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In Situ Synchrotron X-Ray Diffraction during High-Pressure Torsion Deformation of Ni and NiTi

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A down-sized high-pressure torsion device is developed to be used in an INSTRON deformation machine available at the High Energy Materials Science beamline at PETRA III. This setup allows to obtain synchrotron diffraction patterns in situ during severe plastic straining. Two different materials are studied: in pure Ni, the dislocation density and coherently scattering domain size are analyzed; in NiTi shape memory alloy, amorphization and a reverse martensitic phase transformation are investigated. The in situ experiments facilitate the characterization of the microstructural evolution of these materials depending on uniaxial loading, hydrostatic pressure, and torsional strain.

1. Introduction

The processing of materials using extreme plastic deformation under hydrostatic pressure, severe plastic deformation (SPD),[1] has been applied to a wide range of materials and material categories within the past two decades. It involves deformation methods providing hydrostatic pressure of up to about 10 GPa and achieving ultrahigh strains far beyond conventional plastic deformation. Both pressure and strain are fundamental to obtain materials with unique combinations of strength and plastic properties due to grain refinement down to the nanometer scale and the introduction of an enormous amount of lattice defects. SPD can lead to nanocrystallization and even complete amorphization in the case of NiTi shape memory alloys.[2] Furthermore, within the past years, the interest of researchers also turned to the application of SPD methods to materials with functional and tunable properties (thermoelectrics, hydrogen storage, magnetic, biomedical)[3-6] and even geomaterials.[7]

However, the characterization of the microstructure and other properties is always conducted after the complete SPD processing, whereas the dynamic evolution of the microstructure can only be presumed. The exact pathway to the final microstructure remains unclear as accessible in situ parameters are very limited. So, a possibility to investigate the microstructure during such deformation processes is of high scientific interest.

High-pressure torsion (HPT) is an SPD method often used in scientific experiments and refers to a process in which the sample, generally provided as a thin disc, is subjected to torsional straining under a hydrostatic pressure between two anvils, with one of them rotating at a certain speed. The considerably high pressure (between 1 and 10 GPa) provides enough friction between the sample surface and the anvils to enable shear deformation. A modified anvil design with cavities suppresses the outward flow of material and enables a defined deformation. The true torsional strain, γ, is given by γ torsion = ε⊥/h, where r is the distance from the center of the disc, φ is the torsional angle in radians, and h is the sample thickness. The true equivalent strain, ε, can be calculated using the relation ε vanMises = √3 γ torsion using the van Mises criterion of plastic flow. If there is some outward flow of material between the two anvils and a corresponding reduction in the value of h, it can be taken into account by adding the true (compressive) strain. The size of...
the discs used in conventional HPT is quite small (about 10 mm in diameter and 1 mm in thickness) but recent attempts for upscaling the tools have been successful. High-energy X-ray diffraction during this HPT deformation is one among very few possibilities to investigate this process in situ as the sample is deformed by torsion more or less without changing its position. A first promising attempt has been conducted by Kilmametov et al. at European Synchrotron Research Facility (ESRF) using synchrotron diffraction during consolidation of Cu powder torsionally strained at 0.5 GPa. The change of the full width at half maximum (FWHM) of several Cu reflections during deformation could be observed. In the study, newly developed equipment was used to minimize parasitic radiation from the HPT anvils. After the high-quality acquisition of diffraction patterns with adequate time resolution (e.g., deformation strain), state-of-the-art X-ray line profile analysis using physical models to determine crystallite size and distribution as well as dislocation density and arrangement can be applied and enables to characterize the microstructural development during deformation.

