

Microstructure evolution in additively manufactured Ti-15%Nb-12%Zr alloy during plastic deformation over a wide range of strain up to 20,800 %

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ABSTRACT

The evolution of the microstructure during plastic deformation was studied in an additively manufactured Ti-15%Nb-12%Zr (at.%) alloy. The applied equivalent strain ranged extremely widely from 8 % to 20,800 %. Strains below 100 % were achieved by uniaxial compression, while the high strains were obtained by the high-pressure torsion (HPT) technique. In addition to the as-built material, the same investigation was conducted on the alloy after heat treatment at 550 °C for 1 h after additive manufacturing. The as-built alloy had a fully body-centered cubic structure, while the annealing step resulted in the development of a hexagonal close-packed secondary α -Ti phase with a fraction of about 10 %. Compression up to a strain of 70 % resulted in an increase in the secondary phase fraction to 12 % and 22 % for the as-built and heat-treated alloys, respectively. HPT processing at high strains yielded a lower secondary phase fraction due to reverse martensitic transformation. The dislocation density increased to $70\text{--}100 \times 10^{14} \text{ m}^{-2}$ when the strain rose to 70 % during compression. The dislocation density reached extremely large values of $600\text{--}700 \times 10^{14} \text{ m}^{-2}$ at a strain of about 20,800 % achieved by HPT. Although the dislocation density increased by two orders of magnitude and nanocrystallization also occurred when the strain increased to 20,800 %, the hardness was enhanced only by 10–30 %. The unexpectedly low hardness increase after HPT was attributed to unique deformation mechanisms such as the kink pair related dislocation motion and grain boundary sliding.

1. Introduction

β -titanium alloys with body-centered cubic (bcc) structure are highly valued in advanced engineering applications such as aircraft components [1–4], medical devices and implants [5–8], and automobile parts [9] owing to their high strength-to-density ratio [10,11], good corrosion and wear resistance [12,13], excellent biocompatibility [14,15], low elastic modulus [16,17] and fabricability [18]. For such applications, additive manufacturing (AM) is a key enabling technology for producing complex geometries [19–22]. This technique is based on the

layer-by-layer deposition of material using computer-aided design (CAD) models, and offers customization and optimization for patient-specific implants [23]. Due to the rapid cooling and thermal cycles, AM-processed materials have distinctive microstructural features such as epitaxially grown columnar grains, strong crystallographic textures, and dislocation cells [24,25]. These non-equilibrium microstructures profoundly influence the mechanical properties and deformation behavior of these materials [26]. This was exemplified in an SLM-processed Ti-13Nb-13Zr (wt.%) alloy consisting of preferentially oriented β grains, resulting in anisotropic mechanical properties [27].

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Until now, most studies on AM-processed Ti-Nb-Zr alloys have characterized the deformation behavior at relatively low strains [28–33] while investigations at high strains via severe plastic deformation (SPD) have been conducted only on bcc Ti alloys produced by other techniques [34–39]. Therefore, it is unknown whether the unique microstructures produced by AM lead to novel deformation pathways under SPD compared to their conventionally processed counterparts. Consequently, there is no established understanding of the deformation behavior of the AM-manufactured Ti-Nb-Zr alloys across a wide range of plastic strain. Since SPD conditions simulate complex stress states, such study is essential for reliably predicting in-service performance under complex loads.

The present work investigates a Ti-15Nb-12Zr (at.%) alloy processed by laser powder bed fusion (L-PBF) and deformed plastically from low to extremely high strains of about 20,800 %. The low and high strains are achieved by compression and high-pressure torsion (HPT) methods, respectively. This combination overcomes the limitations of each technique used in isolation. Although uniaxial compression is ideal for testing deformation behavior at low strains, it is limited at high strains due to specimen failure. Conversely, HPT is exceptionally effective for studying extreme strains but is less suited for characterizing the initial stages of microstructure development at low strains. In the present study, besides the as-built Ti samples, the specimens with subsequent annealing are also studied in the same way. The microstructure evolution with increasing applied strain is investigated by X-ray diffraction and electron microscopy, and the results are related to the hardness variation. The effect of heat treatment and imposed strain on the deformation behavior of the AM-processed Ti-15 %Nb-12 %Zr alloy is revealed. This study thus provides the first comprehensive analysis of the microstructural evolution and the deformation mechanisms across a wide range of strain in a Ti-15 %Nb-12 %Zr alloy processed by L-PBF.

2. Materials and methods

2.1. Processing of the samples by additive manufacturing and subsequent annealing

The L-PBF technique was used for processing bulk Ti-15 %Nb-12 %Zr (at.%) alloy samples from a pre-alloyed powder with a median particle size of 31 μm supplied by Z3DLAB SAS company, Chaumontel, France. The L-PBF process was performed at the Z3DLAB facility using an SLM 125HL machine (manufacturer: SLM Solutions Group AG, Germany) with a 200 W ytterbium fiber laser. The building platform temperature was maintained at 200 °C to manage residual stress. The Meander Hatching Pattern strategy, with a 67° rotation after each layer, was used for the fabrication of the samples. After trials, the following optimal set of L-PBF parameters for dense and defect-free parts was determined: the laser power of 200 W, hatch spacing of 0.12 mm, scanning speed of 720 mm/s and layer thickness of 0.03 mm. This combination corresponds to a volumetric energy density (VED) of 77.16 J/mm³. This VED value is in close agreement with previously reported ones applied successfully for the densification of similar alloys [40]. The initial material was printed in the form of cubes with the dimensions of 10 × 10 × 10 mm³ and cylinders having both the diameter and the height equal to 10 mm.

A heat treatment after L-PBF processing was performed by Z3DLab company on selected samples using an argon-protected oven (Nabertherm P115) at a soaking temperature of 550 °C for a 1-h dwell time. A custom-designed and fabricated stainless steel box with a volume of 10 cm³, featuring two temperature probes positioned near the manufactured parts to ensure accurate temperature measurement, was employed during heat treatment. The box was purged with argon gas three times and preheated to 200 °C before the L-PBF build platform was placed inside. After the platform was put into the steel box, an additional triple argon flush was applied, and then the box was placed in the oven. The heating was carried out rapidly to prevent undesired phase transformations. For cooling, the box was removed from the oven and

allowed to reach RT under high-pressure argon. In this study, the as-built material is denoted as AB while the alloy subjected to subsequent heat treatment is referred to as AB + HT.

2.2. Deformation methods for strains up to 100 %

Rectangular compression samples were cut from the cube specimens with the dimensions of 4 × 4 × 6 mm³ and the longest edge was parallel to the building direction (and the loading axis as well). Uniaxial compression loading was carried out by an MTS-810 universal mechanical test machine at RT. The specimens were wrapped with a Teflon tape to minimize friction. In order to reduce the effect of the surface roughness on the compression curves, the surface was prepared by grinding up to 2500 grit SiC sandpaper. The initial strain rate was 1.6 × 10^{−3} s^{−1}. The change of the sample height was determined by using an extensometer. The true strain, ϵ , was calculated as $\epsilon = -\ln(1 - e)$, where e is the engineering strain determined from the changes in height. We assumed that the porosity was negligible and the solid was incompressible, hence, the true stress, σ , was determined using the following equation: $\sigma = \frac{F}{A_0}(1 - e)$. Here, F is the force and A_0 is the original cross-sectional area.

The microstructure of the uniaxially compressed samples was studied at the strain values listed in Table 1. These are within the range between 0.10 and 0.77. In some cases, the strain values for samples AB and AB + HT are slightly different.

2.3. Plastic deformation for high strains up to 20,800 % using HPT technique

High compressive straining was applied by utilizing a conventional HPT facility with a quasi-constrained set-up [41,42]. The surface of the HPT discs was perpendicular to the building direction of additive manufacturing. For the compression only and with torsion using HPT processing, the cylindrical AB and AB + HT specimens were cut into discs with a cross-section diameter of 10 mm and a thickness of ~0.85 mm. Before torsional deformation, the discs were loaded in order to supply the frictional force needed for slippage-free torsion. Processing was operated at RT under 6.0 GPa at a rotational speed of 1 rpm for 1/2, 1, 5 and 10 turns. The thickness of the discs was about 0.7 mm after HPT for all numbers of turns. The equivalent strain was calculated using the following formula [43]:

$$\epsilon = \epsilon_0 + \frac{2\pi r N}{\sqrt{3}t}, \quad (1)$$

where r is the distance of the studied location from the disc center, N is the number of turns, t is the thickness of the HPT-processed disc and ϵ_0 is the compressive strain caused by the initial loading in the HPT facility, which is 0.08. The microstructure of the HPT-processed samples was studied in the center and at the edge of the discs. Since the largest

Table 1

The deformation methods and the corresponding equivalent strain values applied in this study on samples AB and AB + HT.

Deformation method, measured location within disc	Equivalent strain
Compression in HPT facility	0.08
Uniaxial compression	0.10
Uniaxial compression	0.39 (AB + HT), 0.41 (AB)
Uniaxial compression	0.68 (AB), 0.77 (AB + HT)
1/2 turns of HPT, close to center	1.38
1 turns of HPT, close to center	2.67
1/2 turns of HPT, close to edge	10.45
5 turns of HPT, close to center	13.04
1 turns of HPT, close to edge	20.82
10 turns of HPT, close to center	26.00
5 turns of HPT, close to edge	103.80
10 turns of HPT, close to edge	207.51

dimension of the XRD spot on the sample surface was about 2 mm (see the next section), the center and the edge parts correspond to an average distance from the center of 0.5 and 4 mm, respectively, as demonstrated earlier [44]. The equivalent strain values for these distances from the disc center for the applied numbers of turns were calculated using eq. (1) and listed in Table 1. The highest equivalent strain was ~ 208 , i.e., 20, 800 %.

2.4. X-ray diffraction study on the evolution of phase composition, texture and microstructure

The phase composition of the AB and AB + HT alloys was studied by X-ray diffraction (XRD) using a Smartlab diffractometer (manufacturer: Rigaku, Tokyo, Japan). Bragg-Brentano diffraction geometry, CuK α radiation (wavelength: $\lambda = 0.15418$ nm) and a D/Tex Ultra 250 one-dimensional detector were applied in the XRD experiments. The data were taken in the diffraction angle range $2\theta = 30\text{--}145^\circ$ with a step size of 0.02° and at a rate of $2^\circ/\text{min}$. Before XRD experiments, the surface was mechanically polished using 800, 1000, 1200, 2500 and 4000 grit papers, and subsequently colloidal alumina suspension with $1\text{ }\mu\text{m}$ particle size. Finally, the surface was etched with a 40 % HF solution for 20 s. Due to etching, the uppermost surface layer with a thickness of $5\text{--}10\text{ }\mu\text{m}$ was removed. The diffractograms were evaluated with the PDXL2 software (manufacturer: Rigaku, Tokyo, Japan) using the ICDD-2018 database. According to XRD, the main phase was bcc-Ti (β -Ti). The average lattice constant of this phase was determined from the diffraction peak positions using the Nelson-Riley method [45]. The XRD intensity fraction of the secondary phase was calculated as the ratio of the sum of the areas under the peaks of the secondary phase and the same for all reflections in the pattern. The peak areas were determined by fitting the reflections with pseudo-Voigt functions while the background was approximated with a spline using the Origin software (manufacturer: OriginLab, Northampton, MA, USA). In this way, the integrated intensities of all peaks were obtained individually. The crystallographic texture was measured by the same XRD facility. The texture was characterized by $\langle 110 \rangle$, $\langle 200 \rangle$ and $\langle 211 \rangle$ pole figures (PFs) measured with parallel-beam optics. 3D-Explore software (manufacturer: Rigaku, Tokyo, Japan) was utilized to plot PFs.

The microstructure of the samples was investigated by X-ray line profile analysis (XLP). The patterns were measured by a high-resolution rotating anode diffractometer (type: RA-MultiMax9, manufacturer: Rigaku, Tokyo, Japan) using CuK α_1 radiation (wavelength, $\lambda = 0.15406$ nm) and a parallel beam. The height and the width of the rectangular X-ray spot on the sample surface were 2 and 0.2 mm, respectively. The step size in 2θ was 0.01° . The measured peak profiles of bcc-Ti were evaluated by the convolutional multiple whole profile (CMWP) fitting procedure [46]. In this method, the diffraction pattern was fitted by the sum of a background spline. The diffraction peaks were obtained as the convolution of the instrumental peaks and the theoretical line profiles related to the crystallite size and the dislocations. The instrumental peaks were measured on a NIST SRM660a LaB $_6$ peak profile standard material. The reflections appearing in the 2θ range between 30 and 130° were evaluated.

