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In situ quantitative study of plastic strain-induced phase transformations under high pressure: Example for ultra-pure Zr

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First in situ quantitative synchrotron X-ray diffraction (XRD) study of plastic strain-induced phase transformation (PT) has been performed on $\alpha - \omega$ PT in ultra-pure Zr as an example under different compression-shear pathways in rotational diamond anvil cell (RDAC). Radial distributions of pressure in each phase and in the mixture, and concentration of ω -Zr, all averaged over the sample thickness, as well as thickness profile were measured. The yield strength of both phases is estimated to be practically the same, in strong contrast to known estimates. Minimum pressure for the strain-induced $\alpha - \omega$ PT, 1.2 GPa, is smaller by a factor of 4.5 than under hydrostatic loading. Theoretically predicted plastic strain controlled kinetic equation was quantified and verified; it is found to be independent of the loading path. Thus, strain-induced PTs under compression in DAC and torsion in RDAC do not fundamentally differ. Obtained results open new opportunity for quantitative study of strain-induced PTs and reactions with applications to material synthesis and processing, mechanochemistry, and geophysics.

Keywords: Plastic Strain-Induced Phase Transformation in Zr; High Pressure; Strain-controlled Kinetics; Yield Strength of α - and ω -Zr; In Situ X-ray Study

PTs caused by large plastic shear deformations under high pressures play an important role in various processes in different material systems. One of the mechanisms of deep earthquake can be related to the instability due to shear straininduced PT [1]. Friction, wear, and surface processing (polishing, cutting, etc.) are accompanied by large plastic shear and can be optimized by involving shear-induced PTs, e.g., in Si, Ge, and strong ceramics [2]. Also, plastic shear: (a) drastically reduces pressure for various PTs in different material systems [3-9]; (b) leads to formation of new phases which were not produced without shear [3, 4, 9, 10]; (c) substitutes a reversible PTs with irreversible ones [3–5], which allows to use the high-pressure phases at normal pressure in engineering applications. These empirical results show potential in the development of the economic routes for synthesis of new and known high-pressure phases at low pressure.

The basic difference between the plastic strain-induced PTs under high pressure and pressure-induced PTs was formulated in [11, 12]. Pressure- and stress-induced PTs occur mostly by nucleation at the pre-existing defects (e.g., dislocations) below the yield. Strain-induced PTs occur by nucleation at new defects generated during plastic flow. Straininduced PTs require completely different thermodynamic and kinetic treatment and experimental characterization. Theoretical and computational studies of the effect of stress tensor and plastic strain on PTs were performed at the atomic scale [13, 14], at the nano- and at the microscale using phase field approach [15, 16], at microscale by developing PT kinetics [11, 12], and at macroscale by studying behavior of a sample under compression in DAC and compression and torsion in RDAC [9, 17-20]. However, no quantitative experimental characterization of strain-induced PTs for any material and, consequently, no verification of the main hypotheses and results of simulations has been reported hitherto.

Strain-induced PTs under high pressures are usually studied using high-pressure torsion in RDAC [4, 6, 9, 10] or metalic/ceramic Bridgman anvils [3, 4, 7, 8, 21–23]. As simulations show [17–20], stress, strain, and concentration of the high-pressure phase fields are very heterogenous and vary during loading. Though radial distribution of pressure, p, is measured routinely in DAC and RDAC [4, 24], *fields of plastic strain and concentration of high-pressure phase, c, required for finding the kinetic equation, have never been reported.*

High-pressure torsion in metalic/ceramic anvils does not allow in situ studies of heterogeneous fields. Pressure is estimated as force divided by area of the sample, which may differ from the maximum pressure in a sample by factor of 3 and more [19, 20]. Plastic shear is evaluated using simple linear distribution for the torsion problem, which significantly differs from much more precise numerical solutions [20]. That is why PT-kinetics determined with such simplifications for some averaged pressures (e.g., in [22]) is far from being correct.

