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Structural phase stability in nanocrystalline titanium to 161 GPa

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Abstract

Nanocrystalline titanium (nc-Ti) metal was investigated up to 161 GPa at room temperature using a diamond anvil cell. X-ray diffraction and electrical resistance techniques were used to investigate the compressibility and structural phase stability. nc-Ti is observed to undergo three structural phase transitions at high pressures, starting with $\alpha \to \omega$ at 10 GPa and followed by $\omega \to \gamma$ at 127 GPa and $\gamma \to \delta$ at 140 GPa. The observed structural phase transitions, as well as compressibility, are consistent with previously reported values for coarse grained Ti (c-Ti). The high pressure experiments on nc-Ti samples do no show any significant variation of the $\alpha \to \omega$ transition pressure under varying non-hydrostatic conditions. This is in sharp contrast to c-Ti, where a significant decrease in the $\alpha \to \omega$ transition pressure is observed under increasing non-hydrostatic conditions. This would indicate that the decrease in grain size in nano grained titanium makes the $\alpha \to \omega$ phase transition less sensitive to shear stresses as compared to bulk or c-Ti.

Keywords: high pressure, diamond anvil cell, titanium, electrical resistance

1. Introduction

There is great scientific interest in nanocrystalline (nc) materials, in part driven by desire to understand changes in material properties resulting from a decrease in grain or crystallite size. One needs only to browse recent scientific reports to gain a sense of magnitude and research efforts dedicated to understanding and developing nc materials. Generally speaking, a reduction

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. in grain size is expected to increase the mechanical strength of materials, as described by the Hall-Petch relationship [1]. However, when the grain size becomes too small, an inverse Hall–Petch relationship may also occur [2]. Reduction in grain size leads to a larger interface to volume ratio and an increase in the relative number of atoms at the grain boundary. The atoms near the grain boundaries are bonded less regularly and this gives rise to grain boundary energy, which is dependent on the mis-orientation of adjacent grain boundaries. As a result, grain boundaries may be more susceptible to having larger impurity concentrations. In high pressure experiments, both static and dynamic, decreases in grain size may affect stress distributions and deformation mechanisms during compression. This in turn may influence compressibility, structural phase stability, and both kinetics and nucleation/growth of new phases. Recent studies suggest that nc materials may deform by a mechanism not accessible to their coarsegrained counterparts [3], and a number of high pressure experiments have been done in order to gain a better understanding of the effects of grain size on structural phase stability and compressibility of materials when subject to high pressures. Furthermore, high pressure studies performed on nc materials are not only important in understanding the general behavior associated with the decrease in grain size, but are also important in understanding and interpreting other high pressure data obtained on materials which have larger or coarser grains initially.

A majority of static high pressure experiments are carried out using a diamond anvil cell (DAC), where the sample is placed in a gasket chamber and then compressed mechanically by two diamonds, which sit in an opposing anvil geometry [4]. Experiments are either performed under hydrostatic conditions, by surrounding the sample with a fluid or gas pressure media, or non-hydrostatic conditions without a pressure medium. However, even when pressure media are used, hydrostatic conditions are attainable only to a certain pressure before the medium itself solidifies. Non-hydrostatic high pressure studies performed on nc gold powder samples with a starting crystallite size of 30 nm and 120 nm at room temperature and pressure (RTP) showed that, at 60 GPa, the crystallite size was reduced to 9 nm and 49 nm, respectively [5]. In some cases crystallite size may not have a significant effect on the compressibility of materials, as shown by studies performed on nc nickel [6]. However, experiments performed on spinelstructure Si₃Ni₄ nanocrystals, indicated a possible 'critical pressure' size-induced weakening of elastic stiffness in nc Si₃Ni₄ [7]. In [7], it was suggested that nc Si₃Ni₄ has a rather large bulk modulus of 685 GPa up to a 'critical pressure' of 40 GPa, followed by a change in compressibility and reduction in the bulk modulus to 415 GPa above this pressure. The suggested change in compressibility was, however, later attributed to the hydrostatic conditions of the sample rather than an internal property of the nc material studied. By studying nc 3C-SiC using various pressure media, as well as without pressure media, it was concluded that a 'critical pressure' change in compressibility may be brought about by performing studies on nc samples under non-hydrostatic conditions [8]. This study further showed that when the experiment is performed under hydrostatic conditions the compressibility of 30 nm 3C-SiC is comparable to a bulk, coarser sample.

