ID31 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a 5 kN micro-tensile machine. The high-resolution ID31 beamline offers a high-energy incident X-ray beam ($\lambda = 0.040002106$ nm) coupled with a nine-channel multi-analyzer detector. The transmitted diffracted beams were collected over the 2θ angular range $4-28^\circ$ with a scanning step of 0.005° . The *in situ* cyclic tensile test under synchrotron radiation was realized on a single crystal specimen with the same geometry than for tensile tests (gauge width of 3 mm and thickness of 0.5 mm) with strain increments of 0.5 % until 5.5 %. SXR scans were therefore obtained after each strain increment for both loading and unloading conditions. More details can be found in [56,12].

2.2. Variant selection

Each variant of α'' martensite can be obtained from β phase orientation by application of BOR. The transformation of a β crystal into α'' martensite leads to 6 equivalent lattice correspondence variants (CV) given in Table 1. Under uniaxial applied stress, activated variants are expected to be the ones leading to the highest transformation strain along the stress direction [53,58,57].

Table 1. Lattice correspondence variants (CV) derived from β and α'' crystals and transformation lattice strain of each CV along the $[101]_\beta$ tensile axis.

Variant	$[100]_{\alpha''}$	$[010]_{\alpha''}$	$[001]_{\alpha''}$	Strain
CV1	$[100]_\beta$	$[011]_\beta$	$[0\bar{1}1]_\beta$	1.51%
CV2	$[100]_\beta$	$[0\bar{1}1]_\beta$	$[01\bar{1}]_\beta$	1.51%
CV3	$[010]_\beta$	$[101]_\beta$	$[10\bar{1}]_\beta$	4.31%
CV4	$[010]_\beta$	$[10\bar{1}]_\beta$	$[\bar{1}0\bar{1}]_\beta$	3.99%
CV5	$[001]_\beta$	$[110]_\beta$	$[\bar{1}\bar{1}0]_\beta$	1.51%
CV6	$[001]_\beta$	$[\bar{1}10]_\beta$	$[\bar{1}\bar{1}0]_\beta$	1.51%

Twinning systems are usually described by their twinning elements: K_1 , η_1 , K_2 , η_2 and P [46] as shown on Fig 1. Variant selection during mechanical twinning of β and α'' phases can be determined using a Schmid factor analysis adapted to this deformation mechanism [17,27]. Schmid factor, written m , is defined similarly to slip as:

$$m = \cos \lambda \cos \phi$$

where λ is the angle between tensile direction (TD) and \vec{K}_1 and ϕ the angle between TD and $\vec{\eta}_1$. Contrarily to dislocation slip, values of λ and ϕ are taken between 0° and 180° in order to obtain m values ranging between -0.5 and 0.5. Using this convention, a twin variant can be activated in tension if its associated Schmid factor is positive. The sign of m plays then a key role in the present study. So, signs of K_1 and η_1 have to be chosen carefully with respect to Fig. 1, as detailed in Appendix A of [27]. Twinning elements of each system are identified in section 3.4.

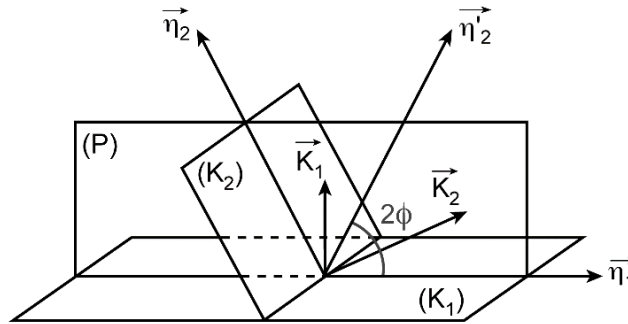


Fig. 1 The four twinning elements contained in the shear plane (P).

In the present study, two twinning systems for each phase will be considered: $\{112\}\langle 111 \rangle_\beta$ and $\{110\}\langle 110 \rangle_{\alpha''}$. This notation without minus sign in index of η_1 will be used for the generic denomination of each system. Conversely, signs will be specified when the twinning (t) or the antitwinning (at) sense will be considered: $\{112\}\langle \bar{1}\bar{1}1 \rangle_\beta^t$ and $\{110\}\langle 1\bar{1}0 \rangle_{\alpha''}^t$

correspond then to twinning systems when the sign of η_1 indicates the twinning sense and $\{112\}\{11\bar{1}\}_\beta^{at}$ and $\{110\}\{\bar{1}10\}_{\alpha''}^{at}$ correspond to twinning systems when the sign of η_1 corresponds to the antitwinning sense. In this paper, the twinning sense is always defined as the twinning direction of the classical twinning system of bcc structures, whatever the phase considered.

3. Results and discussion

3.1. Preliminary results: tensile tests and *in situ* SXRD characterization

The main experimental results are summarized in this section. A full description of phase transformations and mechanical behavior of the present Ti2448 single crystal is available in a previous study [56]. Fig. 2a shows the cyclic tensile curve of the $[101]_\beta$ single crystal strained from 0 to 5.5% and the corresponding *in situ* SXRD diffraction profiles under stress (Fig 2b) and when the stress is removed (Fig 2c). The $(110)_\beta$ peak is represented by black circles in SXRD profiles, while $(002)_{\alpha''}$, $(111)_{\alpha''}$ and $(020)_{\alpha''}$ peaks of martensite are labeled with white circles, black squares and stars, respectively. A stress plateau is observed from 0.7% to 3% of applied strain on the tensile curve and corresponds to SIM transformation as shown in SXRD patterns (Fig 2b). From 4.5% of applied strain, no more β phase is detected on loading, highlighting a full SIM transformation. α'' phase disappears and β phase is restored upon unloading until a strain of 4%. Irreversible strain is observed from 4.5% only and residual α'' phase is observed upon unloading. These observations support that plastic deformation mechanisms such as dislocation glide and mechanical twinning do not occur extensively below this strain level.

