Conventional vs Harmonic-structured $\beta$-Ti-25Nb-25Zr alloys: a comparative study of deformation mechanisms

F. Mompioua, D. Tingaudb, Y. Changc, B. Gaultc, G. Dirrasb

Abstract

Harmonic alloys processed by powder metallurgy are constituted by a core of coarse grains embedded in an interconnected small grain shell. They have attracted attention due to their excellent strength combined with large ductility, the two properties being rather antagonist from the classical metallurgical point of view. In contrast, conventional $\beta$-Ti alloys are currently vastly studied owing their excellent properties especially for biomedical applications. In the present study, we explore at the micron scale the deformation mechanisms operating both in standard and harmonic-structured $\beta$-Ti-25Nb-25Zr alloys using transmission electron microscopy (TEM). Although we show some similarities, deformation mechanisms appear significantly different due to the activation of martensitic transformation in conventional samples. The combined use of automated crystal orientation in TEM and in-situ TEM straining reveals that deformation bands nucleate and grow according to a mechanism involving both martensitic transformation and twinning. The comparison between in-situ and post-mortem experiments shows globally a good agreement and highlights a strain relaxation mechanism between martensite and twin. More importantly, a cross-glide mechanism similar to what is observed in dilute solid solutions is proposed to explain the dynamics of dislocation motion. Stress estimations derived from the observations of dislocation curvature between pinning points, show a reasonable good agreement with macroscopic values. The observation of deformation mechanisms operating both in core and shell structures of the harmonic-structured alloy allows us to propose a scenario of plastic deformation in the early stages.

Keywords: in-situ TEM, $\beta$-Ti alloys, harmonic microstructure, dislocation, martensite, twinning

1. Introduction

$\beta$-titanium alloys constitute excellent candidates for biomedical applications requiring both high strength, low Young modulus and biocompatibilities [1]. Thus, their good mechanical properties have motivated studies of the deformation processes at the sub-micron scale. It was found that they operate by a combination of dislocation slip, twinning and stress-induced phase transformation (TRIP/TWIP effect) [2, 3]. The interplay between these mechanisms can be chemically tuned to provide both hardening and good ductility. However the complexity of the deformed microstructure makes the post-mortem analysis of the deformation processes and the sequence of their appearance difficult to interpret [4–6]. Some aspects of the deformation such as the origin of the unusual $\langle 332\rangle (113)$ twinning mode is for instance still a debated question. The complexity of the mechanisms, is clearly determined by the stability of the different phases that are triggered by strain-induced processes such as $\beta \rightarrow \alpha^\prime$ (martensite) or $\beta \rightarrow \omega$ phase transformations [7]. In addition to that, microstructure design using powder metallurgy routes have been recently proposed and applied to a large variety of alloys in order to improve both strength and ductility. This approach exploits mechanical milling and sintering methods to form a multimodal microstructure composed of a matrix core of large grains embedded in an ultra-fine grained interconnected shell [8–11]. Recent studies in pure Ti indicate that the shell constitutes a strong skeleton controlling the deformation in the early stages leading to a higher yield stress than a conventional microstructure [12]. The strength of the shell is classically attributed to a Hall-Petch type effect, while the core is expected to sustain larger hardening providing thus a better ductility. However, the sequence of deformation processes and the interplay between shell and core, especially at their interface has not been currently addressed at the micron-scale. The behavior of both conventional and harmonic-structured (hereafter simply called harmonic) $\beta$-Ti alloys has been reported in a previous study based on simple shear loading tests and microstructure investigations [13]. The harmonic samples exhibit a higher yield stress without ductility loss as expected. In terms of hardening behavior, the conventional alloy which deforms mainly by twinning compete with the harmonic one, due to dynamic grain refinement. Interestingly, the harmonic alloy of the same nominal composition does not deform by twinning, but still maintain a good hardening rate. The question of the microstructure impact on different deformation mechanisms needs then to be addressed. Here, we present a study exploring the deformation mechanisms in both conventional (i.e. a monomodal structure) and harmonic $\beta$-Ti-25Nb-25Zr (wt. %) alloys. Af-
ter presenting the initial microstructures (sec. 3.1), we will focus our attention on the post-mortem observations of deformed samples (sec. 3.2) by transmission electron microscopy (TEM). With an approach using in-situ TEM straining experiments, we expect to explain some characteristics of the elementary mechanisms (sec. 3.3). Post-mortem and in-situ results will then be compared and used to discuss the mechanisms in relation to the microstructure and mechanical properties, in the light of the literature, in sec. 4.