In the present work, in situ HPT is used to study structural changes in two materials, pure Ni and a NiTi shape memory alloy, with fundamentally different deformation properties: face-centered-cubic (fcc) Ni is a very ductile monophase material where plastic deformation is due to generation and movement of dislocations with cross-slip facilitated by high stacking fault energy. Using the adapted Mini-HPT device, the microstructural evolution of pure Ni during severe plastic straining is investigated in situ by recording synchrotron X-ray diffraction profiles. NiTi is one of the most prominent shape memory alloys. Upon cooling or straining, it undergoes a martensitic phase transformation from the cubic B2 phase (the austenite) to monoclinic B19’ lattice structure (the martensite). This transformation is reversible, giving rise to unique thermomechanical properties such as shape memory effect and superelasticity. Depending on the chemical composition, grain size, and defect structure, an intermediate phase, the R-phase, can occur (the R-phase is also martensitic and arises by a slight rhombohedral distortion of the B2 austenite). In its B19’ structure, deformation can occur by the motion of domain boundaries delineating different variants of martensite. When the applied stress exceeds a critical value, plastic deformation mechanisms set in, based both on dislocation glide and on deformation twinning. In addition, NiTi can show a deformation-induced transformation to an amorphous phase, even for rather low degrees of strain (e.g., by cold rolling). In the current work, the adapted Mini-HPT device is used to follow via the in situ synchrotron X-ray diffraction the process of amorphization induced by SPD.

2. Experimental Section

For the implementation of an in situ X-ray diffraction experiment during HPT, the facilities at the High Energy Materials Science Beamline P07 at Petra III/DESY provided the ideal experimental conditions. The INSTRON 100 kN deformation machine attached to the hexa-pod from PHYSIK INSTRUMENTE for heavy loads of up to 1 t allowed to position the whole deformation experiment in the beam with a resolution down to 1 μm. The INSTRON machine provided the necessary compressive force for the application of hydrostatic pressure to the sample. The load cell of the INSTRON device was mounted on the bottom support of the deformation machine to which a self-constructed rotation device of low height was attached, enabling a HPT deformation. With the help of a slew drive and an induction gear motor controlled by a DANFOSS motor driver, the rotation speed was chosen within more than one order of magnitude (see Figure 1).

The lower and the upper anvil—attached to the slew drive and the upper piston of the INSTRON machine, respectively—were down-sized to a sample diameter of 2.5 mm, from the typically used 8–10 mm in conventional HPT experiments. This had two fundamental reasons and advantages: 1) for a maximum hydrostatic pressure of 8 GPa, only 40 kN load was necessary, which perfectly fit the load range of the INSTRON machine and 2) as the sample was hit only in the outermost diameter, the diffraction volume was more defined with respect to the gradient of deformation strain (see sketch in Figure 2).

The disc-shaped samples of diameter 2.5 mm were placed between the two anvils to which pressure was applied (up to 8 GPa). While the upper anvil was fixed, the bottom one rotated and strained the sample by torsion. During this process, the X-ray beam of several tens of micrometers in size and an X-ray energy of 82 keV transmitted the sample through the small gap between the anvils at its outer radius, where the nominal strain was highest. Due to the special shape of the anvils (Figure 2), a thin well-defined ring of sample material formed between the two anvils providing hydrostatic pressure (hindering the sample material from flowing out). This protrusion also preserved a small gap between the two HPT anvils. Within this gap, the synchrotron beam passed the sample at a section going through the outer diameter of the sample (r = 1.15 mm), which made it possible to record an artifact-free diffraction signal (i.e., without or with low-diffraction signal from the anvils material). The initial sample height was optimized in ex situ HPT experiments to minimize the formation of this protrusion. The width of this protrusion was determined to be smaller than 0.1 mm (in terms of radius) after the HPT process. A 2D detector...
PERKIN-ELMER X-ray diffraction (XRD) 1621 was used to record the diffracted signal with an exposure time for one frame of about 0.5–1 s, which yielded a sufficient resolution with respect to the rate of straining. The sample-to-detector distance was about 3.2 m; the exact value was obtained during the diffraction pattern calibration using CeO2 reference (NIST 674b) using the pyFAI software, which also was used for the integration of the Debye–Scherrer ring sectors to obtain line profiles.

2.1. HPT Deformation of Pure Ni

High-purity Ni (99.99%) was deformed at 8 GPa hydrostatic pressure and up to about eight full rotations of the lower anvil, achieving a torsional plastic shear strain of about 140. The value of rotation speed was chosen to correspond to a strain rate of \( \varepsilon = 0.05 \text{ s}^{-1} \), which was about the same rate as that in the conventional HPT deformation. After the integration of the recorded diffraction patterns, the data were prepared for evaluation by X-ray profile analysis (XPA) using state-of-the-art analysis methods.