Finally, the key feature for the present paper is that a full martensitic transformation from β phase to α'' phase is observed on loading, which means that when plastic deformation occurs, the microstructure is only composed of α'' martensite.

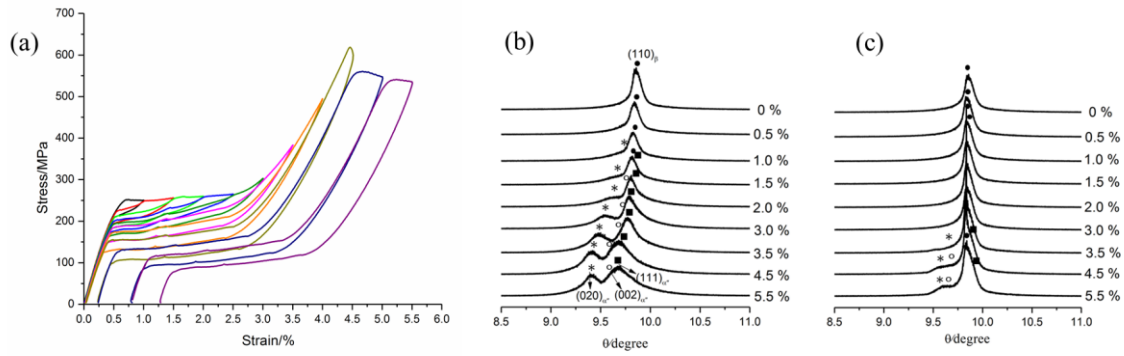


Fig. 2 Cyclic tensile curve of the Ti-24Nb-4Zr-8Sn single crystal (a). *In situ* synchrotron X-ray diffraction profiles during a cyclic tensile test on loading (b) and after unloading (c); black circles correspond to $(110)_\beta$ peak, white circles to $(002)_{\alpha''}$, black squares to $(111)_{\alpha''}$ and stars to $(020)_{\alpha''}$.

3.2. Deformation sequence

It has first to be noted that Schmid factor analysis is required to distinguish the twinning direction from the antitwinning direction of observed twins. In this section, twinning systems are then labeled without signs and twinning/antitwinning directions will be determined in section 3.3.

The microstructure of the Ti2448 single crystal after 4.5% strain is first investigated by optical microscopy. As the single crystal is observed after unloading and according to SXRD results, most of the martensite is reversed into β phase. Fig. 3a shows that two orientations of twins cross the single crystal. These twins were previously characterized by TEM observations and identified as $\{112\}\langle 111 \rangle_\beta$ twins with the presence of a thin layer of interfacial ω phase along the twin boundaries [56]. Another example of such a twin is shown on the Fig. 3b. The corresponding diffraction pattern in Fig. 3c is taken along a $\langle 110 \rangle$ zone axis which is common to both β matrix and $\{112\}\langle 111 \rangle_\beta$ twin. Typical spots of a single variant of ω phase are also clearly visible. As formerly reported, this single variant of ω phase

lies at the twin interface and impedes any direct observation of its atomic structure [56]. Some dislocations are also visible in Fig. 3b. Both dislocation glide and $\{112\}\langle 111 \rangle_{\beta}$ twinning are then activated during plastic deformation.

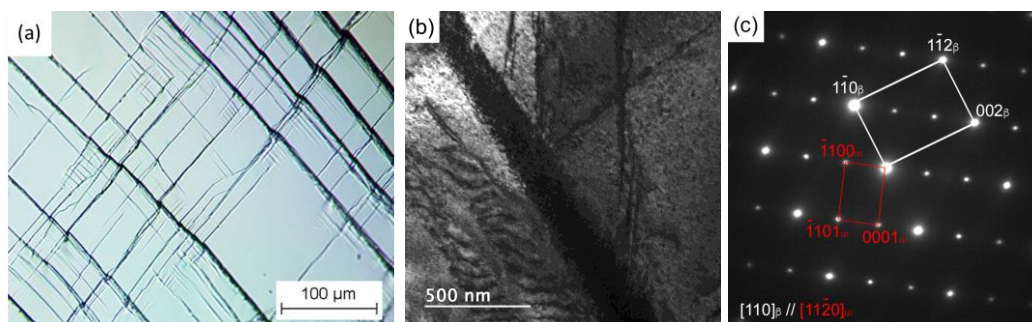


Fig. 3 Optical micrograph of the Ti-24Nb-4Zr-8Sn single crystal after being strained up to 4.5% (a) and TEM observation of a twin (b) and corresponding diffraction pattern showing the presence of interfacial twin boundary ω phase (c).

As mechanical twinning involves unrecoverable plastic deformation, it must occur beyond 4% of strain, i.e. when the microstructure is only composed of α'' martensite. As a consequence, twinning actually occurs in α'' phase according to the $\{110\}\langle 110 \rangle_{\alpha''}$ twinning system as previously evidenced [56]. The deformation sequence can thus be summarized as shown on Fig. 4. After elastic deformation of the β phase, when the strain is increasing:

- β phase is first transformed into stress-induced α'' martensite. Transformation strain along TD is calculated for each possible CV of martensite (Table 1) and leads to the variant selection of CV3, which gives the highest value of transformation strain.
- At higher strain, twinning and dislocation glide of α'' phase occur. According to [56], $\{110\}\langle 110 \rangle_{\alpha''}$ twins are formed into martensite.
- Then, when the stress is removed, the parent crystal and twins reverse each into β phase, leading to the presence of $\{112\}\langle 111 \rangle_{\beta}$ twins into β phase.