2. Experimental

The Ti alloy powder was elaborated by the Plasma Rotating Electrode Process. Conventional specimens were prepared by sintering directly from the initial powder by Spark Plasma Sintering (SPS) (800 °C, 30 min). Harmonic samples were obtained after first a mechanical milling of the initial powder followed by SPS sintering in the same conditions. Details on the sample processing is reported in [14].

Compression tests were conducted at room temperature with a strain rate of $10^{-2}$ s$^{-1}$ up to a strain of 10%.

For in-situ experiments 3 mm x 1 mm TEM samples were cut by electrodischarging machining and eventually mechanically polished and etched by a Struers A3-I solution at -10 °C. Specific areas of the shell structure were analyzed by extracting $10 \mu m \times 5 \mu m$ thin lamella using Focused Ion Beam (FIB). Samples were prepared by a standard lift out method using a Helios FEI nanolab 600i dual-beam microscope equipped with a gallium ion source. TEM observations were performed using a JEOL 2010HC microscope operated at 200 kV using a GATAN straining holder. Video sequences were acquired using a digital recorder and a 25 fps MEGAVIEW III camera. In-situ straining TEM experiments were performed in combination with Automated Crystallographic Orientation Mapping (ACOM-TEM) in a CM20 FEG microscope operating at 200 kV and equipped with a GATAN Orius camera and the Nanomegas Digistar ASTAR system. Orientation maps were obtained sequentially after strain increment complete relaxations. Electron Dispersive Spectroscopy in Scanning TEM (STEM-EDS) or in SEM mode, was performed either using a CM20 FEG TEM equipped with a Bruker detector or a Helios nanolab 600i microscope equipped with an Oxford detector, respectively.

Electron Back Scattering Diffraction (EBSD) observations were carried out on a ZEISS SUPRA 40VP electron microscope equipped with a field effect gun. The step size (from 0.05 to 1.50 μm) was adjusted to the size of the observed microstructures. Crystal orientation, grain size, grain boundary misorientation, Kernel Average Misorientation (KAM) and phase map were obtained by analyzing the data with OIM software version 5 (TexSEM Laboratories). A grain was defined by at least three neighboring pixels with a misorientation lower than 15°. KAM is the average of low misorientation angle (below 5°) between pixels taken into account up to the 5th neighbor.

Specimens for atom probe were prepared specifically from the shell region by using an in-situ lift-out protocol outlined in [15]. The preparation was done on a dual beam FEI Helios PFIB equipped with a cryogenic stage as described in [16]. As proposed by Chang et al. [17], the use of cryo-temperature during specimen preparation is expected to reduce the likelihood of spurious hydride formation during FIB-based specimen preparation reported by Ding and Jones [18]. Atom probe tomography was performed on a Cameca LEAP 5000 XR, equipped with a reflectron-lens and a laser with a wavelength of 355 nm and a pulse duration below 10 ps and a spot-size in the range of 3 μm. The datasets were acquired in laser pulsing mode, with a laser pulse energy of 50 pJ at a base temperature of 70 K and an average detection rate of 2 ions detected per 100 pulses. The data was processed and reconstructed using the commercial package IVAS 3.8.2.