Although the compressibility studies performed on nc samples did not show a significant change as compared to coarse grained materials, studies performed at high pressures have also investigated structural phase stability as a function of grain size. For nc anatase/rutile (TiO₂), it was shown that the rutile phase starts to transform to the ZrO_2 structure at a pressure of 8.7 GPa, which is much lower than the 13 GPa reported for the bulk sample [9]. According to [9] and other studies performed on nc samples, the large surface energy contribution to the total internal

energy will increase the compressibility as the grain size is decreased, while simultaneously causing a reduction in phase transition pressure for materials having a large volume collapse during the phase transition [9, 10].

In this article, we report on measurements performed on nc titanium (nc-Ti) metal samples up to 160 GPa. Ti metal is a part of the group IVa metals along with zirconium (Zr) and hafnium (Hf). Interest in Ti, Zr, and Hf can be attributed to their low weight, high melting temperature, high mechanical strength, and good corrosion resistance. At room pressure and temperature, Ti, Zr, and Hf have a partially filled 3d, 4d, and 5d electron shell, respectively. The relatively narrow d-band is located in the midst of a broad sp-band and under applied pressure, due to uneven shifts in the relative energies of the bands, the number of d-electrons can be increased through $s \rightarrow d$ electron transfer [11, 12]. Increase in d-band concentration is expected to lead to a structural phase transition to a body centered cubic (bcc) crystal structure at high pressures. At RTP, Ti, Zr, and Hf metals crystallize in a hexagonal close packed structure (hcp), referred to as the α phase, and at ≈ 6 GPa, ≈ 7 GPa, and ≈ 38 GPa, respectively, have been observed to undergo a structural phase transition to another hexagonal structure (ω) with three atoms per unit cell [13–16]. The transition pressure is heavily dependant on the concentration of interstitial impurities, which are expected to increase the energy barrier and impede the $\alpha \rightarrow \omega$ structural phase transition [17, 18]. On the other hand, shear stresses resulting from non-hydrostatic conditions reduce the transition pressure [16]. Further compression ultimately leads to a bcc crystal structure in Zr at ≈ 30 GPa [15] and in Hf at ≈ 71 GPa [19]. However, in Ti room temperature compression results in a structural phase transition from ω to an orthorhombic phase (γ) at 116 GPa [20] and then to another orthorhombic phase (δ) at 140 GPa [21]. The appearance of the δ phase, which can be viewed as a distorted bcc structure [21], may suggest Ti's inclination toward a bcc crystal structure. This is further supported by first principle calculations, which suggest that the δ phase may be caused by non-hydrostatic conditions of the experiment, and that the $\omega \to \gamma \to \beta$ is energetically favorable at high pressures [22].

The first part of this work deals with the region below 35 GPa, which concentrates on the $\alpha \rightarrow \omega$ structural phase transition. The second part deals with the high pressure region up to 161 GPa in order to investigate the existence of post- ω structural phase transitions in nc-Ti. Comparison is also made to the values previously reported for coarse grained Ti, referred to as c-Ti in this report.

2. Experiment details

The nc-Ti sample studied in this experiment is of commercial purity and was prepared by equal channel angular pressing followed by cold rolling, which resulted in a grain size of ≈ 200 nm, with some ≈ 100 nm subgrains and dislocation cells [23, 24]. The high-purity, c-Ti sample with chemical composition (in wt%) of 360 ppm O, 60 ppm C, 10 ppm N, 14 ppm H, 4 ppm Al, 3 ppm V, 5 ppm Fe, and balance Ti, was provided by Rusty Gray III from Los Alamos National Laboratory. The experiments described below were performed at beamlines 16ID-B and 16BM-D of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS) of Argonne National Laboratory and beamline B2 of the Cornell High Energy Synchrotron Source (CHESS). For each of them, x-rays in the region from 0.3678 Å to 0.4959 Å were used and the sample to detector distance was calibrated with a CeO₂ standard.