As a conclusion, the observed $\{112\}\langle 111 \rangle_{\beta}$ twins actually correspond to the reversion during reverse SIM transformation of $\{110\}\langle 110 \rangle_{\alpha''}$ twins activated into the stress-induced α'' martensite.

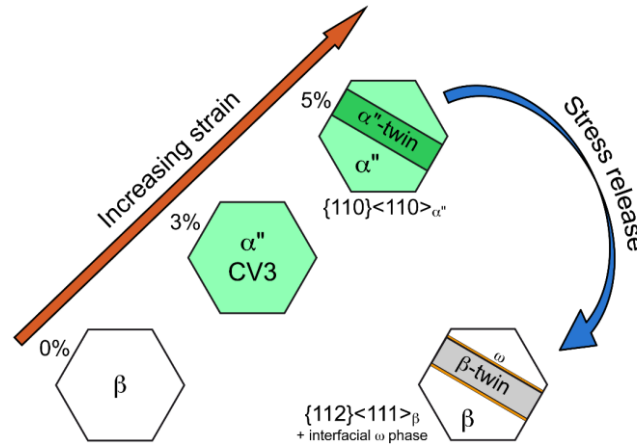
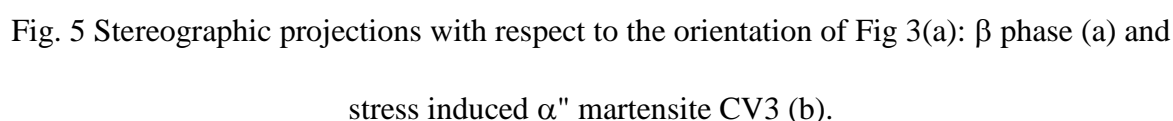


Fig. 4 Deformation sequence of the Ti-24Nb-4Zr-8Sn single crystal under loading and after unloading.

3.3. Schmid factor analysis and twinning system identification

Fig. 5a represents the stereographic projection corresponding to the β phase single crystal orientation where the TD is chosen as $[101]_{\beta}$ and the surface plane is $(\bar{3}53)_{\beta}$ as specified in section 2.1. Using this convention, CV3 is expected to be formed under stress (Table 1). Fig. 5b is then the stereographic projection of the corresponding α'' single crystal obtained by application of the β/α'' orientation relationship for the CV3. This orientation of α'' phase is assumed to be the parent crystal orientation with TD along the $[010]_{\alpha''}$ direction when twins are activated.



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Table 2. Principal twinning elements of the 12 variants of $\{112\}\langle 111 \rangle_{\beta}$ and 2 variants of $\{110\}\langle 110 \rangle_{\alpha''}$ considering the twinning sense η_{1t} and antitwinning sense η_{1at} .

Variant	K_1	η_{1t}	η_{1at}
V1 $_{\beta}$	(112)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V2 $_{\beta}$	(121)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V3 $_{\beta}$	(211)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V4 $_{\beta}$	($\bar{1}$ 12)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V5 $_{\beta}$	($\bar{1}$ 21)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V6 $_{\beta}$	($\bar{2}$ 11)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V7 $_{\beta}$	(1 $\bar{1}$ 2)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V8 $_{\beta}$	(1 $\bar{2}$ 1)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V9 $_{\beta}$	(2 $\bar{1}$ 1)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V10 $_{\beta}$	(11 $\bar{2}$)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V11 $_{\beta}$	(12 $\bar{1}$)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V12 $_{\beta}$	(21 $\bar{1}$)	$[\bar{1}\bar{1}1]$	$[11\bar{1}]$
V1 $_{\alpha''}$	(110)	$[\bar{1}\bar{1}0]$	$[\bar{1}\bar{1}0]$
V2 $_{\alpha''}$	($\bar{1}$ 10)	$[\bar{1}\bar{1}0]$	$[110]$

Schmid factor analysis is used considering both twinning and antitwinning systems for β and α'' phases: $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ and $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$; $\{110\}\langle 1\bar{1}0 \rangle_{\alpha''}^t$ and $\{110\}\langle \bar{1}10 \rangle_{\alpha''}^{at}$ (Table 3). Of course, values of Schmid factors for twinning direction (m_t) have the same absolute values than for antitwinning direction (m_{at}), only the sign is opposite.

Table 3. Schmid factors of the 12 variants of $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ and $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ for a $[101]_{\beta}$ tensile direction and the 2 variants of $\{110\}\langle 1\bar{1}0 \rangle_{\alpha''}^t$ and $\{110\}\langle \bar{1}10 \rangle_{\alpha''}^{at}$ for a $[010]_{\alpha''}$ tensile direction.

Variant	m_t	m_{at}
V1 $_{\beta}$	0,000	0,000
V2 $_{\beta}$	-0,471	0,471
V3 $_{\beta}$	0,000	0,000
V4 $_{\beta}$	0,236	-0,236
V5 $_{\beta}$	0,000	0,000
V6 $_{\beta}$	0,236	-0,236
V7 $_{\beta}$	0,000	0,000
V8 $_{\beta}$	-0,471	0,471
V9 $_{\beta}$	0,000	0,000
V10 $_{\beta}$	0,236	-0,236
V11 $_{\beta}$	0,000	0,000
V12 $_{\beta}$	0,236	-0,236
V1 $_{\alpha''}$	-0,463	0,463
V2 $_{\alpha''}$	-0,463	0,463

As the observed twins are obtained during a tensile test, activated variants are expected to have a high and positive m value. However, the observed $V2_\beta$ and $V8_\beta$ variants have surprisingly a negative m value with high absolute values, close to -0.5 when $\{112\}\langle\bar{1}\bar{1}1\rangle_\beta^t$ is considered. Therefore, the consideration of the classical $\{112\}\langle\bar{1}\bar{1}1\rangle_\beta^t$ twinning system, i.e. twinning in the twinning sense, leads to an apparently incoherent result with observed twins corresponding to a compression of the crystal.