3. Results

3.1. Initial microstructures

Figure 1 shows typical conventional (Fig. 1a) and harmonic (Fig. 1b) microstructures. As expected, the conventional one is constituted by large grains (mean grain size in area of 140 μm) while the harmonic one is composed of a core region with large grains (mean grain size in area of 85 μm) surrounded by a fine shell (typical average thickness of about 12 μm with a grain size in area of 2.5 μm). A FIB specimen was extracted in an area overlapping both the core and shell region, i.e. in an area where the shell is particularly thin (Fig. 1c). The shell grains are usually decorated by small precipitates shown in Fig. 1d. A volume fraction of precipitates of ≈ 3% in the shell can be extracted from image analysis of a large area in electro-polished samples. Electron diffraction analysis shows that they have a fcc structure with a lattice parameter a=0.46 nm. The presence of such precipitates in the shell region suggests that it is associated to the material processing, as previously shown in ball-milled α-Ti50-Zr50 alloys [19] and β-Ti-15-3-3-3 alloy [20]. Their nature, however, is not clear. It is probable that they formed due to contamination by light elements (H,C,N,O) [21], although some other studies speculate from mechanically induced phase transformation [22]. EDS analysis surprisingly shows that they contain a large amount of Zr and are depleted in Nb (Fig. 1d). To look for light elements, atom probe tomography experiments were carried out in the shell region. They show that precipitate are Zr-rich carbides (Fig. 1e). Their morphology is consistent with the results from EDS maps. A composition profile calculated along a 10 nm diameter cylinder positioned perpendicular to the interface is plotted in Fig. 1e. Inset is shown the section of the tomographic reconstruction where the carbide is intercepted. Far from the particle, the composition of the matrix is in the range of Ti69Zr15.5Nb15.5 at. % (i.e. close to the nominal composition, Ti54Zr23Nb23 wt. %) with negligible levels of carbon, comparable to the level of background. In the core of the carbide, the composition in C reaches approx. 33 at.%. Zr is approx. 56 at. %, Ti is 10 at.% and Nb is only ≈ 1 at.%.

The composition profile close to ZrC carbide, which was shown to be energetically rather stable [23]. The crystal structure is however closer to ZrC (Fm-3m, a=0.47 nm [23]). The composition profile of Nb seems to indicate that it tends to be rejected as the carbide grows and accumulate at the interface
between the carbide and the metallic matrix. A slight depletion of Nb appears afterwards, which seems to correspond to a region slightly enriched in Zr. This may be related to the growth of the carbide: Nb is rejected from the carbide, but its diffusivity is too low to equilibrate in the matrix, forming a Nb-rich (up to 30 at. %) shell; the Zr starts to accumulate on the outer edge of the Nb-rich shell. These carbides are hence likely very stable. They are thought to be formed by mechanical alloying due to C contamination in the outer shell of powder particles, during the milling step [24]. During sintering, it is supposed that the carbide particles limit grain recrystallization, by grain boundary impingement, leading to the formation of a shell of fine grains as observed.

At a larger scale, EDS analysis, shown in Fig. 1f, reveals small chemical heterogeneities between shell and core regions. Conventional samples, and shell regions of harmonic samples, present similar compositions, i.e. Ti-22Nb-24Zr and Ti-23Nb-25Zr (wt. %), respectively, while large regions in the center of the core in harmonic samples exhibit composition close to Ti-27Nb-21Zr (wt. %). As shown below, this compositional variation between core and shell may play a significant role in the deformation mechanisms.

3.2. Post-mortem analysis of deformed microstructures in large grains

Both conventional and harmonic samples were observed after 10% of deformation. The observations made in the plane parallel to the compression axis are summarized in Figure 2.

The harmonic microstructure presents typical slip bands as shown in Fig. 2a (noted $S_i$). Dislocations in the bands can be indexed as $a/2\{111\}$ type dislocations with a strong screw character as more easily evidenced on isolated dislocations shown in the inset. The analysis of the slip band plane from the trace analysis direction (noted with dashed lines in Fig. 2a) shows that they correspond to $\{112\}$ planes. Occasionally, $\{112\}$ twins can be identified. In the shell, dislocation tangles with straight segments were observed (Fig. 2b). Their glide planes indicated by dashed lines are here closer to $\{110\}$ planes. The KAM map obtained from EBSD observations of the harmonic alloy reveals that slight misorientations, less than $5^\circ$, are present both in the core and shell (Fig. 2c). In the core, they can clearly be associated to slip bands, originating from grain boundaries and extending in the grains. Moreover, higher misorientations are concentrated in the shell and close to the core/shell interface, indicating that deformation is concentrated in these regions. All these observations tend to indicate that at such strain level, deformation is accommodated both in core and shell.