In the CMWP analysis, the dislocation contrast factors must be given as input parameters in the pattern fitting software. These factors are included in the theoretical diffraction peak profile functions fitted to the experimental peaks and characterize the dependence of the peak broadening on the reflection indices hkl caused by the anisotropic strain field of dislocations. In cubic polycrystals, the average contrast factors of a reflection with the indices hkl ($\bar{C}_{hkl}$) can be expressed as:

$$\bar{C}_{hkl} = \bar{C}_{h00} \left(1 - q \frac{h^2 k^2 + h^2 l^2 + l^2 k^2}{(h^2 + k^2 + l^2)^2} \right), \quad (2)$$

where $\bar{C}_{h00}$ is the contrast factor for reflection types $h00$ and q is a

parameter depending on the anisotropic elastic constants of the crystal and the types of the dislocations. The theoretical values of $\bar{C}_{h00}$ and q for both slip system types $1/2\langle 11\bar{1} \rangle\{101\}$ and $1/2\langle 11\bar{1} \rangle\{112\}$ were calculated from the anisotropic elastic constants of a bcc structure having similar composition (Ti-15 %Nb-22 %Zr in at. %: $c_{11} = 110$ GPa, $c_{12} = 102$ GPa, $c_{44} = 15$ GPa [47]) using program ANIZC [48]. In the case of $1/2\langle 11\bar{1} \rangle\{101\}$ slip systems, for edge dislocations $\bar{C}_{h00}$ and q are 0.58 and 2.3, respectively, while for $1/2\langle 11\bar{1} \rangle\{112\}$ slip systems, these values are $\bar{C}_{h00} = 0.34$ and $q = 1.3$. For screw dislocations with the Burgers vector of $1/2\langle 11\bar{1} \rangle$, $\bar{C}_{h00} = 0.34$ and $q = 2.7$.

The area-weighted mean crystallite size ($\langle X \rangle_{\text{area}}$) and the dislocation density (ρ) were determined by the CMWP fitting evaluation procedure of the diffraction patterns. The value of $\langle X \rangle_{\text{area}}$ was calculated as $\langle X \rangle_{\text{area}} = m \cdot \exp(2.5\sigma^2)$, where m is the median and σ^2 is the lognormal variance of the crystallite size distribution. More details about the XLP evaluation can be found in Ref. [49].

2.5. Microstructure study performed by electron microscopy

The microstructure of the AB and AB + HT samples before deformation and the specimens deformed for the lowest strain of 0.08 were examined by electron backscatter diffraction (EBSD) using a JEOL IT700HR-LA field emission scanning electron microscope (SEM) equipped with an Oxford Symmetry S3 EBSD detector. This study was performed on a plane lying perpendicular to the building direction. During the measurements, an electron beam at 20 kV was applied with step sizes of $0.2\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$, depending on the image magnification. The measured data was evaluated using Oxford AztecCrystal software and the datasets were filtered by a routine cleaning process (wild spike removal and iterative zero solution process) in the AztecCrystal software. In this study, the EBSD results are presented in the form of inverse pole figure (IPF) and grain reference orientation deviation (GROD) maps. The grain size of the samples was determined using equivalent circle diameter parameters and the misorientation threshold of 15° was applied. The minimum pixel number to identify grains was 10. In the determination of the grain size, the option "Close boundaries" with the minimum angle of 2° was applied in the software AztecCrystal. The geometrically necessary dislocation (GND) density was estimated from the EBSD measurements using a step size of $0.2\text{ }\mu\text{m}$ and a kernel size of 5×5 . During this calculation, the Burgers vector of $1/2\langle 110 \rangle$ was assumed and scaled with an alpha parameter of 3.

The surfaces of the samples for the SEM study were first mechanically ground with 1200, 2500 and 4000 grit SiC abrasive papers, and then the polishing was continued with a colloidal alumina suspension with a particle size of $1\text{ }\mu\text{m}$ and then $0.3\text{ }\mu\text{m}$. In the final step of mechanical polishing, the samples were polished with a colloidal silica suspension (OP-S) with a particle size of 40 nm. Finally, the surfaces were electropolished at 32 V and 1 A with Struers A3 electrolyte.

A higher magnification microstructure study on the initial AB and AB + HT samples was performed by transmission electron microscopy (TEM). TEM was also used to investigate the nanostructure formed at the highest applied strain (about 208) achieved close to the edge of the disc HPT-processed up to the highest number of turns (10). Thin sections were cut perpendicular to the radius and the circular surface of the disc by a dual-beam FIB/SEM instrument Scios II using a focused Ga $^+$ beam. Accelerating voltages of 30 and 5 kV were used for cutting and polishing, respectively. After the FIB process, the sample surface was cleaned with the Technoorg Linda GentleMill instrument using the same parameters as in Ref. [50]. The cleaned thin sections were studied by a Themis 200 kV image-corrected transmission electron microscope with a nominal point resolution of 80 pm (manufacturer: Thermo Fisher Scientific, Waltham, MA, USA). Images showing individual dislocations were recorded in high-resolution TEM (HRTEM) mode (without any objective aperture), while the search for these objects was done in bright field (BF) mode. During imaging, no structural changes were observed in the

samples due to beam damage or heating, i.e., the specimens were stable under the electron beam even at high magnifications with concentrated illumination. The average grain size was determined from dark field (DF) images since in these pictures the orientation differences can be seen better than in the BF micrographs. Most grains were elongated; therefore, the area-weighted equivalent circle diameter was used for the characterization of the grain size. In this calculation, the grain area (A) was determined by ImageJ software [51] and the equivalent circle diameter (d) was calculated as $d = 2\sqrt{A/\pi}$. The HRTEM images were analyzed using Gatan Digital Micrograph software 3.6. A fast Fourier transform (FFT) was computed from the region of interest (ROI) selected within the HRTEM image.

2.6. Hardness test

The Vickers microhardness of the AB and AB + HT samples before and after deformation at different strains was measured using a Zwick Roell ZHμ microindenter (manufacturer: ZwickRoell LP, Kennesaw, GA, USA) with a Vickers head, an applied load of 500 g and a dwell time of 10 s. For the HPT-processed specimens, hardness was measured along the whole disc diameter with an indent spacing of 0.5 mm at RT. At each radial position, ten indents were made, and then the mean hardness values was calculated for each studied distance counted from the disc center.

3. Results

3.1. Microstructure of the initial alloys

Fig. 1 shows the XRD patterns obtained from the initial AB and AB + HT alloys. The diffractograms reveal that while alloy AB is a single-phase bcc material (i.e., β -Ti) with a lattice parameter of 0.3326 ± 0.0002 nm, material AB + HT contains an hcp secondary phase (α -Ti) beside the main β -Ti alloy matrix, having a lattice constant of 0.3334 ± 0.0002 nm. The XRD intensity fraction of the α -Ti phase in the initial AB + HT material is about 10 %. The XRD patterns also suggest that in both alloys the bcc matrix has a crystallographic texture where the $\langle 100 \rangle$ direction is preferably lying parallel to the building direction. This texture is confirmed by the XRD pole figures shown in Fig. 2 and obtained for the main bcc phase in the AB (upper row) and AB + HT (lower row) alloys before deformation.

Fig. 3a and b shows EBSD-IPF maps with different magnifications for the alloy AB before deformation. The black lines represent high-angle grain boundaries (HAGBs) corresponding to the misorientation limit of 15° . The grain size was determined from the image with lower magnification for better statistics. The average grain size is 17 μm while the

area-weighted mean is 44 μm . Fig. 3c and d present GROD maps for the same areas as shown in the IPF maps, Fig. 3a and b, respectively. The white lines in these maps show low-angle grain boundaries (LAGBs). The LAGB fraction is about 70 % of the grain boundaries in Fig. 3d. In a significant fraction of the grains, considerable GROD values are observed, which suggests that lattice strains developed during 3D printing. This lattice strain has an inhomogeneous spatial distribution in the sample as revealed by the GROD maps in Fig. 3c. The GND density of $4 \times 10^{14} \text{ m}^{-2}$ was estimated from the misorientations measured on the EBSD image in Fig. 3b by Oxford AztecCrystal software using the setting conditions given in section 2.5.

For the AB + HT alloy, the EBSD-IPF maps are shown in Fig. 4a and b, and the GROD maps in Fig. 4c and d, with the same magnifications used for sample AB in Fig. 3. The average grain size is 17 μm , similar to that of specimen AB. The area-weighted mean grain size is 40 μm , which is only slightly lower than that of sample AB. The GROD maps in Fig. 4c and d shows significant misorientations in many grains and their inhomogeneous spatial distribution. The LAGB fraction determined from Fig. 4d is about 80 %. The GND density is estimated as $6 \times 10^{14} \text{ m}^{-2}$.

The microstructures of samples AB and AB + HT were studied with a higher magnification using TEM. Fig. 5a shows an STEM-BF micrograph and the corresponding EDS elemental maps of the main constituents (b) Ti, (c) Nb and (d) Zr for specimen AB. No chemical heterogeneity is observed. On the other hand, for sample AB + HT, lamellae with dark contrast are visible in the HAADF image shown in Fig. 6a. These lamellae, with a thickness of about 40 nm, appear in bright contrast in BF images in Fig. 6b. A detailed view of this microstructure is presented in the BF image in Fig. 6c and the corresponding EDS elemental maps are shown in Fig. 6e and f for Ti, Nb and Zr, respectively, revealing that these lamellae are depleted of Nb and Zr. The crystal structure of a lamella was determined from an HRTEM analysis. The HRTEM micrograph in Fig. 7a shows a lamella, and the FFT pattern of the rectangular area in (a) is presented in Fig. 7b, revealing that the lamella corresponds to hcp α -phase. The local chemical compositions in bcc β and hcp α structures captured in Fig. 6c were determined quantitatively by STEM-EDS and listed in Table 2. Indeed, the Nb concentrations in the β and α -phases are 15.5 and 7.8 at.%, respectively, while the Zr contents in the same phases are 12.6 and 10.1 at.%, respectively. Thus, the single bcc structure was not stable during heat treatment at 550 $^\circ\text{C}$ and decomposed into α and β -phases. The slightly higher lattice parameter of the β -phase in the AB + HT specimen of 0.3334 ± 0.0002 nm, relative to the value of 0.3326 ± 0.0002 nm in the AB sample as observed by XRD can be attributed to the increase in concentration of Zr in the bcc phase, having a much larger atomic radius compared to Ti. It is noted that a small amount of Al (about 0.9 at.%) was also detected in the samples. The presence of Al in the alloy was unintentional, resulting from contamination in the initial powder used for AM. The pre-alloyed

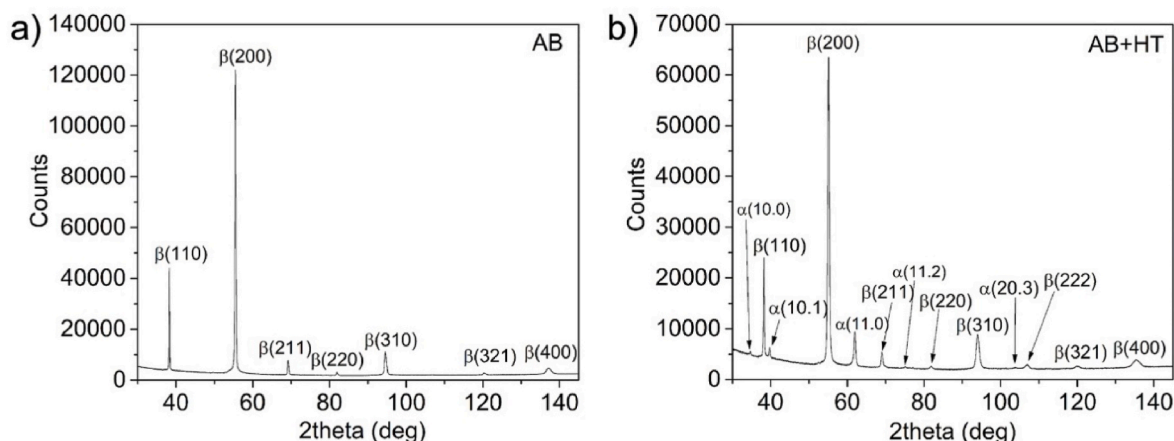


Fig. 1. X-ray diffraction patterns for (a) AB and (b) AB + HT alloys before deformation. The indices of reflections are given in parentheses.