Here, we report the first in situ quantitative XRD study of strain-induced $\alpha - \omega$ PT in ultrapure strongly plastically predeformed Zr (for which strain hardening is saturated and some critical microstructure is reached) under compression in DAC and shear under fixed force in RDAC. We determine radial distributions (averaged over the sample thickness) of pressure in each phase and in mixture and concentration of ω -Zr using XRD, as well as sample thickness profile variation using X-ray absorbtion. The yield strength of both phases is surprisingly the same, while in [25] ω -Zr was estimated to be 6.6 times stronger than α -Zr. Strain-controlled kinetic equation derived based on nanoscale mechanisms [11, 12], after simplifications and modification, is presented as

$$\frac{dc}{dq} = k(1-c)\frac{p_{\alpha}(q) - p_{\varepsilon}^{d}}{p_{h}^{d} - p_{\varepsilon}^{d}} \quad \text{for} \quad p_{\alpha} > p_{\varepsilon}^{d}.$$
(1)

Here q is the accumulated plastic strain defined by \dot{q} = $(2/3d_p^{ij}d_p^{ij})^{0.5}, d_p^{ij}$ are components of plastic deformation rate, p_{ε}^{d} and p_{b}^{d} are the minimum pressures for the straininduced and pressure-induced $\alpha - \omega$ PT, respectively, k is a parameter, and $p_{\alpha}(q)$ is the pressure in the α phase - accumulated plastic strain loading path, which material particle undergoes. Generally, Eq.(1) includes the term for the reverse PT and the ratio of the yield strengths of phases [11, 12]. Since we obtained that strain-induced reverse $\omega - \alpha$ PT in Zr does not occur and yield strengths of phases are the same, general kinetic equation was simplified to Eq.(1). Another simplification is in the choice of linear functions in terms of c and p_{α} . Also, we changed pressure in mixture p to p_{α} in Eq.(1) because PT occurs in α -Zr and we do not need to assume the same pressure in both phases as in [11, 12], because we can measure them.

Eq.(1) is calibrated and verified at the sample symmetry axis, where accumulated plastic strain q can be easily evaluated based on the initial and current sample thicknesses. Independence of the main parameter in Eq.(1), $p_{\varepsilon}^d = 1.2$ GPa, of the pressure - strain state path is proven, because p_{ε}^d was the same at the center (without shears) and at periphery (with large plastic shears). This demonstrates that the straininduced PTs under compression in DAC and torsion in RDAC do not fundamentally differ in terms of kinetics, and, consequently, physical mechanisms, and modeling. Thus, it is not just plastic shear but any plastic deformation reduces PT pressure by the same amount in comparison with hydrostatic loading, and the difference between processes in DAC and RDAC are in the loading path only. Pressure p_{ε}^d is smaller by a factor of 4.5 than the PT pressure under hydrostatic loading p_h^d .

For annealed Zr, strain-induced $\alpha - \omega$ PT in RDAC has been observed at 2.3 GPa at the center of a sample (where plastic strain is small and critical microstructure is not reached) and at 1.2 GPa at the periphery (where large plastic strain produces critical microstructure before PT), the same as at the center of pre-deformed Zr. The difference between minimum PT pressure for annealed Zr under compression at the center and shear at the periphery is not because plastic shear reduces PT pressure in comparison with compression (which was a traditional interpretation [3, 4, 7, 8]), but because at the periphery large plastic strain produces critical microstructure before pressure reaches $p_{\varepsilon}^d = 1.2$ GPa and at the center it does not.

Material. Zr and its alloys have applications in the aerospace, nuclear, and biomedical industries due to their mechanical strength, stiffness, resistance to degradation and corrosion, and light weight. PTs in Zr are studied in numerous papers to understand basic features of PT in solids in general and more specifically in the group IV transition metals. We do not know any in situ XRD studies of strain-induced PT in Zr and any studies of strain-induced PT in ultrapure Zr. Note that in

all known studies of commercially pure Zr (99.98% trace metals basis), Zr contained 45000 ppm of hafnium, which is very difficult to remove. Our Zr sample, purchased from Ames Laboratory, is ultrapure as it contains <55 ppm of Hf, similar to Zr in [25, 26]. Samples were plastically pre-deformed through cold rolling from initial thickness of 1.25 mm down to 140 μ m or 90 μ m. After such large plastic straining strain hardening is saturated and the yield strength does not change, i.e., some critical microstructure is reached [3, 27]. To study the effect of initial state, one sample was subsequently annealed at 650°C for 2 hours. Several compression and shear experiments (runs) were performed, both using steel gasket and without gasket. Experiments details and experimental runs are described in supplemental material [28].