The microstructure of deformed conventional samples appears significantly different. Although $a/2\{111\}$ screw dislocations gliding in $\{110\}$ planes were observed (not shown here), the microstructure is mainly characterized by long deformation bands. Observed by EBSD, the bands are found crossing entirely the grains and misorientation measurement shows that they are $\{332\}$/$\{113\}$ twins (Fig. 2g). The microstructure of the bands themselves is usually complex as shown in Fig. 2d. Dislocations emerging, sometimes forming small angle
3.3. In-situ TEM observations

3.3.1. Dislocation glide

Several mechanisms were observed during straining. They are described below.

In both harmonic and conventional samples, dislocation nucleation and motion were identified. Figure 3a shows typical features of dislocation slip in a coarse grain of an harmonic sample. The glide planes are found to be locally either close to (011) or (112) but at larger scale, the slip traces appear curved indicating cross-slip between those planes (Fig. 3a).

Further straining usually leads, in harmonic samples to the formation of dense deformation bands as shown latter (Fig. 8). As seen in Fig. 3b, dislocations have in average long straight screw segments that are slightly curved between pinning points. It should be noted here that the pinning points cannot be attributed to precipitates. The dynamics of dislocation motion is depicted in Fig. 3c-f as a sequence of pictures extracted from a video sequence (see video 1 in the supplementary materials). Their motion appears very jerky, with rapid pinning and unpinning, on both edge and screw segments, usually within few frames, i.e. few 1/100 of seconds. Fig. 3d-f show for instance the formation by double cross-slip of a dipole at point p1 that eventually extends and moves along the dislocation line to the position p2, i.e. in the b direction. This is easily seen on the image difference shown in Fig. 3g. The displacement of the screw (ds) and edge (de) segments yields a speed of 4.5 nm/s and 28 nm/s, respectively. This difference tends to indicate a mobility difference thus explaining why observed moving dislocations have mainly a screw character. The dipole formed eventually becomes completely pinned in p3 and thus further extends (Fig. 3f and the corresponding image difference in 3h). Other video sequences reveal the presence of a large number of debris in the wake of dislocations which are the direct consequence of the closing of the dipoles by cross-slip. The dislocation mechanism will be further discussed in the section 4.

In conventional samples, dislocations were observed being emitted from a crack on the right side of Fig. 4a (see the video 2 in the supplementary materials). In front of the crack tip, martensite or twin laths noted La were observed alongside with a large density of dislocations. Their role in the deformation is discussed below. A third phase identified as a \( \alpha \) phase can be evidenced.
Figure 3: Dislocation motion in harmonic samples. a) Large BF view showing dislocations and slip plane traces (tr.) b) evidences pining points along screw segments. c)-e) BF snapshots of dislocation motion showing the pining of a screw dislocation and the formation of a dipole. g) and h) are image differences highlighting dislocation motions between snapshots.

Figure 4: Dislocation motion in conventional samples. a) Large view of deformation near a crack. Note the presence of martensite or twins laths ($La$), large dislocation density and $\alpha_2$ precipitates (see the corresponding diffraction pattern). b) shows slip traces of $\alpha/2\{111\}$ dislocation ahead of crack tips and the Schmid factors for the closest planes. c) and d) are BF and the corresponding DF using $\hat{g} = (01\bar{1})_{\alpha_2}$ taken during dislocation motion. Red arrows points in both images on pinning points ($P$), super-jogs ($SJ$), and prismatic loop ($L$).

Figure 5: BF images extracted during in-situ straining revealing the nucleation and propagation of martensite from a crack tip in a conventional sample a)-c) and a complex band formation at further strain d).
in this area (see the diffraction pattern close to [200] zone axis) [25]. Further ahead of the highly deformed area, dislocations with a Burgers vector $a/2[111]$ were observed. Their glide planes have traces distributed around the (211) plane. With the strain axis $T$, the Schmid factors for all the principal crystallographic planes close to the observed traces show very small differences (Fig. 4b). The fan-shaped distribution of the glide planes can thus be attributed to a combination of glide, by cross-slip, in these planes, as a result of local variation of the stress field in front of the crack tip. Dislocation motion dynamics is very similar to what was observed in harmonic samples: straight screw dislocations move jerkily due to the presence of pinning points ($P$)(Fig. 4c-d). This leads to the formation of super-jog ($S/J$)(i.e. large kink on the dislocation line) or prismatic loops ($L$). Corresponding DF images using $\vec{g} = (01\bar{1}1)$ diffraction vector, reveal the presence of nanometer size $\alpha_2$ precipitates. The pinning point on Fig. 4c can be identified as a precipitate when comparing both BF and DF images. In Fig. 4d, the correspondence between the pinning point and super-jog with precipitates is however not clear. The presence of a large precipitate at the loop location ($L$) tends to indicate that the loop itself results from the previous pinning of the dislocation.