2.1.1. XPA Evaluation

The method of XPA is a powerful tool to characterize the microstructure of crystalline materials, such as bulk or powder samples with respect to their lattice defects, especially after plastic deformation. New-generation high brilliant synchrotron radiation sources allow in situ investigations with high temporal and spatial resolution, even in highly distorted and/or plastically deformed materials. The principally ideal narrow diffraction pattern in reality broadens due to numerous effects that are related to the microstructure of the material-like peak broadening originating from finite sizes of crystallites and the presence of microstrains, strain gradients, and chemical heterogeneities. Anisotropic peak broadening possibly combined with asymmetric peak shapes arise from anisotropic crystallite shapes, anisotropic strain, long-range internal third-order strains, or planar faulting.

According to the kinematic theory of scattering, diffraction profiles result from the convolution of size (S) and distortion (D) profiles. The Fourier transform of this is Warren–Averbach’s equation:

\[
A(L) = A^S(L)A^D(L)
\]  

where \( A^S(L) \) is the size transform, \( A^D(L) \) is the distortion transform, \( L \) is the scattering vector, and \( A(L) \) is the total transform.

The resulting fitting parameters describe the state of the material in terms of size and strain: the median \( m \) and variance \( \sigma \) of a log-normal function describing the size distribution of the coherently scattering domains (CSD) representing the smallest perfect lattice volume that scatters coherently. The strain part provided information on the dislocation structure: the parameter \( \rho \) describing the average dislocation contrast, the dislocation density \( \rho \), and the outer cutoff radius \( R_e \), characterizing the extension of the strain field of the dislocations. The experimental data were evaluated using the Convolutional Multiple Whole Profile (CMWP) fitting procedure, which yields dislocation density and CSD size data.
2.2. HPT Deformation of NiTi Shape Memory Alloy

A Ni–50.1 at.\% Ti alloy that is martensitic at room temperature (RT; martensite finish temperature at ≈50 °C) was used to obtain discs with a diameter of 2.5 mm and a thickness of about 0.4 mm by spark erosion. The specimens were subjected to in situ HPT with a maximum pressure of 6 GPa (corresponding to a uniaxial load of 30 kN) and up to torsional shear strain $\gamma_{\text{torsion}}$ of 135 (about seven rotations). These sample states were denoted by $p/\gamma_{\text{torsion}}$, where $p$ is the applied hydrostatic pressure (in GPa) and $\gamma_{\text{torsion}}$ the torsional shear strain.

Synchrotron diffraction profiles were recorded in the initial state, applying a hydrostatic pressure only (1, 4 and 6 GPa), applying a hydrostatic pressure of 6 GPa in combination with a shear strain $\gamma_{\text{torsion}}$ of 3, 5, 8, 13, 21, 39 and, finally, after the maximum torsional straining of 135 and unloading ($p = 0$ GPa). In addition, samples subjected to HPT ex situ with a pressure of 6 GPa were used to obtain thin foil specimens by electropolishing. These specimens were analyzed by transmission electron microscopy (TEM) using a Philips CM200 operated at 200 kV.

Synchrotron profiles were shown by plotting the intensity as a function of the modulus $Q$ of the scattering vector $Q = k - k_0$, where $k_0$ and $k$ are the wave vectors of the incident and scattered beam, respectively, with $|k_0| = |k| = 2\pi/\lambda$. Using synchrotron profiles of the initial undeformed state, the lattice parameters and volume fraction of the martensite were measured applying Rietveld refinement methods. As the incident beam also might partially hit the anvils of the HPT device, the synchrotron profile of the anvils only were taken as a reference and subtracted from the synchrotron signals if necessary by fixing the positions of the anvil peaks during Rietveld fitting. Fortunately, little overlap of the positions of lattice reflections of NiTi and the anvil material was encountered. During loading and straining, an estimate of the amorphous volume fraction was obtained by modeling the amorphous phase and the crystalline phase via Rietveld method. The initial data were used to determine the overall background, which was used as a basis for all profiles by scaling it to the background level at the very low angles. Then, the crystalline and the amorphous phases were added. After fitting the ratio of the areas of the amorphous and crystalline phases, they were used to determine the amorphous phase fraction (APF).\(^{[40]}\)

3. Results and Discussion

3.1. HPT Deformation of Pure Ni

More than 130 frames were recorded including the loading and unloading of the sample (i.e., applying and releasing the hydrostatic pressure before starting and after ending the torsional deformation). About 40 measurements were chosen for evaluation to characterize the microstructural evolution during the HPT process with sufficient resolution regarding the deformation strain.