As the positions of $\{110\}_{\alpha''}$ planes and $\langle 110 \rangle_{\alpha''}$ directions of $V2_{\alpha''}$ and $V1_{\alpha''}$ are very close to $\{112\}_\beta$ planes and $\langle 111 \rangle_\beta$ directions of $V2_\beta$ and $V8_\beta$ respectively (Fig. 5a and 5b), similar m values close to -0.5 are also found for $\{110\}\langle\bar{1}\bar{1}0\rangle_{\alpha''}^t$ twinning (Table 3). Whatever β or α'' phase is considered, Schmid factor calculations for twin variants in the twinning sense (m_t) show that the observed twin variants lead to a compression of the single crystal along its tensile direction. This is of course not observed as the single crystal is elongated during the present tensile test. Therefore, $\{112\}\langle\bar{1}\bar{1}1\rangle_\beta^t$ or $\{110\}\langle\bar{1}\bar{1}0\rangle_{\alpha''}^t$ twins cannot be activated. This means that the observed twins are not the classical $\{112\}\langle 111 \rangle_\beta$ twinning system of bcc structures, and, in turn, are the non-classical $\{112\}\langle 11\bar{1} \rangle_\beta^{at}$ twinning system with a shear in the antitwinning sense regarding the classical $\{112\}\langle 111 \rangle_\beta$ mode. If twinning is then considered to occur in the antitwinning sense but in the same plane, Schmid factors (m_{at}) will have high and positive values for the observed twin variants (Table 3). Considering the activation of this non-classical $\{112\}\langle 11\bar{1} \rangle_\beta^{at}$ system, the crystal will be elongated along the tensile direction with the two observed twin variants. Therefore, this careful Schmid factor analysis allows to determine that the observed $\{112\}\langle 111 \rangle_\beta$ twins does not correspond to the classical twinning mode of bcc structures but to the non-classical $\{112\}\langle 11\bar{1} \rangle_\beta^{at}$ twinning system shearing in the antitwinning sense. $\{112\}\langle 111 \rangle_\beta$ twinning in the antitwinning sense

was never observed, as its activation energy is much higher than the one in the twinning sense due to a much higher value of atomic shuffle as detailed in the next section.

3.4. Twinning elements

As stated in the introduction, the classical $\{112\}\langle\bar{1}\bar{1}1\rangle_{\beta}^t$ mode and the non-classical $\{112\}\langle11\bar{1}\rangle_{\beta}^{at}$ mode in the antitwinning sense have the same principal twinning elements but different secondary twinning elements. Consequently, the same feature will be found for twinning systems in α'' phase due to the orientation relationship between β and α'' phases.

Table 4. Twinning elements for twinning systems in the twinning and antitwinning senses in β and α'' phases and associated shear (s) and shuffle magnitudes.

Twinning system	K_1	η_1	K_2	η_2	P	s	shuffle magnitude
$\{112\}\langle\bar{1}\bar{1}1\rangle_{\beta}^t$	(121)	$[\bar{1}1\bar{1}]$	$(\bar{1}2\bar{1})$	[111]	(10 $\bar{1}$)	0.707	0
$\{112\}\langle11\bar{1}\rangle_{\beta}^{at}$	(121)	[1 $\bar{1}$ 1]	(3 $\bar{2}$ 3)	[131]	(10 $\bar{1}$)	0.354	1/2 [1 $\bar{1}$ 1]
$\{110\}\langle1\bar{1}0\rangle_{\alpha''}^t$	(110)	[1 $\bar{1}$ 0]	(1 $\bar{1}$ 0)	[110]	(001)	0.821	1/5 [1 $\bar{1}$ 0]
$\{110\}\langle\bar{1}10\rangle_{\alpha''}^{at}$	(110)	$[\bar{1}10]$	$(\bar{1}30)$	[310]	(001)	0.259	1/5 [$\bar{1}$ 10]

Principal and secondary twinning elements of each twinning system can be calculated using the Bilby and Crocker theory and can be found in the following references for $\{112\}\langle\bar{1}\bar{1}1\rangle_{\beta}^t$ and $\{112\}\langle11\bar{1}\rangle_{\beta}^{at}$ [46,47] and for $\{110\}\langle1\bar{1}0\rangle_{\alpha''}^t$ and $\{110\}\langle\bar{1}10\rangle_{\alpha''}^{at}$ [55]. These elements are given in Table 4 for each considered twinning system and in Table 5 for each twin variant. As each twinning element is commensurable, these twinning systems are all of compound type. Fig. 6 shows these twinning elements on stereographic projections in β phase (Fig. 6a) and in α'' phase (Fig. 6b) and the associated dichromatic diagrams with respect of the orientation relationship in β phase (Fig. 6c) and α'' phase (Fig. 6d). The pole of K_1 is on the top of the stereographic projections and the pole of the shear plane P is normal to the surface of projections. η_1 directions of the β and α'' twinning systems point both to the right of the

projections whereas η_1 directions of antitwinning systems point to the left. Secondary twinning elements K_2 and η_2 are also shown on these figures for each system. Shear values are calculated using the formula $s = 2\cotan(2\phi)$ where ϕ is the angle between η_1 and the secondary twinning direction in the twinned crystal η'_2 (Fig. 1).

Table 5. Twinning elements of the 12 variants of $\{112\}\langle\bar{1}\bar{1}\bar{1}\rangle_\beta^t$, $\{112\}\langle 11\bar{1}\rangle_\beta^{at}$ and the 2 variants of $\{110\}\langle 1\bar{1}0\rangle_{\alpha''}^t$ and $\{110\}\langle\bar{1}10\rangle_{\alpha''}^{at}$.