Under hydrostatic loading, $\alpha - \omega$ PT started at pressure $p_h^d = 5.4$ GPa and finished at 6.6 GPa. The third order Birch-Murnaghan equation of state fitting on pressure-volume data for α and ω phases provides: initial volume $V_0 = 23.272(2)$ \mathring{A}^3 and 22.870(8) \mathring{A}^3 (per formula unit); initial bulk modulus $K_0 = 92.2$ GPa and 102.4 GPa, and pressure derivative K' =3.43 and 2.93, respectively. The $\omega - \beta$ PT started at 34.6 GPa and finished at 35.5 GPa. Reverse $\beta - \omega$ PT started at 34.2 GPa and finished at 32.9 GPa; ω -Zr retained at ambient pressure on complete pressure release. All results for hydrostatic loading are very close to those for commercially pure Zr [7, 23, 29].



FIG. 1. Radial distribution of pressure in α and ω phases of Zr and volume fraction of ω -Zr phase in experimental run $\sharp 1$. Inset shows axial force and rotation angle of an anvil φ .

Strain-induced PT. For plastically pre-deformed sample without gasket, the radial distribution of pressure in α and ω phases, pressure in mixture, and volume fraction of ω phase,

averaged over the sample thickness for different compression/torsion stages are shown in Fig. 1. Pressure in ω -Zr is slightly lower than in α -Zr because of volume reduction. This difference reduces with increasing radius, because plastic strain increases with radius and relaxes internal stresses between phases. Pressure distribution in mixture does not exhibit any visible signature of PT, like plateaus or change in slope [4, 17, 19, 20]. It is practically linear in the major part of a sample, like in simulations without PT or with PT and equal yield strength of phases [17]. The yield strength σ_{y} determined based on simplified equilibrium equation combined with plastic friction and von Mises plasticity criterion $dp/dr = -(2/\sqrt{3\sigma_u/h})$ is ~0.4 GPa for both phases. This result is very different from 0.18 GPa for α -Zr and 1.18 GPa for ω -Zr for ultrapure Zr [25] determined based on x-ray peak broadening. Our results on peak broadening at the center of the sample are very close to those in [25], i.e., based on peak broadening we would have similar yield strengths of ω and α -Zr as in [25]. Consequently, the difference between current results and those in [25] are not due to different material composition, type of loading (unconstrained plastic flow with large pressure gradient here and constrained compression with small pressure gradient in [25]), and saturated strain hardening here and unspecified initial state in [25]. Thus, evaluation of the yield strength based on peak broadening contains significant error in comparison with the much-better-justified method based on pressure gradient. For commercially pure Zr, ω -Zr has about two times larger hardness than α -Zr [8, 22], which means that Hf produces larger solute strengthening in ω -Zr than in α -Zr.

The minimum pressure for the strain-induced $\alpha - \omega$ PT, $p_{\epsilon}^{d} = 1.2$ GPa, was the same using two methods: minimum pressure at the center of a sample during compression at which ω -Zr was first detected, and based on pressure at the largest radius where ω -Zr was observed, after different compression/torsion loadings. Thus, plastic straining reduced the minimum PT pressure by a factor of 4.5 in comparison with hydrostatic loading. Both with torsion and without torsion, at the center of a sample there are no shears and straining is on average uniaxial compression, but at the periphery there are large plastic shears and multiple complex compression/shear paths. The same minimum pressure p_{ε}^{d} means that at least initiation of strain-induced PTs, and consequently, corresponding physics and mechanisms are *independent of plastic stain* state and its path, which are very complex both in DAC and RDAC [17-20]. This also means that there is no advantage in the shear mode of plastic straining, any plastic straining path produces the same effect. Consequently, PT processes under compression in DAC without hydrostatic medium and torsion in RDAC should be treated in the same way. This was postulated in [11, 12], utilized in kinetic Eq.(1), and used in all simulations of the processes in DAC and RDAC [17-20], without any experimental confirmation. However, in most experiments [3, 4, 7–9], it was claimed that plastic shear reduces PT pressure in comparison with uniaxial compression, while this statement was not supported by precise in situ measurements.