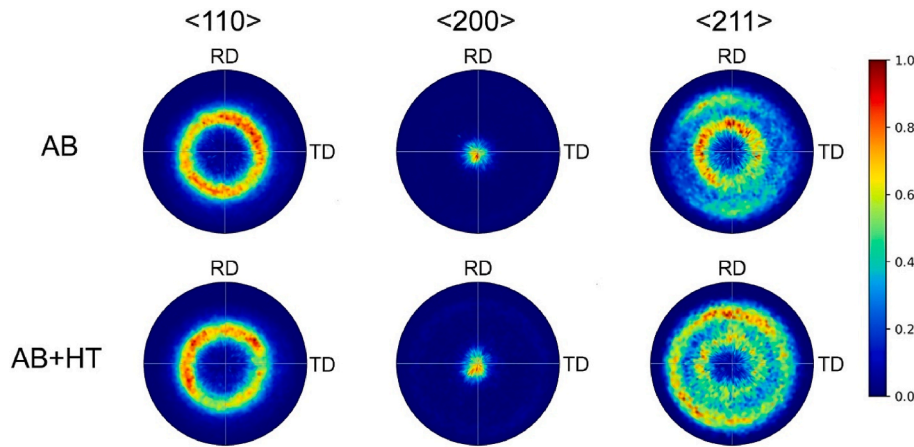


Fig. 2. XRD pole figures for the main bcc phase in the AB (upper row) and AB + HT (lower row) alloys before deformation.

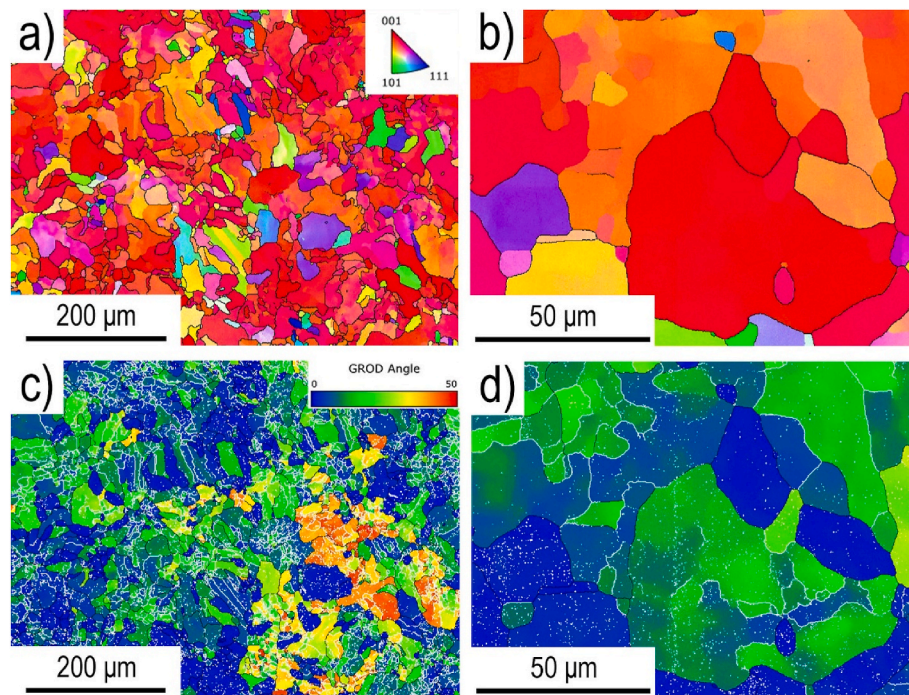


Fig. 3. IPF (a and b) and GROD (c and d) maps for the alloy AB before deformation. The black lines represent HAGBs while the white lines in c and d show LAGBs.

powder was produced by gas atomization of a forged bar. Aluminum may originate from Al-containing master alloys employed in the addition of Nb or Zr to Ti. However, due to its low amount and limited influence on the stability of α - and β -phases, Al did not markedly affect phase transformation or deformation mechanisms. It is worth noting that no porosity was observed in either the AB or AB + HT samples by EBSD or TEM.

The dislocation density in the bcc β -phase was determined by the XLPA method using the CMWP fitting procedure. Fig. 8 shows representative results of the CMWP fitting for samples AB and AB + HT before deformation. The estimated dislocation density values in the specimens AB and AB + HT are $(1.8 \pm 0.3) \times 10^{14} \text{ m}^{-2}$ and $(9 \pm 1) \times 10^{14} \text{ m}^{-2}$, respectively. These values have the same order of magnitude as the GND density obtained from the EBSD micrographs (see Figs. 3 and 4), suggesting that most dislocations are GNDs formed during manufacturing through 3D printing (at least for sample AB). It is noted that for specimen AB, the GND density obtained by EBSD is slightly higher than the total dislocation density (geometrically necessary and statistically stored

ones together) determined by XLPA. This difference can be explained by the very local observation made by EBSD compared to XLPA. Indeed, the sample volume involved in the analysis by XLPA of $\sim 10^6 \mu\text{m}^3$ is orders of magnitude higher than that investigated by EBSD of $\sim 10^2 \mu\text{m}^3$. In addition, the resolution of EBSD is limited by the step size of 0.2–1 μm , which is not the case for XLPA. Therefore, the dislocation density determined by XLPA is statistically more reliable than that obtained by EBSD. The higher dislocation density in the initial AB + HT sample compared to that in specimen AB can be caused by the formation of hcp precipitates during annealing since the difference between the densities and the thermal expansion coefficients of the hcp and bcc phases can induce stresses. These stresses might yield the formation of dislocations in the two phases.

XLPA estimated the crystallite size in the initial samples before deformation. For sample AB, the calculated crystallite size is larger than the detection limit of about 1 μm in the present XLPA measurements. On the other hand, for specimen AB + HT, CMWP estimated the crystallite size of about 60 nm. It should be noted that the crystallite size

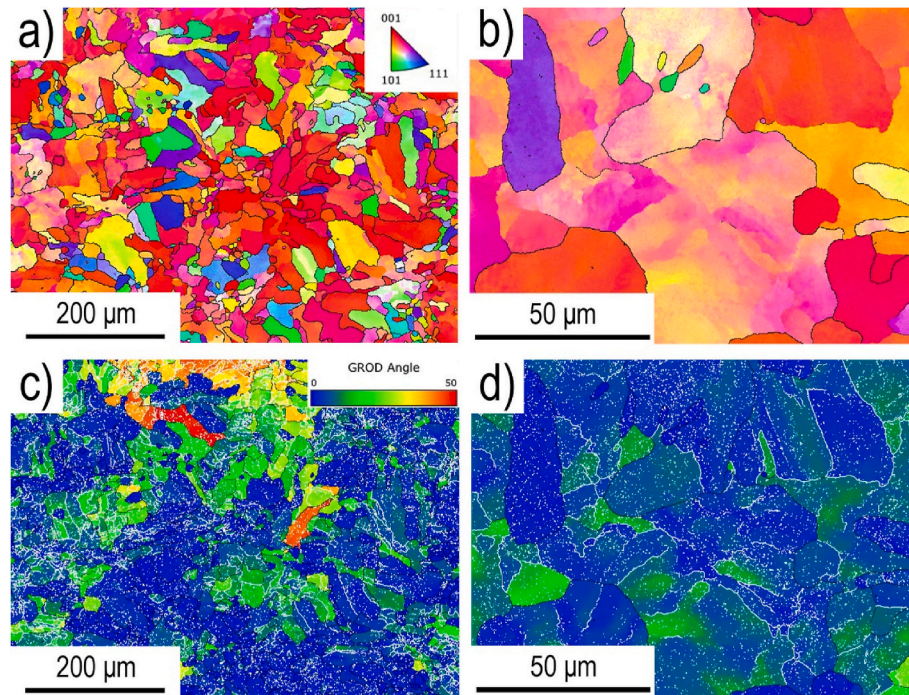


Fig. 4. IPF (a and b) and GROD (c and d) maps for the alloy AB + HT before deformation. The black lines represent HAGBs, while the white lines in c and d show LAGBs.

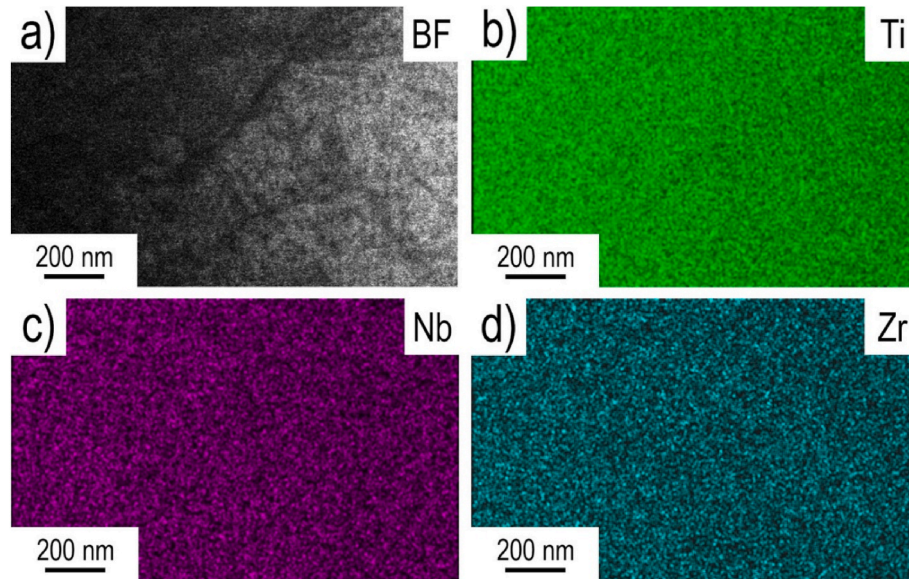


Fig. 5. (a) STEM-BF micrograph and the corresponding EDS elemental maps for (b) Ti, (c) Nb and (d) Zr for the alloy AB before deformation.

corresponds to the coherently scattering domain size in the XRD experiments, which often differs from the grain size determined by microscopic methods, such as EBSD or TEM. Namely, the crystallite size is usually smaller than the grain size since the coherency of X-ray scattering may be destroyed by small misorientations inside the grains [49]. Therefore, the crystallite size obtained by XLPAs measures rather the size of subgrains or dislocation cells in metallic materials. In the present case, the refinement of the crystallite size during heat treatment of sample AB was most probably caused by the development of dislocations due to thermal stresses, as discussed earlier, and their arrangement into low-energy configurations, such as LAGBs and dipolar walls.