3.3.2. Martensitic transformation, twinning and band formation

Apart from dislocation glide, conventional samples present deformation mechanisms leading to the formation of localized deformation bands. Figure 5 shows images extracted from a video taken during straining while a crack opened. In Fig. 5a, typical screw dislocations ($d$) can be easily seen at the crack tip, similarly as shown in Fig. 4a. Upon further deformation, the rapid nucleation of a band is observed (see the video 3 in the supplementary materials). Electron diffraction analysis performed during various experiments on similar laths (see the supplementary materials for details), reveals that it corresponds to a martensite lath ($Ma$) that can be indexed with the lattice parameters $a=0.37$ nm, $b=0.484$ nm and $c=0.462$ nm, close to the X-ray diffraction determination and DFT calculation [26]. Orientation relationships were found to be in agreement with literature, i.e. $[100]_\beta || [100]_\alpha$, $[010]_\beta || [011]_\alpha$ and $[001]_\beta || [011]_\alpha$ [27]. Although not determined, the trace of the habit plane is compatible with (575), close to (111), as typically expected in $\beta$-Ti alloys [27, 28]. Further straining leads to several nucleation and propagation of parallel martensite laths (Fig. 5c). As the crack opens, deformation tends eventually to localize in a larger band where martensite laths can be distinguished at the borders (Fig. 5d). Subsequent deformation leads to further band thickening, but because of heavy foil distortion, the nature of the band interior remains difficult to interpret. To get a clearer picture of the deformation mechanisms, a combination of in-situ straining and orientation mapping using ASTAR was conducted. Indeed because electron diffraction is not sensitive to heavy deformation, it allows the identification of phases/grains in the band [29].

Figure 6 shows the result of such experiment in a conventional sample. The phase map combined with the reliability map in Fig. 6 shows that in an original $\beta$ grain (noted $M$ for matrix), thin $\alpha''$ martensite laths ($Ma$) have grown from the rim of the hole close to a crack. In addition, a $[112](111)$ twin ($T$) can be determined from the orientation map (Fig. 6b). Interestingly, the twin is bounded by the martensite phase, especially in the thicker area. Fig. 6c highlights the growth of a micro-twin (pointed by a red line) during deformation. This event occurs concomitantly with lengthening of the martensite lath (not shown but similar to Fig. 5). This leads to the situation where both twins and martensite have grown and thickened as illustrated in Fig. 6d.

The interplay between twinning and martensitic transformation was captured in another straining experiment and shown in Fig. 7 where both BF images and ASTAR phase/reliability maps were acquired (see the video 4 and 5 in the supplementary materials). A large martensite lath ($Ma_1$), nucleated under stress in the $\beta$ matrix ($M$) gradually disappears due to the nucleation of a $[112](111)$ twin ($T$) (Fig. 7a-b). Although a twin was observed nucleated near a crack tip and penetrated in the martensite as in Fig. 6, the lateral shrinkage of the martensite tends to indicate that twinning occurs first at the
Figure 7: a)-c) are BF pictures taken in a deformation band within the matrix $T$, in a conventional sample. The band initially contains a martensite lath ($Ma_1$) that gradually disappears due to the nucleation and the lateral growth of a $\{112\langle111\rangle$ twin ($T$). In c) a second martensite variant ($Ma_2$) is nucleated in the twinned region. The same process is followed on the phase+reliability maps d). Phase e) and IPF-z f) maps reveal another complex band structure composed of martensite laths ($Ma$) and twinned regions ($T$).