Torsion of transformed ω -Zr was produced during reduction of load and consequently pressure. However, at pressure as low as 0.2 GPa at the periphery and rotation of 180° reverse PT was not observed. This is different from commercially pure Zr, for which pressure for reverse strain-induced PT was the same as for direct PT in the range of 2-2.5 GPa [4, 21]. Consequently, Hf destabilizes ω -Zr at low pressure against strain-induced PT to α -Zr.

Due to pressure gradient and existence of the minimum PT pressure p_{ε}^{d} , PT starts during compression at the center, and then propagates during further compression and torsion toward periphery. Similar, PT completes first at the center and single phase ω -Zr region spreads toward edge of the culet. Note that for commercially pure Zr $\alpha - \omega$ PT does not complete even at averaged pressure of 6 GPa and 10 anvil turns [22].

Due to impossibility to measure strongly heterogeneous fields of plastic strain in the entire sample and its large indeterminacy, we suggested to limit data for determination of the kinetic equation to the X-ray spot focused at the sample center. At the symmetry axis, shear strains are zero. During compression and torsion (note that thickness h reduces during torsion as well), each point at the symmetry axis undergoes uniaxial compression in the axial direction and radial expansion determined from the condition of plastic incompressibility, i.e., like in the test on uniaxial compression. Since pressure and volume fraction of ω -Zr are averaged over sample thickness, plastic strain should be averaged as well. For uniaxial compression $q = ln(h/h_0)$ and we assume this equation for averaged accumulated plastic strain over the thickness and small region within X-ray spot. Then c, p_{α} , and q in Eq.(1) are determined and we can check this equation. We neglect small reduction of q due to elastic and transformational strain and small increase due to local transformation-induced plasticity.

All experimental points obtained in three compression and compression/torsion loadings (runs) produce three different $p_{\alpha} - q$ paths shown in Fig. 2(a). They were approximated by splines and substituted in the integrated Eq.(1)

$$c = 1 - \exp\left[-\frac{k}{p_h^d - p_\varepsilon^d} \int_{q_0}^q (p_\alpha(q) - p_\varepsilon^d) dq\right], \quad (2)$$

where q_0 corresponds to $p_\alpha = p_\varepsilon^d$, i. e., to initiation of PT. Experimental points for all three paths in coordinates $c - \int_{q_0}^q (p_\alpha(q) - p_\varepsilon^d) dq$ are presented in Fig. 2. They are close to the analytical Eq.(2) with k = 26.5 determined from the best fit. Thus, kinetic Eq.(1) derived based on nanoscale mechanisms in [11, 12] received first experimental confirmation for quite complex loading paths.

For annealed Zr, $p_{\varepsilon}^{d} = 2.3$ GPa at the center during compression, but away from center, after much larger compression-shear plastic straining, minimum pressure at which ω -Zr is observed is the same $p_{\varepsilon}^{d} = 1.2$ GPa as in the center of pre-deformed Zr. Traditional interpretation of these



FIG. 2. Pressure in α -Zr p_{α} - accumulated plastic strain q loading paths for three experimental runs described in [28] (a) and kinetics of plastic-strain induced $\alpha - \omega$ PT in Zr. Line in (b) corresponds to Eq.(2) with k = 26.5.

results would be that plastic shear reduces PT pressure in comparison with plastic compression. However, since it is not true for heavily preliminary deformed Zr, we suggest different interpretation. Minimum pressure p_{ε}^{d} depends on the initial microstructure (grain size, dislocation density) and sufficient obstacles to produce strong stress concentrators, e.g., at dislocation pileups [11, 12, 15, 16]. After some critical preliminary plastic strain, the yield strength reaches its maximum value and does not change anymore [3, 27] and critical microstructure is achieved, after which p_{ϵ}^{d} does not change after further plastic straining. During compression of annealed Zr, pressure at the center exceeds 1.2 GPa before plastic strain reaches critical microstructure and PT starts at 2.3 GPa, which is the p_{ε}^{d} for the achieved plastic straining. Eq.(1) should be generalized for pre-critical initial states by using $p_h^d(q)$ and $p_{\varepsilon}^d(q)$, where q is evaluated from the annealed state, which will be done in the future work.