3.2. Evolution of the microstructure during deformation at low and high strains

In the relatively low strain regime of $\varepsilon < 1$, deformation was achieved by compression in the HPT facility and uniaxial compression of samples. For the latter case, the true stress – true strain curves for samples AB and AB + HT are shown in Fig. 9. The yield strengths for specimens AB and AB + HT are about 710 and 780 MPa, respectively, while the maximum compressive stresses reach 1120 and 1230 MPa. It is worth noting that for sample AB, the stress-strain curve has a small plateau at the beginning of deformation, while for specimen AB + HT, strain hardening is considerably higher even at low strains. This

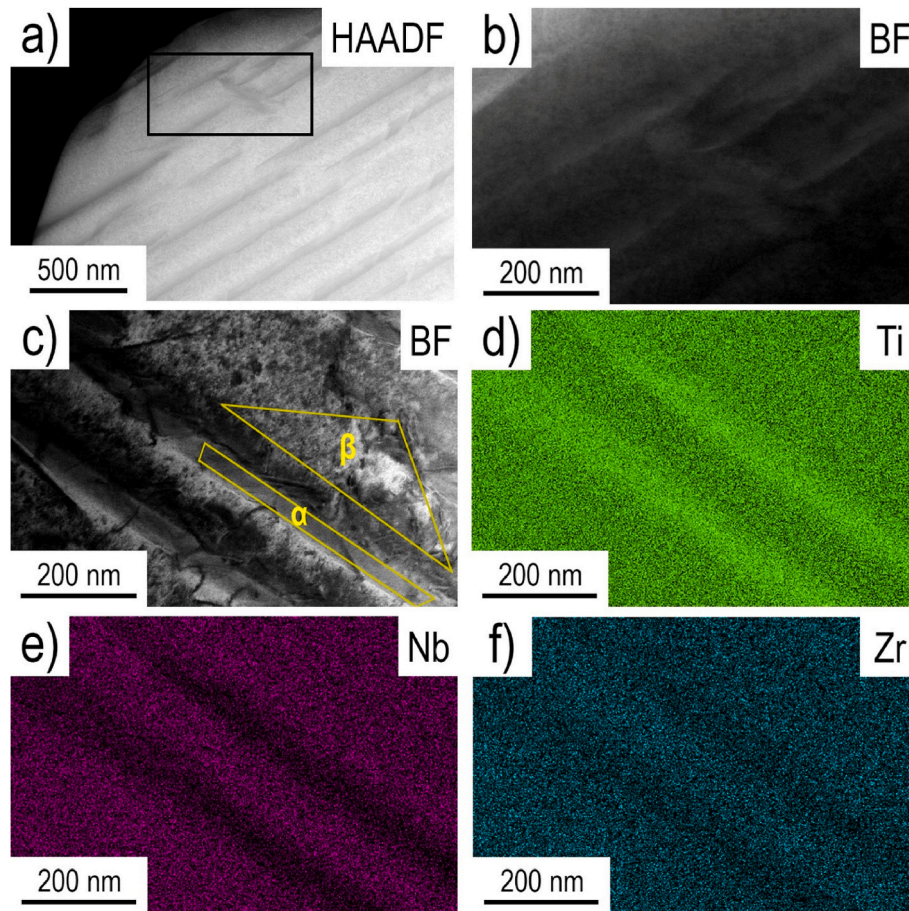


Fig. 6. (a) HAADF micrograph obtained by STEM on the alloy AB + HT before deformation. (b) and (c) show BF images taken in the black rectangle shown in (a). (c) also shows areas corresponding to bcc β - and hcp α -phases. For the area presented in (c), the elemental maps measured by EDS for (d) Ti, (e) Nb and (f) Zr reveal the variation of the chemical composition. The corresponding element concentrations are listed in Table 2.

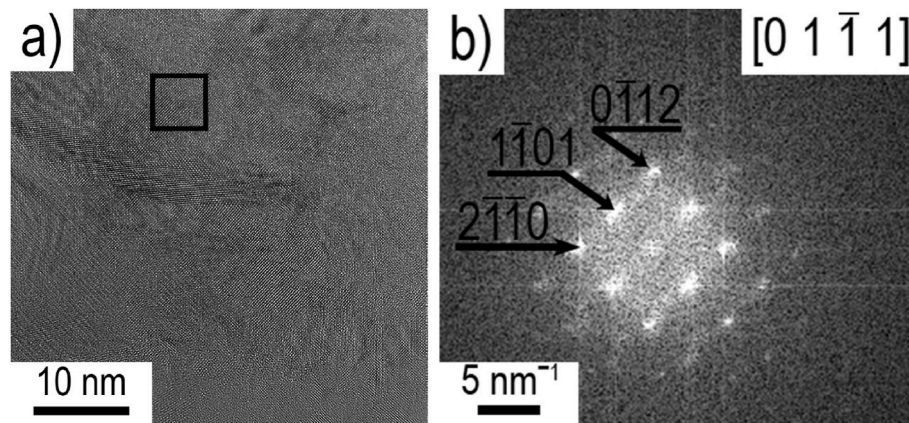


Fig. 7. (a) HRTEM micrograph taken on the alloy AB + HT before deformation. (b) FFT of the rectangle in (a) indicates an hcp phase area. The indices at the top right corner indicate the zone axis. For some diffraction spots in (b), the corresponding indices are shown by black numbers.

difference can be explained by the significant twinning activity in alloy AB, as will be shown later. Indeed, in bcc metals, including Ti alloys, twinning and/or martensitic phase transformation can produce a plateau or low strain-hardening region in the early stage of plastic deformation due to strain being accommodated by twin formation and growth as well as formation of martensite [52,53]. In the stress-strain curves plotted in Fig. 9, the solid points indicate the deformation states where the microstructures were studied by XLP. As shown in Table 1, these samples tested under uniaxial compression are deformed

only up to strains below 1. Equivalent strains higher than 1 were achieved instead by torsion in the HPT facility.

Fig. 10 plots the XRD intensity fraction estimating the secondary phase fraction against the equivalent strain up to (a) 3.0 and (b) 240 for samples AB and AB + HT. Some examples of the XRD patterns used for the determination of the phase content are shown in Fig. S1–1 in the Supplementary material. XRD revealed that the non-deformed sample AB + HT contains only secondary hcp α -phase. For the deformed samples, additional small peaks related to an orthorhombic martensite

Table 2

Chemical composition of the bcc and hcp phase areas shown in Fig. 6c for the alloy AB + HT before deformation as determined by STEM-EDS.

Chemical element	Concentrations in bcc phase (at.%)	Concentrations in hcp phase (at.%)
Ti	71.0 ± 3.9	81.2 ± 2.9
Nb	15.5 ± 2.5	7.8 ± 1.4
Zr	12.6 ± 2.1	10.1 ± 1.8
Al	0.9 ± 0.1	0.9 ± 0.1

α'' -phase were also detected in the XRD patterns in both materials AB and AB + HT. Due to the strong overlapping of most peaks of α - and α'' -phases, their fractions were not separated. Therefore, in Fig. 10, the sum of the intensity fractions of the two secondary phases is considered and evaluated. In the lower strain regime of $\varepsilon < 1$, the secondary phase content increased monotonously with increasing strain for both AB and AB + HT, with the maximum secondary phase fractions of 12 and 22 %, respectively. In the high strain regime, the hcp phase fraction of sample AB + HT remained the same, even up to a strain of about 208. On the other hand, for specimen AB, the XRD intensity fraction of the secondary phase decreased from about 7 to 0.4 % when the strain increased from 1.4 to 208. Thus, it seems that deformation yielded first the formation of stress-induced α'' -martensite which then transformed back to β -phase at high strains, and nearly the initial phase composition was restored. The values of the secondary phase fraction obtained by XRD and the microstructural parameters (crystallite size and dislocation density) determined by XLPAs are listed in Tables S2-1 and S2-2 in the Supplementary material.

Fig. 11a and b shows the evolution of the dislocation density in the low and high equivalent strain ranges. Up to a strain of about 0.7, the dislocation density increases monotonously with increasing strain, and the maximum values are around $130\text{--}140 \times 10^{14} \text{ m}^{-2}$ for both AB and AB + HT specimens. When the samples receive high strains >1 , the dislocation density is lower, about 100 and $70 \times 10^{14} \text{ m}^{-2}$ for AB and AB + HT samples, respectively. Then, the dislocation density increases again with increasing strain to the highest applied strain of 208. The maximum dislocation density values for specimens AB and AB + HT are $(730 \pm 90) \times 10^{14} \text{ m}^{-2}$ and $(590 \pm 70) \times 10^{14} \text{ m}^{-2}$, respectively. Thus, although the dislocation density is higher in sample AB + HT initially, deformation results in reverse results, where, at the highest strain, the dislocation density in specimen AB is only negligibly higher than in specimen AB + HT. In summary, except for a minor non-monotonic behavior, the dislocation density increases with increasing imposed

equivalent strain in both samples. The crystallite size decreases monotonously with increasing strain for both samples and its minimum value at high strains is about 10–20 nm, as shown in Fig. 11c.

To complete the XLPAs study of microstructure evolution during deformation, EBSD and TEM investigations were performed on samples deformed at the lowest and highest strains, respectively. Fig. 12a and b show IPF maps with different magnifications taken by EBSD on the alloy AB compressed for $\varepsilon \approx 0.08$ in the HPT facility. The average grain size is 13 μm , which is slightly lower than 17 μm measured for the non-deformed AB sample. The area-weighted mean grain size is also reduced from 44 to 35 μm . This slight refinement of the microstructure can be attributed in part to considerable twinning. Indeed, Fig. 12b reveals that inside the coarse grains, there are long lamellar volumes bounded by $\{332\}\langle 11\bar{3} \rangle$ twin boundaries that are $\Sigma 11$ boundaries with the misorientation angle between the parent and twinned volumes of about 50.5° and the axis of rotation of $\langle 110 \rangle$. In the Supplementary material, Fig. S3-1a shows the twin boundaries in an EBSD image quality (IQ) map taken on sample AB compressed in the HPT facility. For this strain (0.08), about one-half of HAGBs are twin boundaries. In addition, the fraction of LAGBs is about 40 %, i.e., lower than before deformation of 70 %, which can be caused at least partly by the

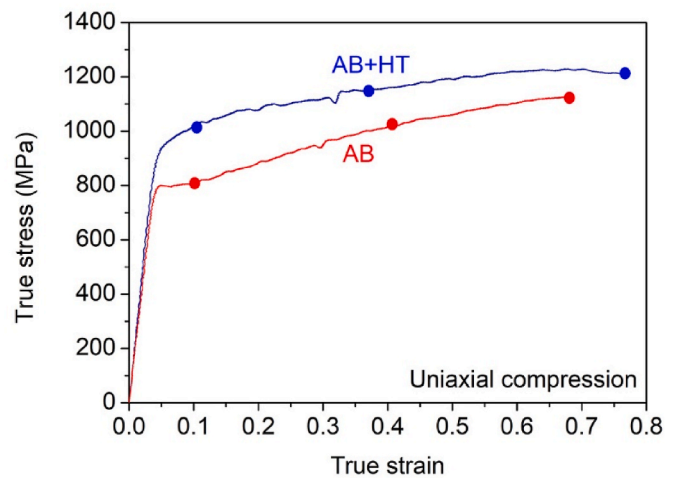


Fig. 9. Representative true stress versus true strain curves obtained by uniaxial compression for materials AB and AB + HT. The spots indicate the strains where detailed microstructure analysis by XLPAs was performed.

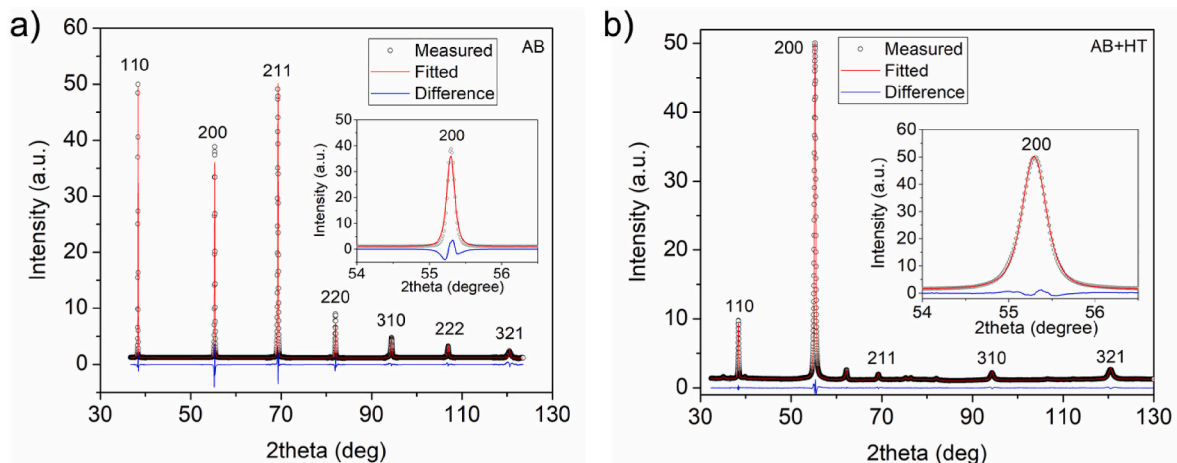


Fig. 8. CMWP fitting for the bcc β -phase in the samples (a) AB and (b) AB + HT before deformation. The open black circles and the red solid line represent the measured and calculated XRD patterns, respectively, with their difference shown by the blue line. The inset shows peak 200 at a higher magnification in order to illustrate the quality of fitting. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

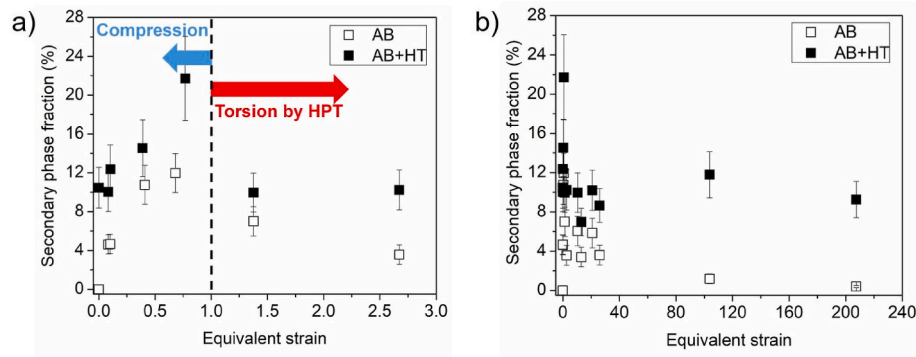


Fig. 10. (a) The fraction of the secondary phase for samples AB and AB + HT versus the equivalent strain up to 3. The data below and above the strain of 1 were obtained by compression and torsion by HPT, respectively. (b) The fraction of the secondary phase for specimens AB and AB + HT versus the equivalent strain up to 208.