3.4. Core-shell effect on the deformation mechanisms

In order to probe differences in the deformation of core and shell, in-situ experiments were carried out on samples where both shell and core area were strained simultaneously. Fig. 8a shows a panorama composed of pictures taken after the deformation of an area located between two TEM holes. Although the stress state and intensity may be different, both parts are subjected to the applied stress. On the lower left area, the microstructure is composed of small grains of the shell while the upper right part corresponds to a large grain of the core. Under strain, the shell deforms and a thick slip band is formed. Note that the dislocations seen in this grain are also shown in Fig. 3b. Thus, the band lies close to (112). Fig. 8a shows that this band extends to the shell area but rapidly vanishes. However, the dislocation activity in the shell grains continues but is spread in several grains ahead of the bands. Several slip planes which traces are indicated by the red dashed lines can be observed. Further straining leads to the propagation of an intragranular ductile crack from both the lower right side or in continuation of the slip band. The deformation mechanisms in the shell grains were analyzed in few grains (see the videos 6 and 7 in the supplementary materials). Fig.8b shows numerous slip traces in one of these sub-micronic grains. Contrary to large grains of the core, the first stage of deformation consists here in the nucleation of dislocations from the grain boundaries at different locations. Fig. 8c, indeed shows the emission of dislocations within 0.2 s, easily revealed by the image difference. The dislocation motion is similar with the formation of several debris and loops by cross-slip in the grain interior. This is for instance shown in Fig. 8d where the motion of a screw dislocation $d$ in average close to the (231) plane leads to the formation of a prismatic loop $l$. Further straining leads eventually to the formation of dense tangles, either by the multiplication of dislocations, by cross-slip or the formation of stable spiral sources. Hence, a large hardening is expected in the small grains. This effect might be also reinforced by the possibility of forming new dislocation sources close to the fcc precipitates (cf. Fig. 1c).

4. Discussion

The observations reported above, both from in-situ and post-mortem experiments give interesting insights of the deformation mechanisms occurring in the investigated $\beta$-Ti-25Nb-25Zr alloys.
Figure 8: a) A panorama of deformation of both core and shell in an harmonic sample during an in-situ experiments. Note that the deformation in the core leads to the formation of a thick slip band. The transmission of the deformation in the shell develops in front of the band by dislocation slip in several grains. b) shows the homogeneous deformation in a shell grain. c) are two snapshots and the corresponding image difference showing dislocation emission from a grain boundary. d) are snapshots showing the wavy motion of the dislocation $d$ leading to the formation of a prismatic loop by double cross-slip.
4.1. Dislocation mechanisms and effective stress estimation

In both conventional and harmonic samples, dislocation mechanisms were found to be active with specific characteristics: screw dislocations glide in a jerky way close to [112] or [110] planes. They cross-slip easily and are pinned on obstacles which leads to the formation of debris (prismatic loops as in Fig. 8d). Similar observations were made in metastable obstacles which leads to the formation of debris (prismatic loops by fitting the shape between anchoring points (the line tension line that provides a strengthening effect). Screw segments appear straight, kinks are nucleated in di- 

by Castany et al. [2, 30]. These two studies point to the presence of small $\alpha_2$ precipitates are expected to act as pinning points along the dislocation line. An average value of $\tau_\text{eff} = 104$ MPa is obtained. The second approach consists in considering pinning jogs/dipoles as strong and impenetrable obstacles and in the approximation of a constant line tension that the overcoming stress is the Orowan stress, i.e. that $\tau \approx \frac{\mu b}{\pi d}$ [37]. Measuring the distance $d$ between anchoring points (Fig. 9b) yields an average value of $d = 63$ nm, which leads to $\tau \approx 128$ MPa, close to the measured in the first approach. Similar results are obtained in both conventional and harmonic samples. These values have to be compared to the yield shear stress of 220 MPa and 150 MPa obtained during shear test in harmonic and conventional samples, respectively [13]. Taking an average Taylor factor of 1.5, the average critical resolved shear stress should be ranging between 100 and 147 MPa, which is close to the measured values. The obtained value can also be compared to those obtained in Fe-Si solid solution by Caillard [31]. Considering that a similar mechanism operates, then the expected pinning stress in bcc Ti can be derived from values obtained from Fe-Si solid solution, i.e. $\tau_{\text{eff}} = \tau_{\text{Fe-Si}} \frac{d_{\text{Fe-Si}}}{d_{\text{Fe}}}$, $d_{\text{Fe}} = 385$ nm, $d_{\text{Fe-Si}} = 275$ nm and $d_{\text{Fe-9Si-1}} = 140$ nm and $\tau_{\text{Fe-9Si}} = 50$ MPa, $\tau_{\text{Fe-3Si}} = 95$ MPa and $\tau_{\text{Fe-9Si}} = 190$ MPa leads to $154 \text{ MPa} \leq \tau_{\text{eff}} \leq 164$ MPa, comparable to the one measured.