Note that transformation to β -Zr for annealed sample within steel gasket was not observed even at maximum pressure of 13 GPa and total rotation of 200°. This is consistent with atomistic simulations [30], in which Zr has imaginary phonon frequencies and is dynamically unstable below 25 GPa. This is very different from results for commercially pure Zr, where a mixture of $\omega + \beta$ phases was reported after compression at 1 GPa in [8], and at 0.5 GPa after 5 anvil turns in [23]. While due to strong stress heterogeneities these numbers should be multiplied by a factor of 3 to 5 [19, 20], still Hf strongly promotes strain-induced PT to β -Zr while practically does not affect pressure-induced PT.

In summary, the first in situ quantitative characterization of plastic strain-induced $\alpha - \omega$ PT in ultrapure Zr under high pressure in RDAC is performed utilizing synchrotron XRD. The radial distributions of pressure in each phase and in mixture and concentration of ω -Zr were determined. Kinetic Eq.(1) is calibrated and verified for the first time, using measurements at the sample symmetry axis, where accumulated plastic strain q can be easily evaluated. The minimum pressure for the strain-induced $\alpha - \omega$ PT, $p_{\epsilon}^{d} = 1.2$ GPa, is independent of the p - q path. Consequently, the strain-induced PTs under compression in DAC and shear in RDAC do not fundamentally differ in terms of kinetics, and, consequently, physical mechanisms, and modeling. In contrast to traditional wisdom, it is not plastic shear only but any plastic straining produces the same effect and PT kinetics. One cannot claim that plastic shear in RDAC reduces PT pressure in comparison with uniaxial compression in DAC. Plastic straining reduces PT pressure in comparison with hydrostatic loading, by a factor of 4.5 for $\alpha - \omega$ PT in ultrapure Zr. The difference between processes in DAC and RDAC are in the p - q path only. The great advantage of RDAC is that under the proper design of an experiment [18], it allows one to run PT to completion at pressure as low as p_{ε}^{d} by increasing shear. At the same time, the increase in plastic strain during compression in DAC leads to significant increase in pressure, even while it is not necessary for PT. The yield strength of α and ω phases is surprisingly the same, while in [25] ω -Zr was estimated to be 6.6 times stronger than α -Zr based on XRD peak broadening, which demonstrates the inapplicability of that method. Comparing our results for ultrapure Zr and commercially pure Zr, we may conclude that impurities, mostly Hf, weakly affect pressure-induced PTs between α , ω , and β phases. However, for strain-induced PTs: (a) Hf allows one to obtain β -Zr at averaged pressure of 0.5 GPa (which with our correction leads to p_{ε}^{d} between 1.5 and 3 GPa [19, 20]) and keep β -Zr down to zero pressure [7, 8, 23]; for ultrapure Zr β phase does not appear even at 13 GPa and rotation of 200°. (b) Hf promotes reverse $\omega - \alpha$ PT [4, 21] which we could not obtain for ultrapure Zr here even at 0.2 GPa and rotation of 180° . (c) For $\alpha - \omega$ PT, $p_{\varepsilon}^{d} = 1.2$ GPa here for ultrapure Zr and 0.75 GPa (with our correcting factor 3) for commercially pure Zr [8]. In annealed Zr, $p_c^d = 2.3$ at the center of a sample (where

In annealed Zr, $p_{\varepsilon}^{a} = 2.3$ at the center of a sample (where plastic strain is small and critical microstructure is not reached before PT) and $p_{\varepsilon}^{d} = 1.2$ GPa at the periphery (where large plastic strain produces critical microstructure before PT), as at the center of pre-deformed Zr. The difference between these two numbers is not due to traditional interpretation [3, 4, 7, 8] that plastic shear reduces PT pressure in comparison with compression, but because at the periphery large plastic strain produces critical microstructure before pressure reaches $p_{\varepsilon}^{d} = 1.2$ GPa and at the center it does not. Eq.(1) should be generalized for pre-critical initial states by using $p_{h}^{d}(q)$ and $p_{\varepsilon}^{d}(q)$, where q is evaluated from the annealed state, which will be done in the future work.