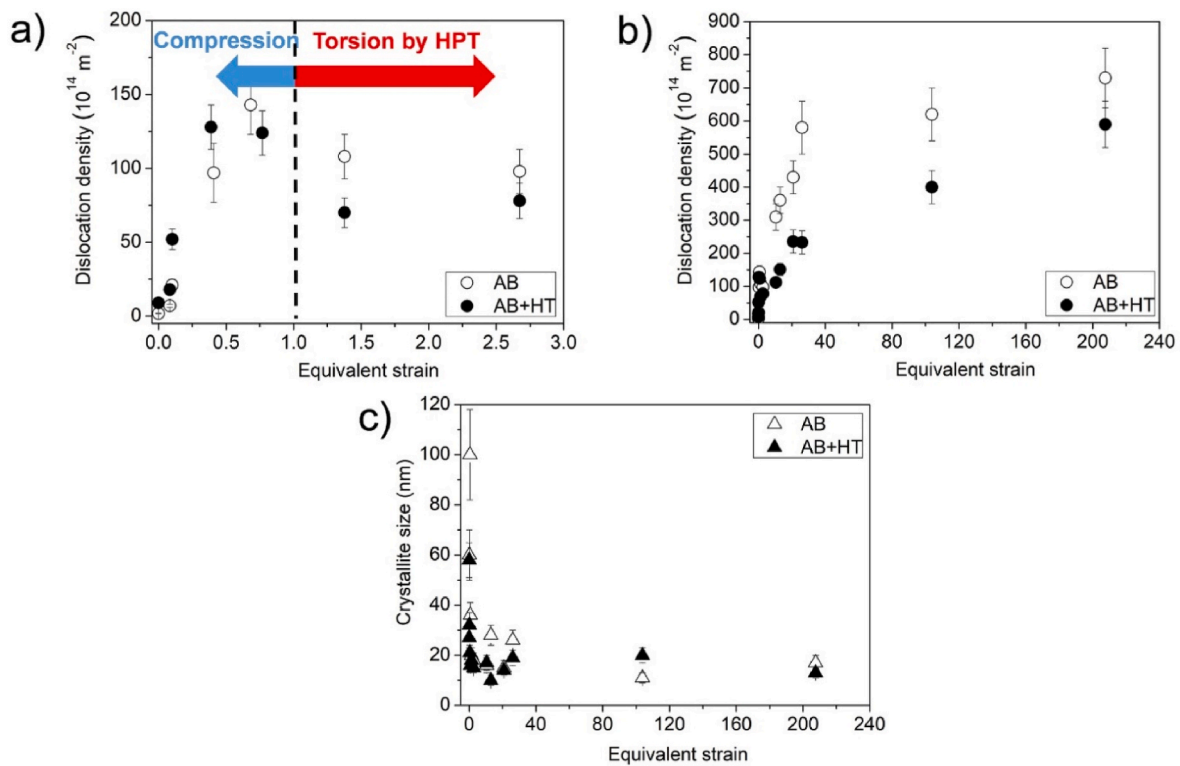


Fig. 11. (a) The variation of the dislocation density obtained by XLPD for the bcc phase in samples AB and AB + HT for the equivalent strain range up to 3. The data below and above a strain of 1 were obtained by compression and torsion by HPT, respectively. In (b), the same is shown for the large strains up to 208. The crystallite size versus the equivalent strain in the entire strain range is plotted in (c).

formation of twin boundaries. However, the transformation of LAGBs to HAGBs during deformation cannot be ruled out as a contributing factor to grain refinement. GROD maps in Fig. 12c and d suggest an inhomogeneous spatial lattice strain distribution in the deformed AB sample. For alloy AB, when the strain increases from 0.08 to 1.38 (corresponding to the close vicinity of the center of the disc HPT-processed for $\frac{1}{2}$ turn), twin boundaries are only rarely observed in the IQ map as shown in Fig. S3–1b in the Supplementary material, suggesting that twinning becomes marginal among the deformation mechanisms.

Fig. 13 shows IPF and GROD maps for material AB + HT compressed in the HPT facility to the lowest strain of $\epsilon \approx 0.08$ applied in this study. The average grain size is reduced slightly from 17 to 12 μm . The area-weighted mean grain size also decreases from 40 to about 33 μm . Unlike sample AB, twin boundaries are not observed; thus, twinning does not contribute to grain refinement. The LAGB fraction is about 58 %

which is lower than the $\sim 80\%$ observed before deformation, and this result is similar to that observed for sample AB. This effect is most probably caused by the transformation of LAGBs to HAGBs during compression in the HPT facility which is in accordance with the reduction of the grain size. Most probably, if the initial material had been processed by casting, the LAGB fraction would have been low and the deformation would have increased its value. The decrease of LAGBs during compression of sample AB + HT is due to the high initial LAGB fraction which is a fingerprint of AM processing. The spatial inhomogeneity in the GROD maps for specimen AB + HT shown in Fig. 13c and d resembles that of sample AB. The GND density does not change significantly in both samples during compression to a strain up to 0.08 in the HPT facility. On the other hand, XLPD reveals an increase in the total dislocation density by a factor of 2–4 in samples AB and AB + HT. It indicates that most of the dislocations formed during deformation are

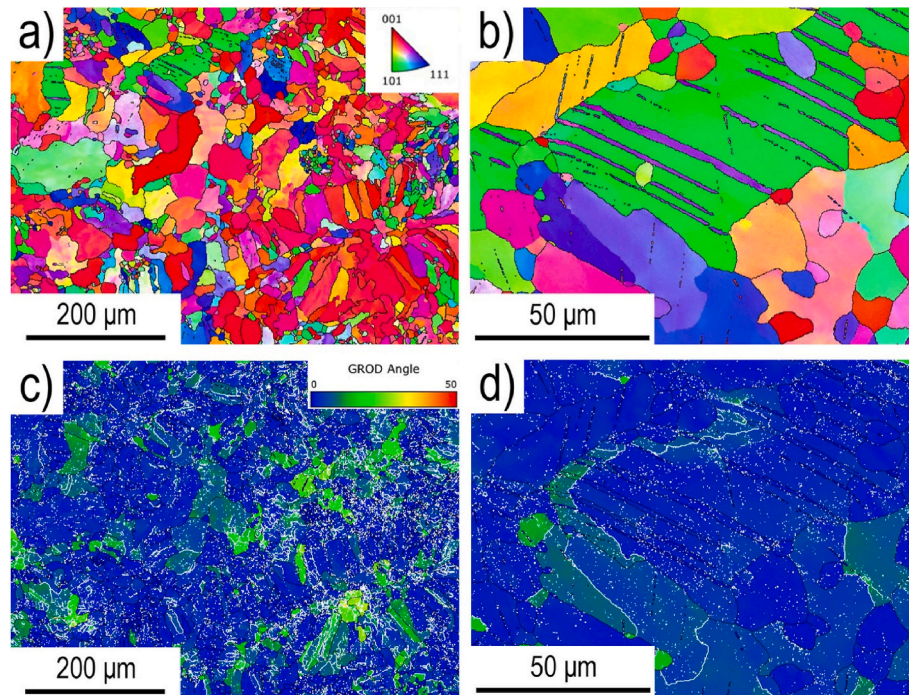


Fig. 12. IPF (a and b) and GROD (c and d) maps for sample AB compressed in the HPT facility (strain ≈ 0.08). The black lines represent HAGBs, while the white lines in c and d show LAGBs.

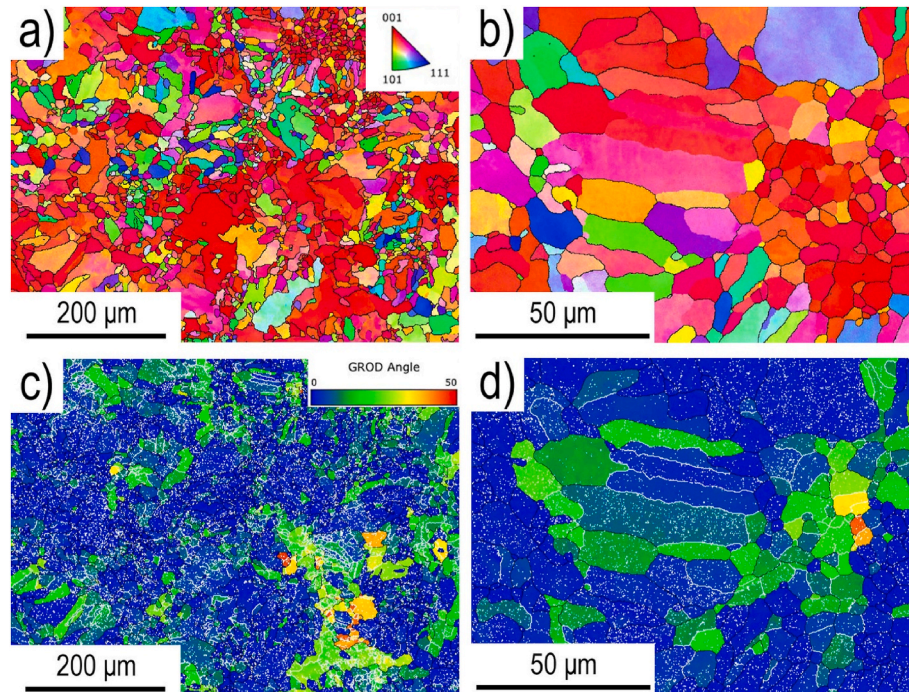


Fig. 13. IPF (a and b) and GROD (c and d) maps for sample AB + HT compressed in the HPT facility (strain ≈ 0.08). The black lines represent HAGBs, while the white lines in c and d show LAGBs.

statistically stored.