Figure 3, 4 show the results of the CWMP evaluation for the CSD size $d$ as well as the dislocation density $\rho$ as functions of deformation strain. Generally, the filled circles depict the sample state at a hydrostatic pressure $p = 0$ GPa, and the circles mark the sample state of the maximal hydrostatic pressure $p = 8$ GPa; after the torsional straining to $\gamma_{\text{torsion}} \approx 140$, the pressure was released sequentially in steps from $\Delta p = 1$ GPa to 0, which is represented by the circles shaded in gray. As shown, there are no results for the completely undeformed state ($\gamma_{\text{torsion}} = 0$ and $p = 0$ GPa) as they lie below the resolution limit of the XPA method (i.e., $d \geq 500$ nm and dislocation density $\rho \leq 10^{13}$ m$^{-2}$).

After the application of hydrostatic pressure, the sample undergoes its first plastic deformation by being pressed into the anvil shape. This is in principle compression deformation of $\varepsilon_{\text{true}} \approx 10 – 20\%$ true strain, which is negligible compared with the subsequent torsion deformation of $\varepsilon_{\text{vAMiS}} > 8000\%$. However, the effect is considerable: while the domain size $d$ takes a value of about 60 nm, the dislocation density, $\rho$ increases to the order of $10^{15}$ m$^{-2}$, an amount usually found after high deformation of more than 100% (e.g., by conventional torsion).\(^{[41]}\)
The much more drastic effects follow the start of the torsional plastic straining. A steep drop in domain size to about one-half occurs, followed by a gradual decrease to about 20 nm, which remains quite stable throughout the whole deformation process. In parallel, the dislocation density strongly increases to values in the range of \(5 - 6 \cdot 10^{15} \text{ m}^{-2}\), which is considerably higher than the values obtained from investigations after HPT deformation. \(^{42,43}\) Both quantities, domain size and dislocation density, remain at their values even when the torsional deformation is stopped but with the hydrostatic pressure still being applied.

However, the situation changes significantly when the hydrostatic pressure load is incrementally released. Both domain size and dislocation density change to higher and lower values, respectively, which have been already observed in investigations by Schafler et al.\(^{43-45}\) In Figure 5, 6, the values obtained during this release are shown against the hydrostatic pressure showing the unloading effect in detail.

The effect is attributed to the presence of the high hydrostatic pressure \(p\) as it has considerable influence on the deformation conditions. Compared with conventional deformation at ambient pressure, the following properties are affected and have been already considered in terms of deformation modeling\(^{46}\): 1) the Young’s modulus \(g_B = \frac{m_B}{h}\) (where \(m\) is the repulsive part of the atomic potential \(U = A/xm + B/x\)); 2) the flow stress due to the work necessary to generate the excess volume of deformation-induced dislocations and vacancies against the external hydrostatic pressure \(p\); and 3) the enthalpy of vacancy migration, which is connected to a locally changing volume via continuous mass transfer, by which a certain hydrostatic pressure \(p\) induces extra work when a vacancy migrates through the lattice. This has a strong effect on microstructural evolution: due to the extreme strains, an enormous amount of dislocations is generated, resulting in generation of vacancies\(^{47}\) because of their interaction. At these high deformation levels, nonconservative dislocation motion, that is, dislocation climb, that is governed by vacancy migration, plays an essential role for dislocation annihilation. As a consequence, even at the relatively low deformation, when the hydrostatic pressure is applied, the dislocation density remains high. The enormous high amount of dislocations also has strong influence on the CSD size.

Due to the reduction of the hydrostatic pressure, the enthalpy of vacancy migration recovers to its original value; hence, all defects become mobile again, the vacancies enable the annihilation of dislocations via climb processes, also supported by the high internal stresses due to the extreme lattice distortions. Consequently, the measured dislocation density decreases considerably and also the domain size is influenced and grows. However, the decrease in dislocation density is not continuous: at 7 GPa it is higher than that at 8 GPa; here, no proper explanation can be made; yet, a possible measurement/evaluation inaccuracy is rather likely than a microstructural cause.