ER and XRD

XRD

nanocrystalline sample, and c is for the coarse grained sample.				
Exp. #	Sample	Highest P reached	Sample loading conditions	Measurement(s)
1	nc	23.3 GPa	Hydro (M:E)	XRD
2	nc	34.5 GPa	Hydro (M:E)	XRD
3	nc	23.8 GPa	Hydro (M:E)	XRD
4	nc	9.9 GPa	Non-hydro	ER and XRD
5	nc	27.7 GPa	Non-hydro	ER and XRD
6	nc	21 GPa	Non-hydro	ER and XRD
7	nc	13 GPa	Non-hydro	ER and XRD
8	с	13.6 GPa	Non-hydro	ER and XRD

Non-hydro

Non-hydro (M:E)

Table 1. Details of experiments performed. In this table, abbreviations used are as follows: XRD is for x-ray diffraction, ER is for electrical resistance, Hydro is for hydrostatic conditions, Non-hydro is for non-hydrostatic conditions, nc is for the nanocrystalline sample, and c is for the coarse grained sample.

2.1. Lower pressure region

9

10

с

nc

Below 35 GPa, two sets of experiments were performed. In the first set of experiments, the sample was investigated at high pressures using a DAC and the angle dispersive x-ray diffraction (ADXD) technique. Experiments were performed up to 23.3 GPa (exp. 1), 34.5 GPa (exp. 2), and 23.8 GPa (exp. 3). Experiments 1, 2, and 3 were performed under hydrostatic conditions using methanol–ethanol (4:1) pressure media and using Cu as a pressure marker. All were loaded in a 90 μ m sample hole drilled in a pre-indented spring steel gasket. A fourth experiment, up to 9.9 GPa (exp. 4), was performed under non-hydrostatic conditions.

7 GPa

161 GPa

For the second set of experiments designer diamond anvils [25] were used in the DAC in order to measure electrical resistance as a function of applied pressure. Three electrical resistance measurements were performed on nc-Ti up to the highest pressure of 27.7 GPa (exps. 5–7). In addition, electrical resistance experiments were performed on a high-purity c-Ti metal up to 13.6 GPa for comparison (exps. 8–9). All high pressure electrical resistance measurements were performed under non-hydrostatic conditions, because the use of pressure media prevents electrical contact between the sample and contact probes. Furthermore, in order to avoid possible interference from Cu, ruby fluorescence was used for determining pressure. All measurements were performed using the four-probe van der Pauw method, in which two-probes are used to supply constant current while the other two are used as voltage pickup probes [25, 26].

2.2. High pressure region

The highest pressure experiment, up to 161 GPa (exp. 10). This experiment was performed using $150 \,\mu\text{m}$ tip beveled diamond anvil and a $50 \,\mu\text{m}$ gasket chamber drilled in a pre-indented spring steel gasket. The sample and Cu pressure marker were compressed under non-hydrostatic conditions. All experiments performed are detailed in table 1.



Figure 1. ADXD spectra showing: (a) α phase at 1.8 GPa, (b) both α and ω phases at 12.4 GPa, (c) ω phase at 23.8 GPa, and (d) ω phase at RTP after pressure release.