Deformation at low strain of $\varepsilon < 1$ does not trigger an apparent change in the crystallographic texture. On the other hand, HPT at high strains yields a change of the preferred orientation from $\langle 100 \rangle$ to $\langle 110 \rangle$ parallel to the original building direction. As an example, Fig. 14 shows XRD pole figures for the HPT-processed AB and AB + HT sample for the highest applied turns of 10. The $\langle 110 \rangle$ texture parallel to the

disc normal, which is lying in the original building direction, is evident. The evolution of both $\langle 100 \rangle$ to $\langle 110 \rangle$ texture components with increasing strain is characterized using a texture intensity parameter which is described in section S4 of the Supplementary material. It turns out that the initial $\langle 100 \rangle$ texture practically disappears at the equivalent strain of about 10, and further deformation yields a gradual development of a less intense $\langle 110 \rangle$ texture component (see Fig. S4–1

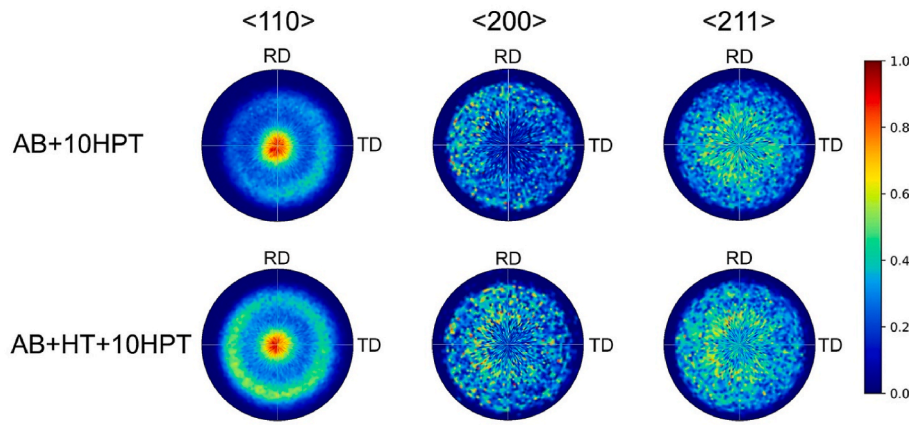


Fig. 14. XRD pole figures for the main bcc phase in the AB and AB + HT samples after deformation by 10 turns of HPT.

in the Supplementary material).

The microstructure of the samples deformed through the highest strain of ~ 208 was investigated by TEM. Fig. 15a shows a TEM-BF image of the alloy AB taken close to the edge of the HPT disc processed by 10 turns. The corresponding diffraction pattern is presented in Fig. 15b. The black circle in Fig. 15b indicates a part of the pattern that was used for taking the DF micrograph shown in Fig. 15c. The area-weighted mean grain size determined from the DF image is 48 ± 4 nm. As can be seen in Fig. 15c, the grains contain darker and brighter areas, indicating the misorientations inside the grains. The area-weighted mean subgrain size was determined from the dimensions of the bright spots, and 11 ± 1 nm is obtained for sample AB at the highest applied strain. This value is in good agreement with the crystallite size of 10–20 nm determined by XLP. In the bcc matrix, a reasonable chemical homogeneity is observed, as confirmed by the STEM-EDS elemental maps shown in Fig. 16.

The microstructure of sample AB + HT deformed by HPT up to the highest strain of ~ 208 is shown in the TEM-BF image in Fig. 17a. The corresponding diffraction pattern is presented in Fig. 17b. Besides the diffraction rings of the bcc β -phase some reflections of hcp α -phase were also detected. A part of the pattern marked by a black circle was used for making the DF micrograph shown in Fig. 17c. The area-weighted mean grain size obtained from this image is 31 ± 3 nm, while the subgrain size corresponding to the bright spots is 8 ± 1 nm. These values differ only slightly from those obtained for sample AB. In addition, the subgrain size is close to the crystallite size determined by XLP.

The HAADF and BF images shown in Fig. 18a and b, respectively, reveal wavy morphology at the edge of the AB + HT sample deformed by 10 turns of HPT. These wavy items are most probably the deformed hcp

α -phase grains which were straight lamellae before HPT processing. Indeed, the STEM-EDS elemental maps in Fig. 18c–e shows that the wavy grains are enriched in Ti and depleted of Nb and Zr as expected for the α -phase. The chemical compositions of α - and β -phase areas shown in Fig. 18f were analyzed quantitatively, and the results are listed in Table 3. Comparing these values with the concentrations before deformation (see Table 2), it seems that during HPT-processing, the difference between the chemical compositions of α - and β -phases slightly changed. In addition, the thickness of the α -phase lamellae decreased from about 40 to 10–20 nm.

Fig. 19a shows an HRTEM micrograph taken on sample AB + HT deformed to the highest applied strain of about 208. Fig. 19b shows the FFT corresponding to the area indicated by the black square. The FFT suggests that the area consists of hcp α -phase.

3.3. Change of hardness over a wide range of strain

The variation of the microhardness as a function of equivalent strain is plotted in Fig. 20. The hardness values for samples AB and AB + HT before deformation are about 2620 ± 90 MPa and 3000 ± 90 MPa, respectively. The higher hardness of specimen AB + HT can be explained by the higher dislocation density and the hardening effect of α -phase lamellae. The Vickers hardness measurement causes a strain of 0.08 in the tested material; therefore, the hardness value can be related to the flow stress obtained at this strain rather than the yield strength [54]. Usually, the estimated hardness in the unit of MPa is about three times higher than the flow stress. In the present case, at a strain of 0.08 the flow stress values are 820 and 1040 MPa for samples AB and AB + HT, respectively (see Fig. 9). Thus, the ratio between the hardness and the

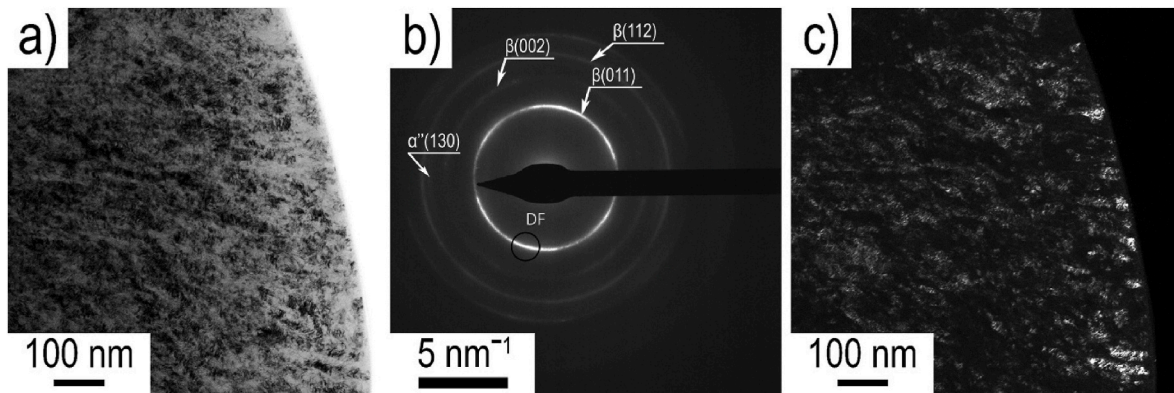


Fig. 15. (a) TEM-BF image taken close to the edge of the HPT disc processed by 10 turns of HPT for sample AB, (b) the corresponding SAED pattern, and (c) the DF micrograph taken from the same area in (a) using the diffraction ring segment indicated by the black circle in (b).

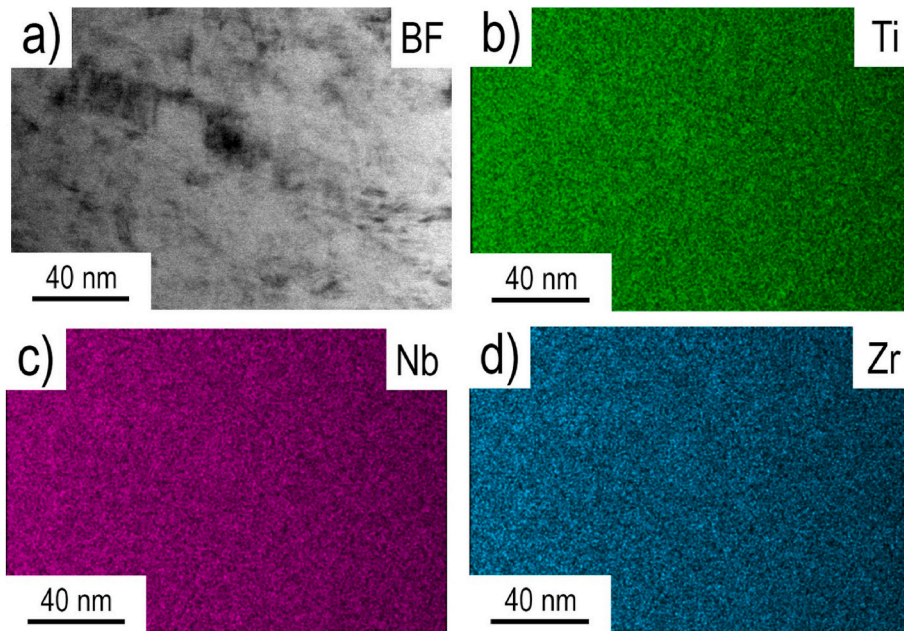


Fig. 16. (a) STEM-BF micrograph, and the corresponding EDS elemental maps for (b) Ti, (c) Nb and (d) Zr for sample AB deformed to the highest applied strain of about 208 (close to the edge of the HPT disc processed by 10 turns of HPT).

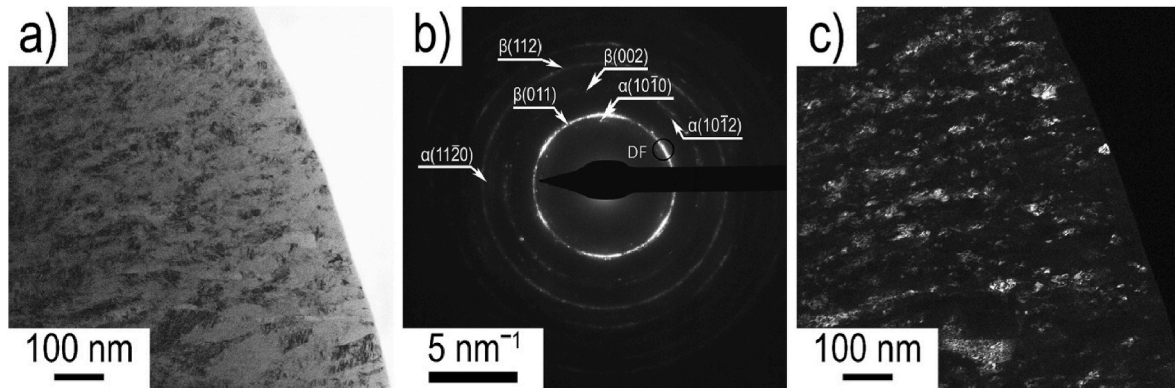


Fig. 17. (a) TEM-BF image taken close to the edge of the AB + HT disc processed by 10 turns of HPT, (b) the corresponding SAED pattern, and (c) the DF micrograph taken on the same area as shown in (a) using the diffraction ring segment indicated by the black circle in (b).

flow stress varies between 2.9 and 3.2 in accordance with the general trend observed for many other materials.

Deformation up to a strain of ~ 0.7 increases the hardness to 3330 ± 90 MPa for both materials. This enhancement is only 10–20 %, suggesting a low strain hardening rate. This observation is in accordance with the character of the stress-strain curves shown in Fig. 9. The hardness at strains of >1 was obtained on the HPT-processed discs. In this study, the microstructure in the HPT-processed discs is investigated only close to the center and the edge parts (see Table 1). On Fig. 20, only the hardness values corresponding to these locations are plotted. It should be noted that the notation “close to the center” means that the hardness was determined by averaging the values measured between the center and the radius value of 1 mm. This calculation of hardness enables comparison with the microstructure parameters determined by XLP, and the latter method studied the material around the center using an X-ray beam with a height of 2 mm (see section 2.4). Close to the disc edge, XLP was performed at the distance of 4 mm from the center; therefore, the hardness values measured at these distances on the two ends of a disc diameter are averaged and plotted in Fig. 20. Fig. 20a reveals that torsion by HPT at the equivalent strain slightly above 1 resulted in a lower hardness in the range of 3000–3100 MPa for both AB

and AB + HT samples than the values obtained by compression at slightly lower strains of ~ 0.7 . Increasing the number of HPT turns from $\frac{1}{2}$ to 10 led only to a moderate increase in the hardness up to 3400 ± 100 MPa at the disc edge. For both materials AB and AB + HT, this is the maximum achievable hardness by severe plastic deformation.