	K_1	η_1	K_2	η_2		K_1	η_1	K_2	η_2
$V1_\beta^t$	(112)	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{1}\bar{1}2)$	$[111]$	$V1_\beta^{at}$	(112)	$[11\bar{1}]$	$(33\bar{2})$	$[113]$
$V2_\beta^t$	(121)	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{1}2\bar{1})$	$[111]$	$V2_\beta^{at}$	(121)	$[1\bar{1}\bar{1}]$	$(3\bar{2}3)$	$[131]$
$V3_\beta^t$	(211)	$[1\bar{1}\bar{1}]$	$(2\bar{1}\bar{1})$	$[111]$	$V3_\beta^{at}$	(211)	$[\bar{1}1\bar{1}]$	$(\bar{2}33)$	$[311]$
$V4_\beta^t$	$(\bar{1}12)$	$[1\bar{1}\bar{1}]$	$(1\bar{1}2)$	$[\bar{1}11]$	$V4_\beta^{at}$	$(\bar{1}12)$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{3}3\bar{2})$	$[\bar{1}13]$
$V5_\beta^t$	$(\bar{1}21)$	$[1\bar{1}\bar{1}]$	$(12\bar{1})$	$[\bar{1}11]$	$V5_\beta^{at}$	$(\bar{1}21)$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{3}23)$	$[\bar{1}31]$
$V6_\beta^t$	$(\bar{2}11)$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{2}\bar{1}\bar{1})$	$[\bar{1}11]$	$V6_\beta^{at}$	$(\bar{2}11)$	$[111]$	(233)	$[311]$
$V7_\beta^t$	$(1\bar{1}2)$	$[\bar{1}11]$	$(\bar{1}12)$	$[1\bar{1}\bar{1}]$	$V7_\beta^{at}$	$(1\bar{1}2)$	$[1\bar{1}\bar{1}]$	$(33\bar{2})$	$[1\bar{1}3]$
$V8_\beta^t$	$(12\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{1}2\bar{1})$	$[1\bar{1}\bar{1}]$	$V8_\beta^{at}$	$(12\bar{1})$	$[111]$	(323)	$[131]$
$V9_\beta^t$	$(2\bar{1}1)$	$[11\bar{1}]$	$(21\bar{1})$	$[1\bar{1}\bar{1}]$	$V9_\beta^{at}$	$(2\bar{1}1)$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{2}33)$	$[3\bar{1}1]$
$V10_\beta^t$	$(11\bar{2})$	$[\bar{1}\bar{1}\bar{1}]$	$(\bar{1}\bar{1}2)$	$[11\bar{1}]$	$V10_\beta^{at}$	$(11\bar{2})$	$[111]$	(332)	$[11\bar{3}]$
$V11_\beta^t$	$(12\bar{1})$	$[\bar{1}11]$	$(\bar{1}21)$	$[11\bar{1}]$	$V11_\beta^{at}$	$(12\bar{1})$	$[1\bar{1}\bar{1}]$	$(3\bar{2}3)$	$[13\bar{1}]$
$V12_\beta^t$	$(21\bar{1})$	$[1\bar{1}\bar{1}]$	$(2\bar{1}1)$	$[11\bar{1}]$	$V12_\beta^{at}$	$(21\bar{1})$	$[\bar{1}1\bar{1}]$	$(\bar{2}3\bar{3})$	$[31\bar{1}]$
$V1_{\alpha''}^t$	(110)	$[\bar{1}\bar{1}0]$	$(\bar{1}\bar{1}0)$	$[110]$	$V1_{\alpha''}^{at}$	(110)	$[\bar{1}\bar{1}0]$	$(\bar{1}30)$	$[310]$
$V2_{\alpha''}^t$	$(\bar{1}10)$	$[\bar{1}\bar{1}0]$	$(\bar{1}\bar{1}0)$	$[\bar{1}10]$	$V2_{\alpha''}^{at}$	$(\bar{1}10)$	$[110]$	(130)	$[3\bar{1}0]$