Obstacles to kinks motion in dilute solid solution are supposed to be solute atoms or cluster of solute atoms as observed in many alloys [31]. In the present case of a highly concentrated solute solutions, supposedly composed of Zr and Nb atoms, their nature is still unclear. In conventional samples, the presence of small $\alpha_2$ precipitates are expected to act as pinning points. So far, it is unclear whether small embryo of such precipitates also exist in harmonic samples. Further dedicated experiments using atom probe tomography should be able to identify atomic clusters along the dislocation line [17]. Because cross-glide can be triggered by atomic size clusters, $\alpha_2$ or other metastable phases may contribute to some hardening without being at the origin of the cross-glide mechanism. From our stress measurements, the contribution of different pinning is difficult to decorrelate. Model alloys with controlled microstructure and composition are required in this case. Recent theoretical developments, applied to fcc high entropy alloys, considering that every atoms can be viewed as a solute atom embedded in an average matrix, can explain a strengthening effect when dislocations interact with local chemical fluctuations [38]. From an experimental point of view, straight $a/2[111]$ screw segments and loops, were recently observed in a deformed bcc equimolar HfNbTaTiZr alloy by Lilenstein et al. [39–41]. Their observations are quite similar to the ones presented here, suggesting that the mechanism, i.e. cross-glide, can control the dislocation mobility in highly concentrated solid solution.
4.2. Twinning and martensitic transformation

The ensemble of post-mortem and in-situ observations presented here bears similarity with some recent works which associate the formation of such twins to martensite transformation. The role of metastability of the $\beta$ phase in the formation of (332)(113) has been clearly pointed out in several studies [42, 43]. Indeed, it is often associated either to the existence of the $\omega$ and/or the $\alpha''$ martensite. Experimental evidence of the formation of $\omega$ lamella either in the twins [44] or at their borders [45, 46] has been frequently found in (332)(113) twins. In the present study however, no $\omega$ phase was detected at or in the twinned structures.

In other studies, the origin of twin has been discussed in relation with martensitic transformation and rearrangement at the interface [47, 48] indicating that twins formed by transformation from martensite. This idea tends to be supported by several studies. In the work of Lai et al. [49], based on SEM/EBSD observations, the authors found that twins initiate within martensite. Martensite relaxation at high temperature leads to the transformation of martensite to the twin structure instead of the parent $\beta$ phase, suggesting the direct relationship between martensite transformation and twin formation. More precisely, Castany et al. [46] propose a mechanism of twin formation related to martensite. They show that, in a Ti-27Nb metastable $\beta$ alloy, (332)(113) twins result from a complex deformation path where martensite is first nucleated and then twinned before being transformed back to the $\beta$ phase when stress is relaxed. Because of the specific orientation relationships of the twinned martensite, the back transformation leads to (332)(113) twins. This study clearly points out the influence of strain relaxation processes as the driving force in twin formation.

The difference between post-mortem and in-situ observations can be related to different relaxation mechanisms during straining. (332)(113) twin has a twinning shear half of those of the (112)(111) twin, but requires that one half of the atoms shuffle to their correct positions [50]. In thin foils, for the observed twin formation, the (111) twinning direction has a large component perpendicular to the foil plane. Because of that, the twinning strain can be accommodated easily at the sample surface. At room temperature and at typical strain rate/stress level, (112)(111) may then be preferred. In bulk sample however, (332)(113) twinning mode starts to be competitive because strain relaxation is constrained by surrounding grains and thus lower shear mode may be preferred despite atomic shuffling is required.

Recent observations from Yao et al. [51] in $\beta$-Ti-24Nb-4Zr-8Sn, reports similar observations of complex band formation from in-situ SEM and TEM experiments. They conclude from post-mortem examination of bands formed during SEM straining, and finite element modeling that martensite nucleates first followed by the apparition of (112)(111) twin at higher stress.