4. Discussion

4.1. Microstructure evolution as a function of strain

EBS investigations reveal that at low strains in the bcc β -phase in sample AB, $\{332\}\langle 11\bar{3} \rangle$ twins are formed, while twinning is absent in specimen AB + HT. It has been shown that the alloying with Nb in bcc Ti alloys significantly influences twinning activity [55]. In general, increasing Nb content above 8 at.% suppresses mechanical twinning in bcc Ti alloys. This is due to the reduction in the driving force for twinning as the lattice becomes more stable and the critical resolved shear stress (CRSS) for twinning increases [56,57]. The addition of Zr together with Nb to Ti can extend the concentration limit of Nb to higher values for which twinning may occur [58,59]. Because of former studies [60],

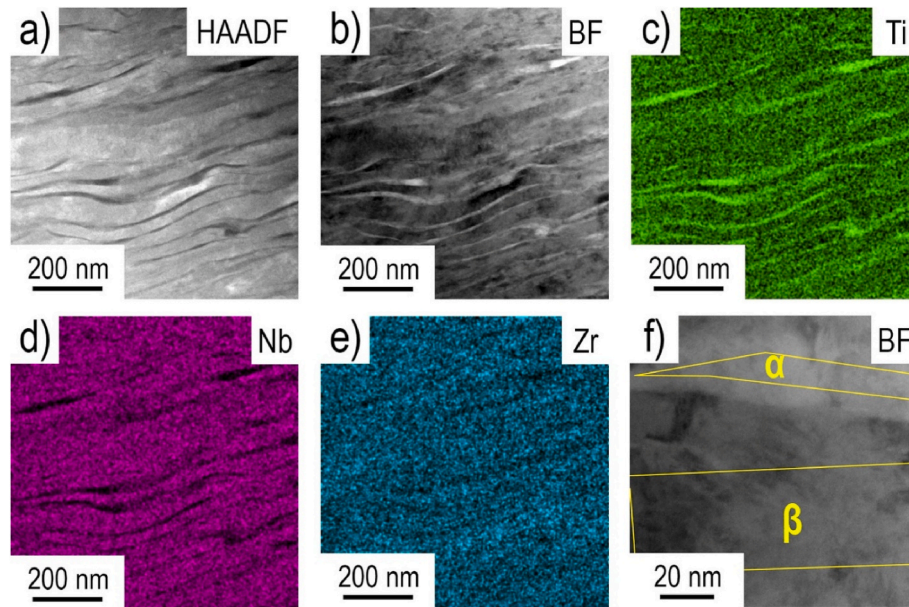


Fig. 18. (a) HAADF micrograph obtained by STEM on specimen AB + HT deformed to the highest applied strain of about 208 (close to the edge of the HPT disc processed by 10 turns of HPT), (b) BF image taken on the same area as shown in (a), and the corresponding EDS elemental maps for (c) Ti, (d) Nb and (e) Zr. The BF image in figure (f) shows bcc β and hcp α phase areas which were characterized by EDS. The corresponding element concentrations are listed in Table 3.

Table 3

Chemical composition of the bcc β and hcp α phase areas shown in Fig. 18f for sample AB + HT close to the disc edge after 10 turns of HPT (equivalent strain: ~ 208) as determined by STEM-EDS.

Chemical element	Concentrations in bcc phase (at.%)	Concentrations in hcp phase (at.%)
Ti	71.1 ± 3.9	86.1 ± 2.3
Nb	15.8 ± 2.6	4.4 ± 0.8
Zr	12.3 ± 2.0	8.5 ± 1.6
Al	0.8 ± 0.1	1.0 ± 0.2

mostly the average valence electron concentration ($\bar{e}/a$) and the compositionally-weighted average atomic radius difference between Ti and the alloying atoms ($\bar{\Delta r}$) determine the propensity of twinning. For the present composition, $\bar{\Delta r} = 0.008 \text{ \AA}$ and $\bar{e}/a = 4.15$. Therefore, according to Fig. 4 in Ref. [60], the main deformation mechanisms in specimen AB are twinning and stress-induced martensite (SIM)

formation. The stress-induced martensite grains and $\{332\}\langle 11\bar{3}\rangle$ deformation twins nucleate at prior β grain boundaries and propagate across grains, forming a substructure which restricts dislocation motion. In sample AB + HT, the Nb and Zr concentrations in the bcc matrix increased due to α -phase precipitation during annealing after 3D-printing (see Table 2); therefore, the propensity of twinning during deformation decreased. A similar effect has been observed in former studies (see e.g., Ref. [61]). With increasing strain, these mechanisms refine the microstructure. At high strains, due to the small grain size, the stress required for twinning and martensitic transformation cannot be provided by the external load, thus dislocation slip becomes the dominant deformation mechanism. Indeed, former studies suggested that when grains become extremely small (typically $<100 \text{ nm}$), twinning is suppressed entirely because the grain size approaches or drops below the minimum size needed for a twin to nucleate and grow [62,63].

The undeformed sample AB is composed of a single β -phase, while the undeformed AB + HT specimen contains an hcp secondary phase with a fraction of about 10 %. This phase is most probably an

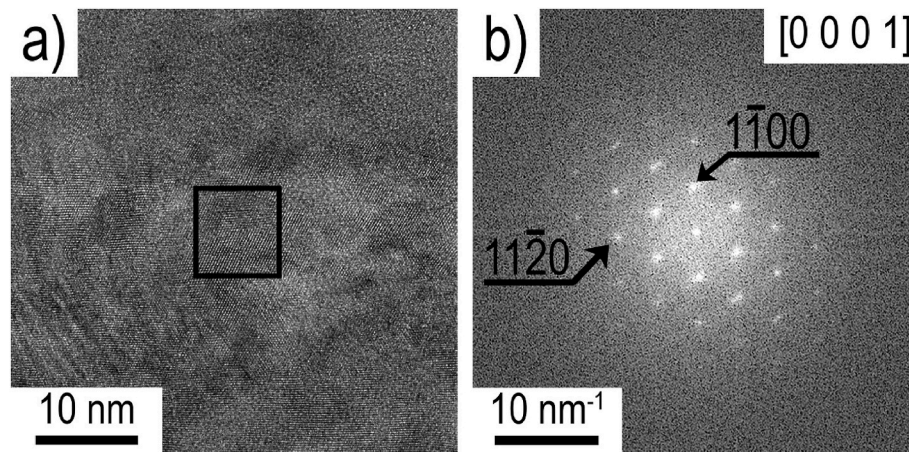


Fig. 19. (a) HRTEM micrograph taken on sample AB + HT deformed to the highest applied strain of about 208 (close to the edge of the HPT disc processed by 10 turns of HPT). The rectangle in (a) indicates an hcp α -phase area as revealed by the FFT pattern shown in (b). The indices at the top right corner indicate the zone axis. For some diffraction spots in (b), the corresponding indices are shown by black numbers.

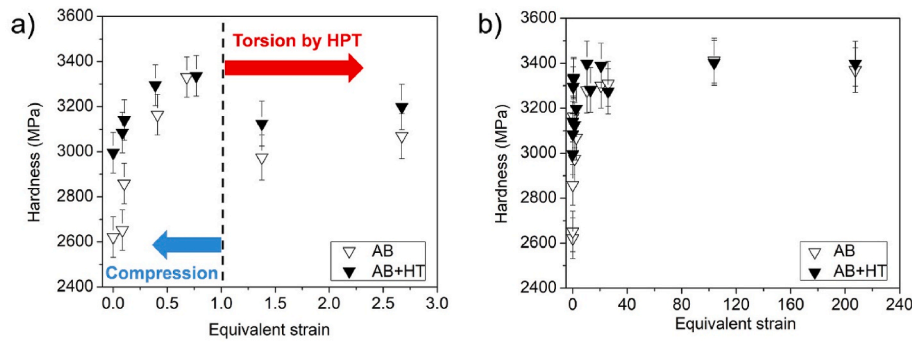


Fig. 20. (a) The variation of the hardness for samples AB and AB + HT in the equivalent strain range up to 3. The data below and above the strain of 1 were obtained by compression and torsion by HPT, respectively. (b) The hardness changes against equivalent strain up to 208.

equilibrium α -phase since it was obtained by annealing of material AB [64]. This is confirmed by the considerable compositional difference between the bcc and hcp phases (see Table 2). On the other hand, the orthorhombic phase formed during plastic deformation is a stress-induced phase since diffusion is strongly hindered at RT, and thus only non-equilibrium phases can develop by martensitic phase transformation [61]. This stress-induced martensitic transformation was also observed in Ti-30Zr-xMo ($x = 5, 6, 7$, and 8 wt%) [65,66], Ti-15Nb-5Zr-4Sn-1Fe (wt.%) [67] and Ti-10Mo-3.5Cu (wt.%) [68] alloys. Therefore, in the deformed AB samples, the orthorhombic phase detected by XRD is solely stress-induced martensite phase, while in the case of the deformed AB + HT alloy the secondary phase fraction includes both equilibrium α -phase formed during preliminary annealing and stress-induced martensite phases developed during deformation. Fig. 10 suggests that during deformation for $\varepsilon < 1$ the secondary phase fraction increases, while at high strains it decreases. The latter effect can be explained by a reverse transformation of the stress-induced martensite phases to β structure in accordance with former studies [69,70]. This reverse martensitic phase transformation can be triggered by a decrease in grain size in α'' -phase during HPT. Indeed, a former thermodynamic analysis revealed that the stress-induced α'' -phase formed during HPT became unstable below a critical grain size and transformed back into β -phase [69]. This instability was due to the very fast increase of the Gibbs free energy of the alloy when the dimension of the martensite grains decreases owing to the interfacial energy between α'' - and β -phases. The former calculations suggested that when the grain size of the martensite phase falls below about 10 nm during HPT deformation, the enhanced Gibbs free energy causes reverse phase transformation to β structure. It has also been shown that further deformation cannot yield a novel martensitic phase transformation since the development of α'' -phase from a nanostructured β -phase would require a very high stress due to the very small grain size and this stress is not provided by HPT-processing [69]. It is noted that the reversed martensitic phase transformation has been observed in Ti-10V-2Fe-3Al (wt.%), Ti73.5-Nb19.6-Ta4.5-Cr2.4 (at.%) and Ti-5Al-5V-5Mo-3Cr (wt.%) alloys [69,71–73].

In the initial AB and AB + HT samples, a $\langle 100 \rangle$ fiber texture is observed. This result is in accordance with the former observations on additively manufactured β -Ti alloys [74–77]. Indeed, in bcc metals, $\langle 100 \rangle$ directions are the fastest growth directions during solidification. During L-PBF, each layer re-melts the previous one partially; thus, the texture cannot weaken even if new crystallites are nucleated and columnar grains with $\langle 100 \rangle$ orientations are grown. This process results in a strong fiber texture with axis $\langle 100 \rangle$ parallel to the building direction. It was observed in the present study that the texture changes from $\langle 100 \rangle$ to $\langle 110 \rangle$ during HPT. The reason for the development of $\langle 110 \rangle$ texture in bcc metals during severe torsion or shear deformation at RT is that the slip occurs favorably in planes $\{110\}$ (beside $\{112\}$) and the grains are reoriented in a way that minimizes the shear resistance. Thus, lattice planes $\{110\}$ become parallel to the shear/torsion plane, i.e., axis

$\langle 110 \rangle$ is oriented parallel to the HPT disc normal [78,79].