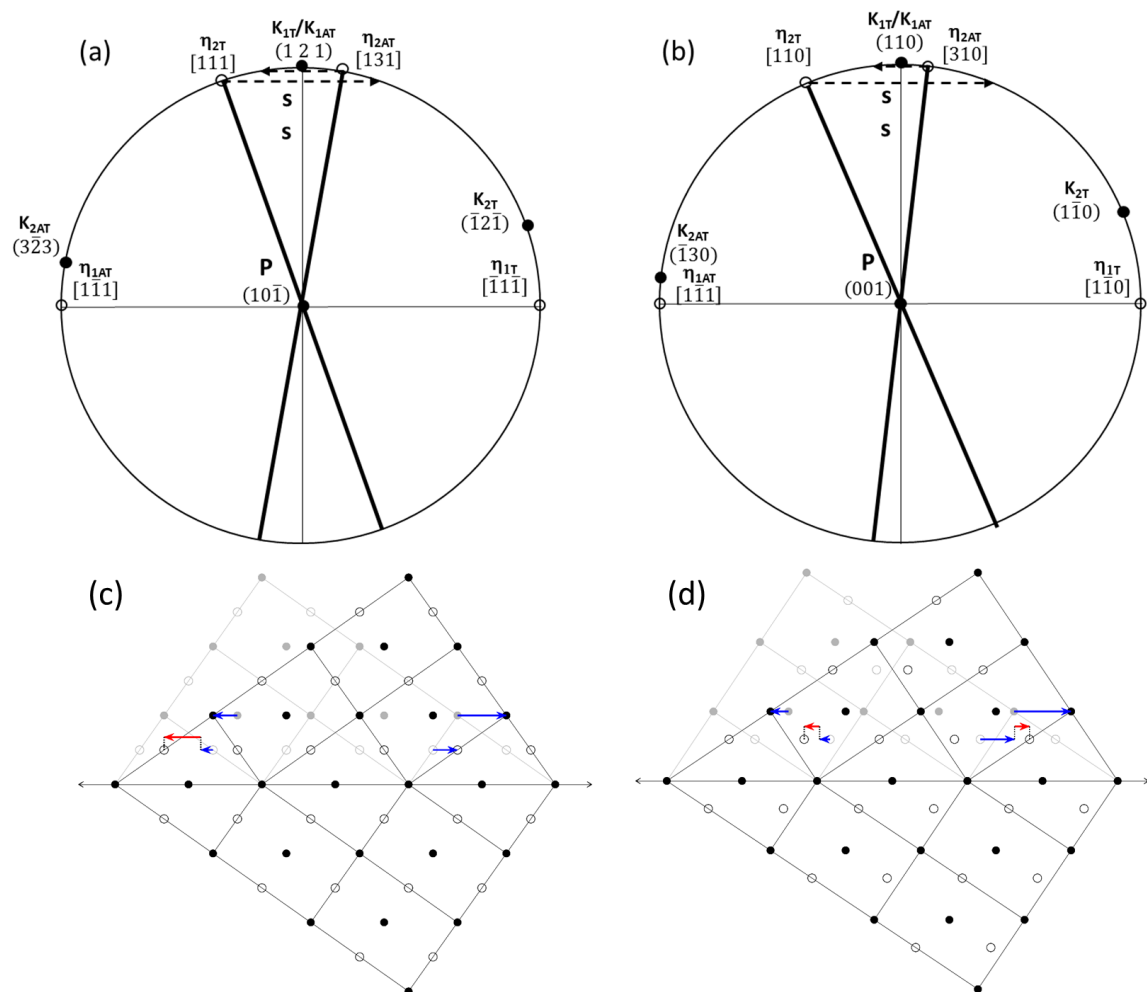


Fig. 6 Stereographic projections showing twinning (T in subscript) and antitwinning (AT in subscript) elements for β phase (a) and α' phase (b) and associated dichromatic diagrams (c and d, respectively). Filled circles correspond to atoms in the plane of the figure and empty circles correspond to atoms above the plane of the figure.

As it is acknowledged that activated twinning systems exhibit low shear and shuffle [46,47], dichromatic diagrams of β and α' phases are used to highlight shear and shuffle values of each twinning system (Fig. 6c and Fig. 6d). Twinning direction points to the right and antitwinning direction points to the left. The obtained shear and shuffle values are summarized in Table 4. They are measured as follows:

- the plane located two atomic layers above the twinning plane of the figure is assumed to undergo simple shear during the twinning operation. This necessary shear is applied to the whole twinned crystal and is represented by blue arrows on Fig 6c and Fig 6d;

- the plane located one atomic layer above the twinning plane needs additional shuffle to reach the twinning configuration. This shuffle, represented by red arrows, is applied to every white atom of Fig 6c and Fig 6d.

Shuffle is an important parameter to take into account to explain twinning of bcc structures.

Whereas shear of $\{112\}\langle 11\bar{1}\rangle_{\beta}^{at}$ is very low, this system is generally not activated in bcc structures due to its high shuffle magnitude ($1/2 [1\bar{1}1]$). Conversely, no shuffle is necessary for classical $\{112\}\langle \bar{1}\bar{1}1\rangle_{\beta}^t$, making it easier to activate in spite of its higher shear value [46].

The case of α'' phase is more complex because several dichromatic diagrams can be obtained from its twinning elements due to its double-layered structure. Investigation by high resolution transmission electron microscopy may reveal the real structure of the α'' twin interface. But this phase disappears when the stress is released and makes this kind of observation difficult. Several configurations were then tested and the most probable configuration, i.e. the one with minimal shear and shuffle magnitudes, is shown on Fig 6d. In this condition, the shear is lower for $\{110\}\langle \bar{1}10\rangle_{\alpha''}^{at}$, than for $\{110\}\langle 1\bar{1}0\rangle_{\alpha''}^t$, and the atomic shuffle is the same for both twinning systems. Thus, $\{110\}\langle \bar{1}10\rangle_{\alpha''}^{at}$ is easier to activate thanks to its low shear and low shuffle magnitudes. Then, as the shuffle value is the same for twinning and antitwinning direction in α'' phase, the twinning direction has to be the one involving the lowest shear. As a consequence, twinning and antitwinning senses are inverted in α'' phase in comparison with β phase.

Finally, observation of twins in the antitwinning sense in β phase is due to the activation of twins in SIM α'' because of lower shear in the antitwinning sense than in the twinning sense

of the prior β phase. In other words, it was firstly assumed that twinning senses are the same in both β and α'' phases, while not. Consequently, what is denoted “antitwinning” in α'' phase actually corresponds to twinning sense in this phase, but corresponds to antitwinning sense in β phase. Despite this, subscripts (t) and (at) in the notation of twinning systems in α'' phase will not be changed in order to keep a coherent notation in the whole paper. Actually, they correspond to the sense of twinning of β phase.