In the already mentioned first that investigations on unloading\(^{43-45}\) the hydrostatic pressure release were "simulated" by warming up the HPT-deformed sample, where the microstructure was "frozen in" by lowering the temperature before the hydrostatic pressure was released. This worked as low temperature has a similar impact on the effective migration enthalpy as hydrostatic pressure. These findings could help with the discussion of experimental results reported in several works, for example, see various studies.\(^{48,49}\)

Another issue which is often discussed when conducting HPT deformation to unlimited strains is that there have to be dynamic relaxation/recovery effects; otherwise, the materials must be pulverized due to successive destruction of the crystal lattice. This is intrinsically indicated by the saturation of the in situ flow curve determined by torque measurement during the HPT process (e.g., see Figure 1 in the study by Schafler et al.\(^{44}\)). The evolution of the dislocation density shown in Figure 4 supports that view: the yield-drop behavior of the dislocation density (see Figure 4, at a strain of about 25) may indicate the onset of this dynamic recovery process.

3.1.1. Influence of the Protrusion Part on the Evaluated Values

As the beam transmitted the sample, not only the sample part was deformed in the cavity between the anvils but also the protrusion part was hit—so the measured signal originated from two
different sample states. While the sample part inside the cavity was well defined with respect to shear and initial compression deformation, the protrusion part only underwent compression and any further state cannot be unde ned. Due to the hardening of that thin layer, it is suggested that the protrusion material mainly slid between the anvils that con ned the cavity. A decomposition of the diffracted signal coming from these two sample parts was not possible. An estimation should put this effect into perspective: Under the previous assumption that the protrusion part deformed under compression only, the absolute values of the CSD and dislocation density increase for the sample volume inside the cavity get somewhat higher and lower, respectively. Considering the sample radius, the measurement position (radius), and the protrusion part dimensions, the volume of the protrusion part penetrated by the beam is about 25% of the whole volume that is transmitted. A simple estimation by linear proportionality would increase a CSD value of 22 nm (during deformation at $\gamma_{\text{torsion}}$ from 25 to 140) and 42 nm (after unloading) to 33 nm and 47 nm, respectively. The dislocation density would decrease during deformation from about $5.2 \cdot 10^{15} \text{m}^{-2}$ to $4.1 \cdot 10^{15} \text{m}^{-2}$ (at $\gamma_{\text{torsion}}$ from 50 to 140) and after releasing the hydrostatic pressure the value would change from $2.7 \cdot 10^{15} \text{m}^{-2}$ to $2.4 \cdot 10^{15} \text{m}^{-2}$. The general characteristics of the evolution of the two parameters would not be affected. In addition, the illuminated volume from the protrusion as compared with the sample volume is small, as shown in Figure 2.

3.2. HPT Deformation of NiTi Shape Memory Alloy

Figure 7 shows synchrotron profiles obtained after different states of deformation. The initial alloy (sample 0/0) shows diffraction peaks that almost entirely arise by the monoclinic B19† lattice structure. (Bragg reflections of the B19† martensite for $Q$ ranging between about 2.6 and 3.2 Å$^{-1}$ are indexed.) Minor reflections can be indexed according to the B2 austenite/R-phase. Rietveld re nement methods yield a phase fraction of the B19† martensite exceeding 95%. Its lattice parameters measured by Rietveld re nement are $a = 0.2913 \text{nm}$, $b = 0.4141 \text{nm}$, $c = 0.4689 \text{nm}$, and $\beta = 97.89^\circ$, in good agreement with the literature. It should be noted that one re ection (103)$_{\text{B19}}$ (marked by an asterisk) exceeds the intensity expected, considering its structure factor by about an order of magnitude.

Due to the small sample radius and tiny cross-sectional area of the synchrotron beam, the scattering volume is rather small. Therefore, a “spotty” or textured pattern of Debye–Scherrer rings is observed in the 2D detector images of the initial sample state 0/0, as shown in Figure 8. Marked by arrows, Debye–Scherrer rings of the B19† martensite for $Q$ between 2.6 and 3.2 Å$^{-1}$

Figure 7. Synchrotron profiles of the sample states $p/\gamma_{\text{torsion}}$, where $p$ denotes the applied hydrostatic pressure (in GPa) and $\gamma_{\text{torsion}}$ the torsional shear strain.