The dislocations activated during deformation in the studied samples are influenced by their crystallographic texture since the Schmid factors for the slip systems $1/2\langle 11\bar{1} \rangle\{112\}$ and $1/2\langle 11\bar{1} \rangle\{101\}$ are different. If the loading orientation is parallel to direction $\langle 100 \rangle$ (in the case of compression at low strains for both samples AB and AB + HT), for $1/2\langle 11\bar{1} \rangle\{101\}$ dislocations in 8 slip systems the Schmid factor is 0.4082, while it is zero for the rest 4 systems (see Table S5–1 in the Supplementary material). For $1/2\langle 11\bar{1} \rangle\{112\}$ dislocations, in 8 slip systems, the Schmid factor is 0.2357, while for the rest 4 systems it is 0.4714 (see Table S5–2 in the Supplementary material). Since the latter value is higher than the maximum Schmid factor of 0.4082 for the $1/2\langle 11\bar{1} \rangle\{101\}$ slip systems, an easier activation of $1/2\langle 11\bar{1} \rangle\{112\}$ dislocations is expected for deformation at low strain in samples AB and AB + HT. The dominance of the latter type of dislocations is confirmed by the XLPAs results. Namely, the experimental value of parameter q in the dislocation contrast factor (see eq. (2)) obtained from CMWP fitting is only about 1.4 at the equivalent strains of 8–10 %. Since the theoretically calculated ranges of q for dislocations $1/2\langle 11\bar{1} \rangle\{101\}$ and $1/2\langle 11\bar{1} \rangle\{112\}$ are 2.3–2.7 and 1.3–2.7, respectively (the exact value depends on the edge/screw character of dislocations), the low experimental q value suggests the dominance of $1/2\langle 11\bar{1} \rangle\{112\}$ type edge dislocations. It is noted that with increasing strain the value of q obtained by CMWP fitting increases considerably and achieves 2.5–2.6 at the highest strains, which suggests the increase of screw dislocation fraction and/or a higher activation of $1/2\langle 11\bar{1} \rangle\{101\}$ dislocations. The more pronounced screw character of dislocations can be explained by the reduced mobility of these dislocations compared to edge dislocations in bcc structures. The difficulty of screw dislocation motion is caused by the dissociation of their core into a non-planar, three-dimensional configuration [80]. On the other hand, the core of edge dislocations is more planar and thus these dislocations have higher mobility than that of screw dislocations. As a consequence, during plastic deformation edge dislocation segments can annihilate more easily than screw ones; therefore, the character of the remaining dislocations becomes more screw.

It is worth noting that the dislocation density at an equivalent strain of about 1 is slightly lower when the deformation method changes from compression to HPT (see Fig. 11a). This effect can be attributed to the relaxation of the dislocation structure after releasing the very high hydrostatic pressure applied during HPT processing. A former study has shown that at the hydrostatic pressure of 4 GPa the dislocation density decreased by 10–40 % upon releasing the pressure [81]. This effect was attributed to the activation of vacancy migration after HPT which triggers edge dislocation annihilation. Indeed, during HPT a very high concentration of excess vacancies forms, however, their motion is highly hindered by the high pressure during HPT. When the pressure is released after HPT, the vacancies are mobilized, yielding dislocation annihilation. This effect is higher for larger strains and pressures applied in HPT

processing, and it is negligible in uniaxial compression. Therefore, this pressure effect can explain the 20–40 % lower dislocation density when comparing the states at strains of 0.7 and 1.4 achieved by compression and HPT, respectively.

4.2. Hardness change with increasing equivalent strain

The hardness values for the coarse-grained samples AB and AB + HT are about 2620 and 3000 MPa, respectively. These high values can be partly attributed to the non-planar, highly spread cores of screw dislocations in bcc crystals that yields a high lattice friction, i.e., a high Peierls stress, irrespective of the microstructure [82]. This is a fundamental crystallographic effect and is valid for all bcc alloys. This effect is more pronounced for β -Ti (and also for Hf and Zr) compared to the other bcc metals such as Fe, Mo and W [83]. Moreover, the alloying of bcc Ti with Zr further increases the yield strength via solid solution hardening due to the large atomic size and elastic moduli misfit between the two elements (e.g., the atomic radii of Ti and Zr are 147 and 160 pm, respectively). The higher hardness for alloy AB + HT can be attributed to the higher α -phase fraction. The α -phase lamellae (see Fig. 6) serve as obstacles against dislocation motion in the major bcc matrix, thereby hardening the material. It is noted that the hcp grains are assumed to be harder than their bcc counterparts due to the limited easy dislocation slip systems in the former phase. The higher dislocation density in the initial sample AB + HT may also contribute to the higher hardness compared to the initial AB specimen but the dislocation forest hardening is usually less pronounced in bcc metals and alloys than the Peierls stress [84].

Fig. 20 shows that for both samples AB and AB + HT, the hardness increases to 3330 ± 90 MPa with increasing strain up to about 0.7, and then slightly decreases to 2970 ± 100 and 3120 ± 100 MPa, respectively, at a strain of ~ 1.4 . This change in hardness can be attributed to variations in dislocation density and the secondary α -phase fraction (see Figs. 10 and 11) since significant texture evolution is not observed for these strains (as shown in Fig. S4–1 in the Supplementary material). Thus, the increase of the hardness from 2620 to 3000 MPa to about 3300 MPa for samples AB and AB + HT, respectively, is caused by the increase of the dislocation density from $(2\text{--}9) \times 10^{14} \text{ m}^{-2}$ to $(120\text{--}140) \times 10^{14} \text{ m}^{-2}$ and the formation of α'' -phase with the fraction of 12 %. For the lowest studied strain achieved by HPT (~ 1.4), 6–11 % lower hardness values are obtained due to the smaller dislocation density and α'' -phase fraction.

The increase of the equivalent strain from 1.4 to 208 leads only to a moderate increase in hardness from 2970 to 3120 to 3400 ± 100 MPa. It can be concluded that the overall hardness increase due to 10 turns of HPT processing (at the disc edge) is low if the initial materials are taken as the reference states: for sample AB, the hardness increases from 2620 to 3400 MPa, while for the specimen AB + HT, the hardness is enhanced from 3000 to 3400 MPa. This behavior is especially interesting when considering the very different microstructures before and after 10 turns of HPT: the grain size and the dislocation density decreases and increases, respectively, by at least two orders of magnitude. Quantitatively, for instance, in the case of material AB + HT, if the initial sample is considered as a reference state, the increase of the square root of the dislocation density at the strain of ~ 208 is 3.7 times higher than that at the strain of ~ 1.4 . Since the secondary phase fraction is practically the same at these two strains as in the initial state, and the grain size reduces significantly at the strain of ~ 208 , a similar or even a higher factor is expected for the hardness change when the strain increases from ~ 1.4 to ~ 208 . On the other hand, the hardness increment is only 3.2 times higher at the strain of ~ 208 than that at the strain of ~ 1.4 . The moderate hardness despite the extremely high dislocation density at high strains is most probably caused by the special features of the deformation mechanisms in metastable β -Ti alloys. Namely, the dislocation character becomes rather screw at very high strains as suggested by XLP, and the mechanism of screw dislocation motion in bcc crystals is

the thermally activated nucleation and propagation of kink pairs along the dislocation line [85]. With increasing mobile dislocation density, the velocity of individual dislocations decreases at a given strain rate. Therefore, thermally activated kink-pair formation occurs more easily, thereby reducing the stress necessary for the motion of dislocations [85]. In addition, due to the very small grain size of 30–50 nm, grain boundary sliding may significantly contribute to plastic deformation; therefore, the high dislocation density can not yield the expected very high hardness. Similarly, low hardening has been observed for other highly alloyed bcc metals such as nanostructured multi-principal element alloys (e.g., HfNbTiZr) processed by HPT at RT [86].

The change in the texture from $\langle 100 \rangle$ to $\langle 110 \rangle$ during HPT processing may also have an effect on the evolution of hardness with increasing strain. Former studies (e.g., Ref. [87]) have shown that for bcc Ti alloys the yield strength measured in direction $\langle 100 \rangle$ were higher than those detected in orientation $\langle 110 \rangle$. This observation can be explained by the higher number of activated slip systems during deformation along direction $\langle 100 \rangle$, which increases the probability of the dislocation lock formation due to interaction between dislocations. The corresponding Schmid factor analysis of the different slip systems can be found in section S5 of the Supplementary material. Thus, a bcc sample with the texture $\langle 100 \rangle$ is expected to be harder than that having $\langle 110 \rangle$ texture. This consideration is valid for samples which are not subjected to preliminary plastic deformation, therefore the number of pre-existing dislocation locks is very low. It should be noted, however, that most of the samples investigated in this study are severely deformed; therefore, all slip systems are expected to contain a lot of dislocation locks even before hardness testing. In addition, Vickers hardness measurement is not a uniaxial deformation; rather, hardness testing results in a complex stress state under the indenter. Therefore, the Schmid factor analysis presented in this study gives only an approximation of the influence of the texture on the hardness variation. In summary, the texture effect on the hardness is marginal in the present case, and the low hardening due to HPT is most probably caused by the kink pair related deformation mechanism and the sliding of nanograin boundaries.

5. Conclusions

In this study, an additively manufactured Ti-15 %Nb-12 %Zr (at.%) alloy was deformed in a wide range of strain from 0.08 up to 208. Below a strain of 1, the deformation was carried out by compression, while above that, HPT was performed on the samples. The evolution of the microstructure was monitored and related to the hardness change as a function of strain. The effect of heat treatment after additive manufacturing on the deformation behavior was also investigated. The following conclusions were drawn from the experimental results.

1. The as-built alloy has a single-phase bcc structure, which contains a significant density of as-grown dislocations ($\sim 1.8 \times 10^{14} \text{ m}^{-2}$). The heat treatment yields a considerable increase in the dislocation density to about $9 \times 10^{14} \text{ m}^{-2}$, which can be caused by the stresses developed due to the formation of an hcp secondary phase with a fraction of about 10 %. The area-weighted mean grain sizes of the AB and AB + HT samples are 44 and 40 μm , respectively. Both materials have a $\langle 100 \rangle$ texture parallel to the building direction.
2. For strains up to about 1 achieved by compression, in both AB and AB + HT samples the secondary phase fraction and the dislocation density increase considerably while the crystallite and grain sizes decrease. In this strain range, the amount of the secondary phase and the dislocation density are higher, while the crystallite size is smaller for the heat-treated material. In alloy AB, besides the dislocation activity, $\{332\}\langle 11\bar{3} \rangle$ twinning is also observed. The lack of twinning in the bcc matrix of the heat-treated sample can be explained by its enrichment in Zr and Nb due to the formation of a Ti-rich hcp secondary phase.

3. In the high strain regime achieved by HPT (between 1 and 208), the texture of the bcc matrix for both AB and AB + HT samples gradually changes from $\langle 100 \rangle$ to $\langle 110 \rangle$ parallel to the building direction. At a strain of about 1, the dislocation density in the HPT-processed sample is slightly lower than in the compressed specimen. Above a strain of 1, the dislocation density increases monotonously up to an extremely large value of $600\text{--}700 \times 10^{14} \text{ m}^{-2}$ at a strain of 208. At the highest strain, a nanocrystalline microstructure forms in both AB and AB + HT specimens. In the high strain regime, the secondary phase fraction decreases back to similar values for both materials as in the initial state before deformation due to reverse martensitic phase transformation. The α -phase formed due to annealing before deformation remains in the sample AB + HT even after HPT processing, although the lamellae of this phase are significantly refined.
4. The initial AB and AB + HT samples exhibit high hardness values of about 2620 and 3000 MPa, respectively. The higher hardness of the latter material can be explained by the higher dislocation density and secondary phase fraction, as well as the smaller grain size. Compression up to the strain of 0.7 increases the hardness to about 3300 MPa for both materials. By changing the deformation mode from compression to HPT, thus at a strain of about 1, a slight decrease in hardness is observed, similar to the dislocation density and the secondary phase fraction for both AB and AB + HT samples. An additional increase in strain up to 208 leads only to a slight increase in hardness to 3400 MPa, although there is a many-fold increase in dislocation density and reduction in grain size. The unexpectedly low hardness increase due to HPT may be caused at least partly by the kink pair related deformation mechanism. Namely, due to the high density of dislocations, their velocity is lower during deformation, which facilitates thermally activated kink pair formation on screw dislocations, thereby reducing the thermal component of the strength. Moreover, the very small grain size of 30–50 nm in the HPT-processed samples can yield an operation of grain boundary sliding during hardness test which usually requires lower applied stress than dislocation glide.

CRediT authorship contribution statement

Kamilla Mukhtarova: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Guy Dirras:** Writing – review & editing, Validation, Funding acquisition. **Megumi Kawasaki:** Writing – review & editing, Investigation, Funding acquisition. **Csilla Kádár:** Writing – review & editing, Validation, Investigation, Funding acquisition. **Márk Windisch:** Writing – review & editing, Investigation, Formal analysis. **Anita Heczel:** Writing – review & editing, Investigation, Formal analysis. **Zoltán Dankházi:** Writing – review & editing, Investigation, Data curation. **György Zoltán Radnóczy:** Writing – review & editing, Investigation, Formal analysis. **Jenő Gubicza:** Writing – original draft, Visualization, Validation, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Editorial board member of MSEA - J.G. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.msea.2026.149842>.

Data availability

Data will be made available on request.

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