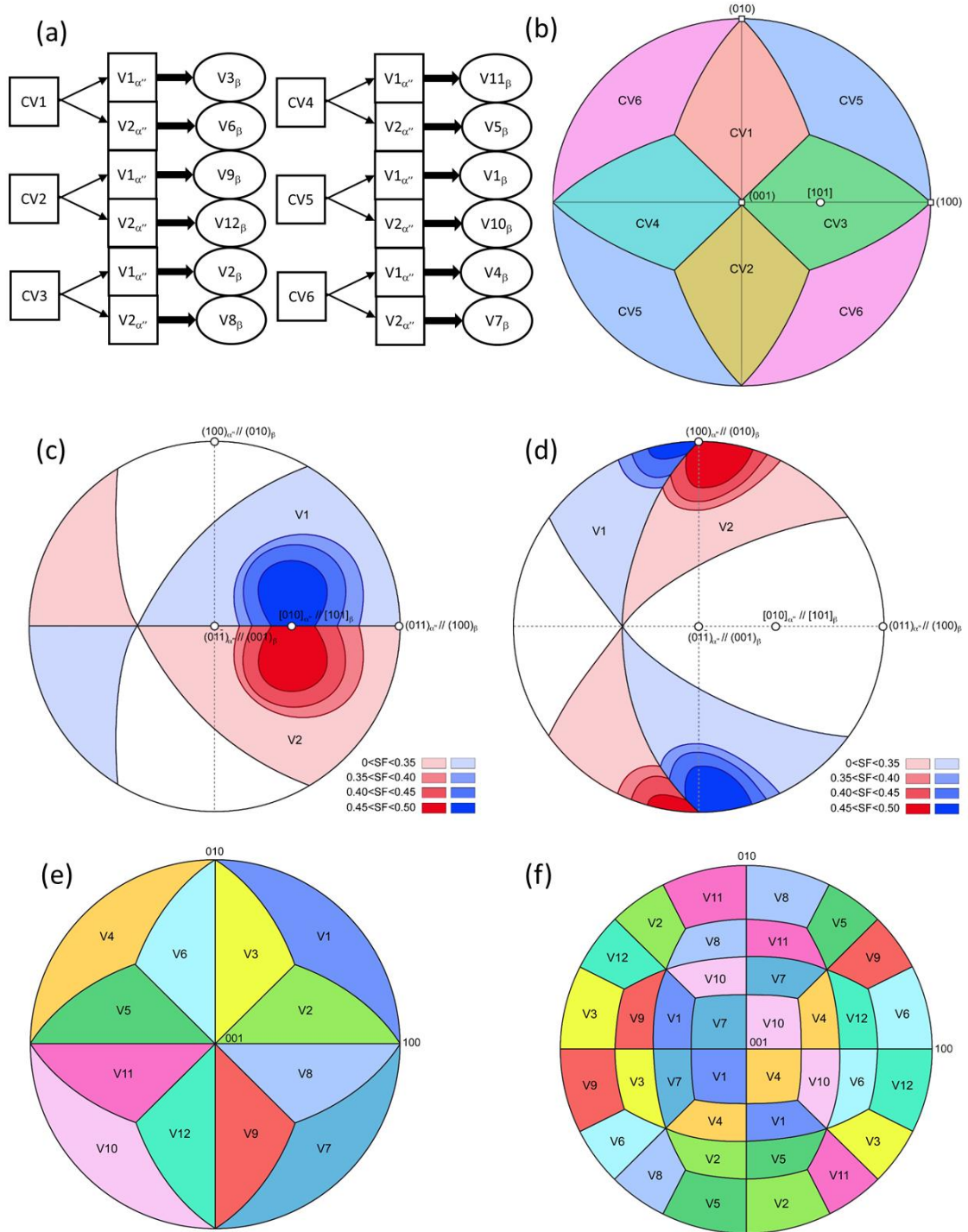


Fig. 7 Correspondences between variants of martensite, twin variants in martensite and twin variants in β phase (a); IPF showing variant selection of α'' martensite as a function of TD (b); IPFs of positive Schmid factor values of $\{110\}\langle 110 \rangle_{\alpha''}^{at}$ (c) and $\{110\}\langle 110 \rangle_{\alpha''}^t$ (d) in CV3 of α'' martensite; IPFs of maximum Schmid factor values of $\{112\}\langle 111 \rangle_{\beta}^{at}$ and $\{112\}\langle 111 \rangle_{\beta}^t$ twinning systems.

3.5. Twinning system activation in alloys exhibiting SIM transformation

Results of previous sections focused on a specific observation in a given single crystal. Let us now generalize these results to any crystallographic orientation. Observed twins in β phase are presently the result of a twinning operation in α'' martensite and a reverse SIM transformation of α'' martensite twins. The formation of each β twin variant actually corresponds to a process composed of two successive variant selections. The first step is the selection between the 6 CVs during SIM transformation and the second step is the selection between the two $\{110\}\langle 110 \rangle_{\alpha''}$ twin variants. As only 2 twin variants exist for $\{110\}\langle 110 \rangle_{\alpha''}$ twinning in α'' , only 2 of the 12 $\{112\}\langle 111 \rangle_{\beta}$ possible twin variants can be observed in β phase for a given CV. In the case of the present single crystal, CV3 is activated by tensile stress. The application of CV3 BOR shows that only $V2_{\beta}$ and $V8_{\beta}$ fit with $V1_{\alpha''}$ and $V2_{\alpha''}$ respectively. However, the six possible CVs offered by SIM transformation combined with the two possible variants of twinning in α'' phase cover the twelve variants of twinning in β phase. Fig 7a summarizes then these correspondences. Note that this process can operate with $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ and $\{110\}\langle \bar{1}10 \rangle_{\alpha''}^{at}$, or with $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ and $\{110\}\langle 1\bar{1}0 \rangle_{\alpha''}^t$. This first step can be drawn as an inverse pole figure (IPF) showing the domains of selected CVs as a function of the orientation of the tensile axis TD (Fig. 7b). The selected CV is then the one leading to the maximum strain along the tensile axis among the 6 CVs as described in section 2.2. Considering the present single crystal, it can be seen on this figure that a $[101]_{\beta}$ orientation of TD leads actually to CV3 under tensile stress.