3. Results

3.1. Lower pressure region

Prior to performing high pressure experiments, a RTP spectrum of nc-Ti was collected using the ADXD technique. The resulting spectrum indicates that the sample has an hcp crystal structure with lattice parameters $a = 2.949 \pm 0.002$ Å and $c = 4.689 \pm 0.002$ Å (c/a = 1.590) and a volume/atom = 17.658 Å³. Both the volume per atom and the non-ideal c/a ratio are slightly lower compared to what has been previously reported for the α phase of c-Ti [16]. In exps. 1–3, performed under hydrostatic conditions, only the α phase is observed up to 9.3 GPa. When pressure is increased to 10.0 GPa, new peaks belonging to the ω phase were observed and indexed accordingly, as can be seen in figure 1. Both α and ω phases are then observed to coexist between 10.0 GPa and 13 GPa. Above this pressure, and up to the highest pressure of 34.5 GPa, only the ω phase is observed. The $\alpha \rightarrow \omega$ structural phase transition pressure, 10.0 \rightarrow 13.0 GPa, observed for nc-Ti in this study is slightly lower compared to 10.2 \rightarrow 14.7 GPa reported from studies performed on commercial purity c-Ti, which used methanol–ethanol (4 : 1) pressure medium as well [16]. Furthermore, comparison of the volume change at the start of the $\alpha \rightarrow \omega$ transition for the case of c-Ti at 10.2 GPa is $V/V_0 = 0.928$, as calculated by the



Figure 2. Change in volume/atom with increase in pressure for α and ω phases and the third order Birch–Murnaghan EOS fit for α of nc-Ti.

equation of state (EOS) values reported by Errandonea *et al* [16], and in the case of nc-Ti at 10.0 GPa, the volume change appears to agree fairly well with a value $V/V_0 = 0.927$.

Under non-hydrostatic conditions, it has been reported that the shear deformation can induce the $\alpha \rightarrow \omega$ structural phase transition and ultimately decrease the transition pressure down to ≈ 4 GPa in c-Ti [16]. In the case of nc-Ti in exp. 4 we observe only a slight decrease in the transition pressure due to non-hydrostatic conditions. In this experiment, the transition pressure was measured at 9.9 GPa. At this pressure, the volume decrease is lower compared to the hydrostatic case and has a value of $V/V_0 = 0.936$. Overall, the compressibility of the α phase of nc-Ti appears to be slightly greater under hydrostatic conditions when compared to data obtained from non-hydrostatic experiments, as shown by figure 2. As the sample undergoes the $\alpha \rightarrow \omega$ structural phase transition, in both hydrostatic and non-hydrostatic cases, a discontinuous change in volume is observed. The measured volume decrease, $\Delta V/V = 1.8\%$, is consistent with the reported value of 1.9% for c-Ti [16, 20]. Figure 2 shows both the experimental volume change with pressure for both the α and ω phase, as well as the resulting Birch–Murnaghan third order EOS, equation (1), fit for the α phase of nc-Ti [27].

$$P = \frac{3}{2}B_0 \left[x^{7/3} - x^{5/3} \right] \left[1 + \frac{3}{4} \left(B_0' - 4 \right) \left(x^{2/3} - 1 \right) \right].$$
(1)

In equation (1), $x = V_0/V$, where V is the volume per atom and V_0 is the RTP volume per atom, B_0 is the isothermal bulk modulus, and B'_0 is the pressure derivative of B_0 . An EOS fit to P–V data reported for Cu [28, 29] results in $B_0 = 121.60$ GPa and $B'_0 = 5.58$, which was then used for pressure calculations in our experiments. Next, using the measured value $V_0 = 17.658$ Å³ at RTP, as reported earlier, we obtained $B_0 = 106.69$ GPa and $B'_0 = 4.54$ for the α phase. The B_0 value obtained for nc-Ti is comparable to the value reported for c-Ti, while the B'_0 is slightly larger. However, both of these values can be influenced by the initial volume used in the fit. It is also important to compare the overall compression, V/V_0 , which appears to be fairly consistent, as mentioned earlier.