Figure 8. 2D detector images of different sample states $p/\gamma_{\text{torsion}}$ ($Q$ ranging from $\approx2.3$ to $6.2 \text{ Å}^{-1}$). Sample states 6/21, 6/39, and 0/135 show rather sharp diffraction rings arising by scattering from the anvils. The contrast of the detector images of sample states 0/0, 6/0, and 6/3 was adapted for better visibility.
of 6 GPa but also significant plastic deformation occurs, especially close to the edge of the sample, where material is allowed to plastically flow in the gap between the anvils.

With the application of load, the fitting results from the refinement show an increase in broadening (see also Figure 9); its magnitude exhibits considerable peak dependence referring again to a textured material (the latter is also visible in the spotty intensity distribution for the sample state 6/0, see Figure 8). The peak broadening is caused by lattice strain due to plastic deformation by compression. The B2/R phase reflection visible in the 2D detector image of the undeformed sample is still present after the application of the maximal uniaxial load (see the dashed arrows of the sample states 0/0 and 6/0 in Figure 8). In addition, a very weak but rather continuous Debye–Scherrer ring shows up with a radius $Q = 2.95 \, \text{Å}^{-1}$ corresponding to $\{110\}_{B2}$. Therefore, for a minor volume fraction, a reverse B19′ martensite to B2 austenite transformation seems to occur already by compression, in agreement with previous results. It was recently reported that in a Ni-rich NiTi alloy with B2 austenite as stable phase at RT; a stress-induced B2 $\Rightarrow$ B19′ $\Rightarrow$ B2′ martensitic transformation can occur under the conditions of large strains/high stresses and elevated temperatures ($B2^T$ denotes twinned austenite). In the present case, the Ti-rich NiTi alloy already contains B19′ martensite in its stress-free state and, by compression in the HPT anvils, a single-step stress-induced reverse transformation occurs even at RT, concomitant with amorphization.

Figure 9 shows that in the range of $Q$ between about 2.6 and 3.3 Å$^{-1}$ with the onset of the torsion (see sample states 6/3, 6/5, and 6/8), the overall diffuse background of the diffracted intensity further increases with torsional strain. Thus, deformation-induced amorphization occurs, concomitant with broadening of the reflections due to grain/crystal refinement, causing neighboring Bragg peaks to overlap. The five characteristic monoclinic reflections seem to gradually merge into a single peak comprising the diffuse halo of the amorphous phase and the superimposed broadened crystalline reflections. A texture is still present for sample states 6/3, 6/8, and 6/13 (see Figure 8). A similar intensity pattern is observed for $Q$ ranging between about 4.5 and 5.5 Å$^{-1}$, where a second weaker corrugated peak forms. An APF of $\approx 60$ and $\approx 70$% is measured for $r_{\text{tension}} = 8$ and 21, respectively. With further straining, the APF seems to increase only slightly, yielding a value of APF of $\approx 80$% for the maximum applied stress at $r_{\text{tension}} = 135$.

Figure 10 shows the synchrotron profile of the samples 6/13, 6/21, 6/39, and 0/135 in more detail; the intensity profile for the initial sample 0/0 is shown as a reference (peaks with large intensity are truncated). In the case of the sample 0/135 (i.e., subjected to maximum strain followed by unloading), the following features are encountered: a first broad peak with a maximum occurring at $Q = (2.94 \pm 0.05) \, \text{Å}^{-1}$ and a weaker and rather shallow second peak at $Q = (5.1 \pm 0.2) \, \text{Å}^{-1}$ that is followed by a shoulder-like peak. A similar diffraction pattern of amorphous NiTi alloys is reported in case of different methods such as TEM, XRD, and XRD by synchrotron radiation. It should be noted that this profile is rather smooth. Contrary to that, in the case of the sample 6/13, weak crystalline reflections corrugate the diffracted intensity profile of the amorphous phase. In addition to the reflections of the B19′ martensite, also, austenite reflections are encountered (see the corresponding arrows in Figure 10); whereas reflections of the B19′ martensite gradually
vanish with increasing strain; still, reflections are observed in the synchrotron profile of the sample 6/39 that can be indexed with respect to the B2 austenite: \(\{110\}_B2, \{002\}_B2, \) and \(\{112\}_B2\) occurring at positions \(Q = (2.93 \pm 0.02), (4.09 \pm 0.04),\) and \((5.15 \pm 0.04) \text{Å}^{-1}\), respectively. Based on these values, a lattice parameter of \(a = (3.03 \pm 0.03) \text{Å}\) is obtained in agreement with the lattice parameter of \((3.0164 \pm 0.0006) \text{Å}\) of bulk undeformed Ni–50.0 at.% Ti.\(^{[50]}\)