Finally, in terms of mechanical properties, the apparition of such dense and complex deformation bands is expected to play the major role in the hardening behavior of the material as pointed out during cyclic deformation by Dirras et al. [13]. Indeed, as second variant martensite nucleation can operate in a band where (112)(111) has grown, the structure is expected to be refined by a sequence of martensite to twin formation (Fig. 7). As dislocation nucleation operates in the early stage and in front of cracks, dislocation glide is thus expected still to control yield stress, which is indeed found to be fairly similar in both harmonic and conventional samples [13].

4.3. Implication of deformation mode in harmonic vs conventional

The sequence of deformation in harmonic samples is more difficult to assess owing the fine scale at which in-situ TEM observations were made. However several points can be discussed in the perspective of unraveling the effect of the core/shell structure. The first point to notice is the fundamental difference in terms of deformation mechanisms, as for harmonic samples, no twinning or martensite transformation was observed. Two hypotheses can be proposed. First, chemical variations between core and shell, may destabilize metastable phases such as martensite. Indeed according to the Bo-Md model proposed to explain the stability of phases in Ti-alloys, an increase of Nb in the core can stabilize the $\beta$ phase [52]. This chemical effect can potentially suppress the formation of martensite and subsequent twins in the core. The origin of such chemical variation is not clear but may be related to material processing. Impurities such as hydrogen incorporated during ball-milling of initial powder could play an important role in forming Zr rich hydrides as observed solely in the shell region. Further investigations are on their way. Secondly despite chemical heterogeneities, we have shown that deformation in the core of the harmonic sample can be efficiently accommodated and redistributed in the shell without localization. This may not be the case in the conventional alloy where strain incompatibilities may promote martensite/twins nucleation. Our observations lead to the following deformation scenario. Coarse grains in the core are expected to yield first and lead to the formation of dislocation band that eventually pile-up against shell regions. As dislocations pile-up, the back stress ($\sigma_{BS} = \frac{N\mu}{d}$, with $N$ the number of dislocations and $d$ the pile-up length, [53]) increases, yielding the initial hardening. As the stress increases in the core, sources closer to the shell can be activated leading to an increase of the density of geometrically necessary dislocations close to shell area, as indicated by EBSD observations (see Fig. 2c) and in agreement with strain gradient plasticity [54, 55]. At a given stress, dislocations start to be emitted in the shell from grain boundary sources. Then, the strain is delocalized progressively in the shell presumably toward the interior (Fig. 8) as observed in a bimodal duplex steel [56]. More generally, such a plastic deformation delocalization has been reported in inhomogeneous structures [57]. Indeed, in the present study, grains in the shell seem to be able to harden significantly as evidenced by the building up of dense dislocation tangles (Fig. 8).

5. Conclusions

This study on conventional and harmonic $\beta$-Ti-25Zr-25Nb alloys has allowed us to draw the following conclusions.
• Plastic deformation in both alloys operate through the motion of \( a/2 \langle 111 \rangle \) dislocations gliding in \( [110] \) or \( [112] \) planes. Straight screw segments pinned on small obstacles, presumably atomic clusters and sometimes on nanoscale \( a_2 \) precipitates, move jerkily and cross-slip often. This strongly suggests that the motion is controlled by a cross-slip mechanism, as observed in dilute solid solution and possibly in concentrated ones such as high entropy alloys. The stress opposed to dislocation motion has been estimated and has led to value in qualitative agreement with macroscopic measurements.

• In the conventional microstructure, the nucleation of martensite is favored in early deformation stages leading rapidly to the formation of complex deformation bands where \( (112) \langle 111 \rangle \) twins nucleate and grow at the expense of the martensite laths. Similar deformation bands were observed post-mortem from bulk materials except they contain \( [332] \langle 113 \rangle \) twins. This result highlights the existence of relaxation mechanisms from martensite to twins that differ in thin foils and bulk materials.

• While deformation in the core of the harmonic microstructure occurs mainly through the formation of slip bands, deformation is more homogeneous in the shell, probably because grain boundaries themselves act as dislocation sources. The dislocations piling up against the shell are expected to smooth the deformation of both core and shell.

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