In order to further investigate the possibility that the $\alpha \rightarrow \omega$ structural phase transition under non-hydrostatic conditions is occurring at lower pressures than what we are able to detect



Figure 3. Change in electrical resistance as a function of pressure for nc-Ti and c-Ti. For each of these, all experiments are shown to indicate the transition pressures measured for both the nc and c-Ti. The inset shows the measured values for c-Ti, while the main graph shows results for the three measurements of nc-Ti.

using x-ray diffraction, we have also performed electrical resistance measurements up to 27.7 GPa. As mentioned earlier, electrical resistance measurements were performed on both nc-Ti and c-Ti for comparison. As shown in figure 3, for both nc-Ti and c-Ti a steady decrease in electrical resistance with increasing pressure is observed to a minimum point, followed by a sudden increase. The initial resistance values depend strongly on the initial thickness of the sample, however subsequent changes with increasing pressure would be related to the physical changes in the sample at high pressures. The subsequent increase in electrical resistance with further pressure increase is the result of the $\alpha \rightarrow \omega$ structural phase transition [30, 31]. For c-Ti, we observe $\approx 5\%$ increase between 6.4 GPa and 11.4 GPa, while for nc-Ti an increase of $\approx 40\%$ between 9.7 GPa and 18.3 GPa is observed in exp. 6. Other than the difference in the percent change in the electrical resistance and the pressure at which the minimum is observed, we do not detect any additional difference in the electrical behavior between the two samples studied here, as well as in comparison to previous high pressure electrical resistance measurements performed on c-Ti [30].

The correlation between the $\alpha \rightarrow \omega$ structural change and change in electrical resistance in nc-Ti is further confirmed using simultaneous, time-resoloved electrical resistance and ADXD measurements. Using a gas membrane equipped DAC [32], sample pressure was increased while continuously performing electrical resistance and ADXD measurements. Electrical resistance measurements were recorded *in situ* every 0.02 s and, during pressure increase from 8.9 GPa to 9.5 GPa, an abrupt increase in resistance was observed, shown in figure 4. Simultaneous ADXD spectra ($\approx 1.5 \text{ min/spectra}$, including exposure and image plate readout time) collected over the same pressure range clearly shows that the abrupt change in electrical resistance can be attributed to the $\alpha \rightarrow \omega$ structural phase transition. As shown in figure 5 at 8.9 GPa, nc-Ti is in the α phase and with pressure increase to 9.5 GPa, the ω phase appears. Subsequent spectra collected at constant pressure of 9.5 GPa, and over the same time span as the electrical resistance measurements in figure 4, shows a continuous increase of intensity of $(101/110)_{\omega}$ peak and decrease in intensity of $(100)_{\alpha}$, $(002)_{\alpha}$, and $(101)_{\alpha}$ peaks. For high-purity c-Ti,



Figure 4. Continuous measurement of change in electrical resistance in nc-Ti, during pressure increase from 8.9 GPa to 9.5 GPa. Sudden rise in resistance with pressure increase is attributed to $\alpha \rightarrow \omega$ structural phase transition in nc-Ti at this pressure.



Figure 5. ADXD spectra collected during pressure increase from 8.9 GPa to 9.5 GPa. Initial spectra at 8.9 GPa shows that nc-Ti is in the α structural phase. Subsequent increase to 9.5 GPa results in the $\alpha \rightarrow \omega$ structural phase transition. Five subsequent spectra collected at 9.5 GPa (\approx 1.5 min/spectra, including exposure and image plate readout time) show the evolution of the ω phase, as seen by intensity increase in (101/110) $_{\omega}$ peak and decrease in (100) $_{\alpha}$, (002) $_{\alpha}$, and (101) $_{\alpha}$ peaks.

we observe the minimum in electrical resistance to occur at a lower pressure than what is observed for nc-Ti. The minimum in electrical resistance measured between 5.9 GPa and 6.3 GPa for c-Ti is consistent with the $\alpha \rightarrow \omega$ structural phase transition pressure reported for studies performed on c-Ti under non-hydrostatic conditions [16], as was the case in this experiment. However, for nc-Ti, there appears to be minor difference between the $\alpha \rightarrow \omega$ transition pressure under either hydrostatic or non-hydrostatic conditions, as confirmed in



Figure 6. ADXD spectra of nc-Ti sample and copper pressure standard collected using x-rays with wavelength $\lambda = 0.4959$ Å. Shown are the three high pressure phases of nc-Ti, starting at the bottom with ω phase at 40 GPa, followed by γ at 133 GPa, and δ at 161 GPa shown on the top.