The second step consists of the twin variant selection from Schmid factor analysis. This is drawn in Fig. 7c and Fig 7d that correspond to IPFs of positive m values as a function of the tensile direction for $\{110\}\langle \bar{1}10 \rangle_{\alpha''}^{at}$ and $\{110\}\langle 1\bar{1}0 \rangle_{\alpha''}^t$ respectively, for the orientation of α'' corresponding to the CV3. The twin variant selection can then be verified from the superimposition of Fig. 7b and Fig. 7c or Fig. 7d in this specific case: The domains of high

positive m values of $\{110\}\bar{1}10\}_{\alpha''}^{at}$ (Fig. 7c) coincide with the CV3 domain of Fig. 7b whereas it is not the case for $\{110\}\bar{1}\bar{1}0\}_{\alpha''}^t$ (Fig. 7d). Therefore, only $\{110\}\bar{1}10\}_{\alpha''}^{at}$ can accommodate a tensile strain when CV3 is selected as in the present single crystal. This result can be now generalized to any variant as detailed hereafter.

The same procedure can be done directly into the β phase for the variant selection of both twinning and antitwinning $\{112\}\langle 111 \rangle_{\beta}$ modes. IPFs of maximal positive m values as a function of the tensile direction of $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ and $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ systems are represented in Fig. 7e and Fig 7f, respectively. The criterion of selection is then the maximum positive m value belong the 12 twin variants. The superimposition of Fig. 7b and Fig. 7e shows a perfect fitting between the domains of activated CVs (Fig. 7b) and activated twin variants of $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ (Fig. 7e). In other words, the CV selection of α'' martensite followed by the twin variant selection in the activated α'' CV leads to the same result than considering directly the variant selection of $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ antitwins in β phase. The CV selection of α'' martensite for a tensile test always gives a crystal of martensite favorably orientated to produce $\{112\}\langle 11\bar{1} \rangle_{\beta}^{at}$ twins after reverse SIM transformation. Conversely, the Fig. 7f shows the variant selection of classical $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ twins in β phase, i.e. the domain of preferential activation of each twin variant if no SIM is considered. Taking again the present single crystal with the tensile direction of $[101]$ as an example, $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ twin variants $V4_{\beta}$, $V6_{\beta}$, $V10_{\beta}$ or $V12_{\beta}$ would be expected to be activated (Fig. 7f). However, the superimposition of Fig. 7f with Fig. 7b shows that the CV3 of α'' martensite is activated, and, regarding the possible twin variants of $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ possibly formed from the reversion of twins in α'' (Fig. 7a), only $V2_{\beta}$ and $V8_{\beta}$ can be produced. Finally, this point highlights that the classical $\{112\}\langle \bar{1}\bar{1}1 \rangle_{\beta}^t$ twinning system can never be formed in β phase due to the CV selection of martensite occurring during a tensile test, whatever the tensile direction. While this CV

selection promotes the formation of non-classical $\{112\}\langle 11\bar{1}\rangle_{\beta}^{at}$ twins in the antitwinning sense through the activation and the reversion of $\{110\}\langle \bar{1}10\rangle_{\alpha''}^{at}$ twins in α'' martensite. Therefore, a careful examination of activated $\{112\}\langle 111\rangle_{\beta}$ twin variants by Schmid factor analysis allows to determine if a SIM transformation has occurred: If the observed $\{112\}\langle 111\rangle_{\beta}$ twins are in the twinning sense of classical bcc structures, twins are directly formed into the β phase, while $\{112\}\langle 111\rangle_{\beta}$ twins in the antitwinning sense are the proof of the reversion of twins previously formed into a SIM α'' phase.

4. Conclusions

A single crystal of metastable β Ti-24Nb-4Zr-8Sn alloy was studied. *In situ* SXRD during cyclic tensile test shows that full martensitic transformation is achieved when plastic deformation begins. Deformation twins are observed *post mortem* after tensile test and are identified as $\{112\}\langle 111\rangle_{\beta}$ twins. Careful Schmid factor analysis of the observed $\{112\}\langle 111\rangle_{\beta}$ twins shows that they are $\{112\}\langle 11\bar{1}\rangle_{\beta}^{at}$ antitwins with a twinning direction opposite to that of classical $\{112\}\langle \bar{1}\bar{1}1\rangle_{\beta}^t$ twins of bcc structure, i.e. along the antitwinning direction.

This unusual observation is explained by the stress-induced martensitic transformation occurring during tensile test. Observed twins in β phase are actually the result of the reversion during the reverse SIM transformation of activated $\{110\}\langle \bar{1}10\rangle_{\alpha''}^{at}$ twins in α'' martensite. The magnitude of shuffle drops then from $1/2 [\bar{1}\bar{1}1]_{\beta}$ if these twins were directly formed in β phase, to $1/5 [\bar{1}10]_{\alpha''}$ after SIM transformation, making it easier to activate in α'' phase. Moreover, variant selection of stress-induced martensite always leads to a martensitic crystal which is favorably oriented for $\{110\}\langle \bar{1}10\rangle_{\alpha''}^{at}$ and unfavorably oriented for $\{110\}\langle 1\bar{1}0\rangle_{\alpha''}^t$ twinning system, according to Schmid factor analysis. Finally, this former feature

demonstrates that the occurrence of α'' SIM transformation promotes the observation of $\{112\}\{11\bar{1}\}_{\beta}^{at}$ antitwins and totally impedes the formation of classical $\{112\}\{1\bar{1}1\}_{\beta}^t$ twins of bcc structures due to a combination of variant selection of stress-induced martensite and occurrence of reverse martensitic transformation.

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Compliance with Ethical Standards:

The authors declare that they have no conflict of interest.

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