While for the sample 0/135 crystalline reflections are not observed in the diffraction profile, at this degree of deformation still, the crystalline phase is retained. Figure 11 shows a TEM bright-field image taken from a NiTi sample subjected to HPT with even a higher degree of deformation \(\gamma_{\text{torsion}} \approx 900\) than that achieved by in situ HPT straining. Nanocrystalline debris embedded in an amorphous matrix is clearly observed. Most of the nanocrystals that frequently form clusters have a size of less than 30 nm.

The observation of the B2 reflections shows that besides amorphization, the martensite is also subjected to a deformation-induced reverse transformation. The significant decrease in grain/crystalline size induced by HPT can strongly shift the phase equilibrium tending to stabilize the austenite.\(^{[20,55,56]}\) Also, the imposed hydrostatic pressure of the HPT can lower the martensite to austenite transformation temperature.\(^{[22,57]}\)

In the case of HPT of a Ni-rich NiTi alloy where a parent B2 to B19’ transformation occurs by the application of pressure during loading, it was argued that in deformation-induced nanograins, the B19’ martensite can revert to the B2 austenite after (or during) release of hydrostatic pressure by unloading, denoted as size baroeffect.\(^{[21]}\) In contrast, in the present case of a Ti-rich NiTi alloy containing stable B19’ martensite in its coarse-grained defect-free state, a size baroeffect is not confirmed. The in situ results clearly show a reverse B19’ to B2 transformation occurring during the ongoing HPT deformation and thus under applied hydrostatic pressure.

Finally, it should be noted that synchrotron profiles can be used to obtain further structural information, for example, by calculating the pair distribution function and changes of the free volume.\(^{[23]}\) Facilitated by the in situ HPT device, this can be used to almost continuously monitor the structural evolution of NiTi as a function of applied strain and load.

4. Summary

The successful implementation of a mini-HPT device favored by the design and instrumentation of the High Energy Materials Science beamline at PETRA III enabled a primal in situ HPT investigation, allowing for quantitative analysis of the enormously plastically strained microstructure. Two different materials were characterized by principally diverse investigations that motivate to further challenge in situ experiments concerning for example, mechanical alloying by SPD, even of immiscible components, deformation-induced phase transformations, or deformation of brittle materials. For these, controlling for possible temperature variation may already be of crucial importance.

4.1. HPT Deformation of Pure Ni

The application of the mini-HPT device enabled the in situ investigation of the microstructural evolution of severely plastically deformed Ni. Very high defect densities already evolve when starting uniaxial loading and increase strongly when torsional straining is added. This is attributed to the strong influence of the applied hydrostatic pressure that reduces the lattice defect mobility considerably, resulting in lowering the potential of defect annihilation. This is supported by the defect density loss upon pressure release and coincides well with previous indirect investigation results. The yield-drop-like behavior of the dislocation density evolution hints at previously suggested dynamic relaxation processes.
4.2. HPT Deformation of NiTi Shape Memory Alloy

Using the specifically designed mini-HPT device, deformation-induced amorphization can be studied in situ as a function of applied load (hydrostatic pressure) and strain. In NiTi, amorphization already starts during uniaxial loading. When additional torsion straining is applied, the volume fraction of the amorphous phase first increases strongly with strain. For values larger than about $\gamma_{\text{HPT}} \approx 20$, only a rather small increase of the amorphous volume fraction with increasing strain is observed. The in situ HPT results show the occurrence of a reverse B19’ to B2 transformation induced by deformation even when the samples are still under pressure.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

amorphizations, in situ X-ray diffraction, martensitic phase transformations, profile analyses, severe plastic deformation

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