Figure 7. Change in axial ratio (*c/a*) as a function of pressure for ω , γ , and δ phases.

electrical resistance at ≈ 10.6 GPa in exp. 1 and at ≈ 9.7 GPa in exp. 2 under non-hydrostatic conditions.

3.2. High pressure region

In the highest pressure experiment, we observe that the sample undergoes two additional structural phase transitions. Initially, above 10 GPa, the sample is observed in the ω structural phase, shown in figure 6. As previously reported [16, 21], the *c/a* ratio of the ω phase has a steady value of 0.612 initially and, as the pressure is increased above 20 GPa, this value increases to 0.626 and levels off above 80 GPa, displayed in figure 7. Once the pressure was increased from 120 GPa to 127 GPa, we observe the structural phase transition from the ω to the γ phase, in figure 6. All of the new peaks belonging to the γ phase were assigned to the orthorhombic Cmcm space group, with four atoms occupying 4c positions at (0, *y*, 1/4), (0, -*y*, 3/4), (1/2, *y*+1/2, 1/2), and (1/2, 1/2-*y*, 3/4), where *y* was set at 0.11 as proposed by Vohra and



Figure 8. Change in atomic volume for α , ω , γ , and δ phases of nc-Ti. Also shown is the third order Birch–Murnaghan EOS fit for the ω phase (solid line) and γ and δ phases (dashed line).

Spencer [20] and Akahama et al [21]. The observed transition pressure is slightly larger than 118 GPa and 124 GPa reported for c-Ti [20, 21]. Furthermore, we observe a discontinuous volume change of 3.2% at this transition, which is almost double that reported for c-Ti [20, 21]. Further compression leads to a structural phase transition from γ to δ at a pressure of 140 GPa, in figure 6, which agrees very well with the transition pressure reported for c-Ti [21]. The δ phase also belongs to the same orthorhombic Cmcm lattice and the four atoms occupy the same 4c positions as the γ phase while the y parameter of 0.30 gives the best fit to the experimental spectra [21]. figure 7 also shows the axial ratio for the γ and δ structural phases of nc-Ti, which are in a good agreement with the values reported for c-Ti [20, 21]. At the onset of the γ to δ structural phase transition, we do not observe any noticeable discontinuous volume change. On the other hand, for c-Ti, a volume decrease of 1.4% was reported [22]. What should be pointed out is that for the c-Ti the *total* volume change as the sample undergoes the $\omega \to \delta$ structural phase transition is 3.0% at 147 GPa, which is almost equivalent to what we observe during the $\omega \rightarrow \gamma$ structural phase transition in nc-Ti. The overall volume for nc-Ti at the highest pressure of 161 GPa is reduced by 0.533 of the initial volume of 17.658 Å³, as compared to 0.532 for c-Ti at the same pressure and calculated from the EOS reported in [21].

The resulting experimental volume change with pressure up to 161 GPa and the third order Birch–Murnaghan EOS fit are shown in figure 8 for ω , γ , and δ phases. One EOS was determined for both γ and δ phases, since we do not observe a significant volume collapse at the onset of $\gamma \rightarrow \delta$ structural phase transition. Using RTP values of $V_0 = 17.370$ Å³, we obtained $B_0 = 116.23$ GPa and $B'_0 = 3.27$ for the ω phase, which are in close agreement with previously reported values [16, 21]. We also point out that the RTP volume per atom value used for the nc-Ti ω phase EOS fit was determined from the spectra collected after the pressure was completely released, shown in figure 1(d), following the third experiment to 23.8 GPa. Recovery of the metastable ω phase after pressure treatment is consistent with previous reports, which indicate that after the pressure release, samples were either recovered in the ω phase or as a mixture of $\alpha + \omega$ [16, 20]. In our experiment, we recovered the sample in the ω phase only. For the γ and δ phase regions from 127 GPa to 161 GPa, the EOS parameters from the fit were determined to be $V_0 = 16.518$ Å³, $B_0 = 123.23$ GPa, and $B'_0 = 3.26$. These V_0 and B_0 EOS parameters are larger and smaller, respectively, compared to the δ phase c-Ti third order Birch–Murnaghan EOS values [21], which used a set value of $B'_0 = 3.24$ in their fit. For further comparison, if we set $V_0 = 14.20$ Å³ and $B'_0 = 3.24$, as in [22], then we obtain $B_0 = 213.90$ GPa for the γ and δ EOS fit, which is only ≈ 2.7 GPa larger than what was reported for the c-Ti δ phase B_0 value [21].

4. Conclusions

In this study, we show that nc-Ti undergoes three structural phase transitions up to 161 GPa. At 10 GPa, under both hydrostatic and non-hydrostatic conditions, we observe the first structural phase transition from $\alpha \to \omega$. It is also important to note that the methanol-ethanol mixture is known to freeze above 10 GPa. As a result, additional experiments have to be performed using gas pressure media, which can provide hydrostatic conditions to higher pressures. This would give further information on the effects of grain size on the $\alpha \rightarrow \omega$ structural transition under hydrostatic conditions. As the grain size is reduced it is possible that the transition will initiate at grain boundaries rather than in the grain interior. Grain boundaries may also contain a higher concentration of impurities, which further help impede $\alpha - \omega$ transformation and this is consistent with our observation of the shift to higher transition pressure in nc-Ti. With the current measurement, using XRD and electrical resistance probes, we are unable to pinpoint the exact origin of transformation (i.e. grain boundary versus interior), but further dedicated investigation of samples recovered after pressure treatment could provide additional insight. In the highest pressure experiment, we also observe the $\omega \rightarrow \gamma$ structural transition in the pressure region from 120 GPa to 127 GPa and then $\gamma \rightarrow \delta$ at 140 GPa. The observed structural phase transitions, as well as the volume change with increase in pressure, are consistent with reported studies done on c-Ti [20, 21]. However, in the case of nc-Ti, the $\alpha \rightarrow \omega$ transition appears to be less affected by non-hydrostatic sample conditions compared to c-Ti. In c-Ti, shear deformation resulting from non-hydrostatic conditions leads to significant lowering of the structural phase transition pressure from 10 down to 4 GPa [16], while in the case of nc-Ti, we observe $\alpha \to \omega$ to occur at ≈ 10 GPa under both hydrostatic and non-hydrostatic conditions. For nc-Ti, a case may be made that the increase in interface to volume ratio, resulting from reduction in grain size, leads to increased resistance to shear deformation and the stabilization of the α phase to higher pressures. Likewise, there may be a larger concentration of interstitial impurities near the grain boundary in nc-Ti, which would increase in the energy barrier of the $\alpha \rightarrow \omega$ tranformation [17].

At ultrahigh pressures, both nc-Ti and c-Ti will undergo a decrease in grain size, which should equilibriate any grain size effects that may be seen. This is confirmed by the consistency in the observed structural phase transition pressures observed for nc-Ti and c-Ti above 100 GPa. One significant difference is that we observe a larger volume change at the onset of the $\omega \rightarrow \gamma$ transition and no significant volume change is detected during the $\gamma \rightarrow \delta$ transition. However, for c-Ti a discontinuous volume change is observed for both $\omega \rightarrow \gamma$ and $\gamma \rightarrow \delta$ transitions [21]. Further investigation of these two structural phase boundaries needs to be performed since the measured volume change is strongly dependent on how accurate the transition pressure is, or rather how close to the onset of the phase transition the volume is determined, as well as other experimental errors associated with performing high pressure experiments.

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