The obtained results allow one to transform popular quali-

tative discussions in literature about the effect of plastic shear on PTs into a new quantitative field of research with applications to material synthesis and processing, mechanochemistry, and geophysics. Current experiments can be combined with our simulations [19, 20] in order to obtain more advanced and precise theoretical and numerical description, extract all material parameters for more advanced models, and then find all fields in the entire sample, even those that cannot be measured (e.g., plastic strain tensor), as it was done for deformation without PT in [31]. Recent advances in measurements of all components of the stress tensor in diamond at the boundary with the sample [32] may significantly improve our boundary conditions, in particular for friction. The results also may lead to scientific fundamentals for creating new, more economical deformation processes for discovering and stabilizing high-pressure phases with novel properties, at much lower pressure.

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Supplemental Material

In situ quantitative study of plastic strain-induced phase transformations under high pressure: Example for ultra-pure Zr

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1 Phase transformations in Zr

Under quasi-hydrostatic loading Zr undergoes the hcp $(\alpha) \rightarrow$ simple hexagonal (ω) PT in the broad pressure range of 2-7 GPa (i.e., with large scatter from different references) and $\omega \rightarrow$ bcc (β) reversible PT at 30-35 GPa [1–3]. After high-pressure torsion, a mixture of $\omega + \beta$ phases was reported at 3-6 GPa in [2], at 1 GPa (even before torsion) in [4], and at 0.5 GPa (after 5 anvil turns) in [3]. The lowest pressure for $\alpha - \omega$ PT was 0.25 GPa after 5 anvil turns [3]. No other papers reported ω - and β -Zr at such low pressures. In particular, ω -Zr under torsion was obtained at 2-2.5 GPa in [5,6] and 6 GPa in [7]. We do not know any in situ XRD studies of strain-induced PT in Zr. We are also unaware of any studies of strain-induced PT in ultrapure Zr.

2 Sample preparation

Ultrapure Zr samples with Hf content < 55 ppm was obtained from Ames laboratory, Ames, IA. Impurity concentrations in Zr sample are given in Table S1. The sample was cold rolled from initial thickness of 1.25 mm down to ~130 to 140 μm and 90 μm for unconstrained and constrained compression experiments, respectively. This was to achieve saturated strain hardening through large plastic straining. For unconstrained compression experiments, 3 mm sample disks were punch cut from thinned Zr foil and were used as gasket. For constrained compression experiments, ~ 300 μm disks were cut using laser micro-machining facility [8] at HPCAT laboratory at APS and loaded in a nearly same size hole drilled in steel gasket pre-indented to the same thickness.

Annealed Zr samples were prepared by annealing Zr under inert Ar environment at $650^{\circ}C$ for 2 hours and subsequently cooling to ambient temperature at a rate of $100^{\circ}C$ per hour.

Element	Impurity in PPM	Element	Impurity in PPM	Element	Impurity in PPM
Al	<20	В	< 0.25	С	32
Cd	< 0.25	Co	<10	Cr	$<\!50$
Cu	<25	Fe	< 50	Н	<16
Hf	<55	Mn	$<\!\!25$	Mo	<10
Ν	<20	Nb	<50	Ni	$<\!\!35$
Ο	70	Р	<3	Pb	<25
Si	<10	Sn	$<\!\!35$	Ta	<100
Ti	$<\!\!25$	U	<1	V	$<\!\!25$
W	<30				

Table S1: Chemical analysis of Zr sample

3 Experimental details

For unconstrained and constrained non-hydrostatic experiments, a Zr sample, with or without a steel gasket were loaded in rotational diamond anvil cell (RDAC). RDAC is similar to conventional piston-cylinder diamond anvil cell (DAC), but with additional degree of freedom of relative rotation of diamond anvils with respect to each other (see Fig. S1).



Figure S1: Schematics of RDAC and its motorized mechanism. Sample is first compressed, like in traditional DAC, and a large shear is then induced by rotating one of the anvils.

Our RDAC has a motorized mechanism to mechanically apply load and/or torque at fixed load using a single stepper motor (see Fig. S1). A servo-motor has been used to switch between load or shear mode by engaging the stepper motor to either compression or torsion mechanisms. The controller unit attached to the RDAC can be connected to a PC through USB port and can be remotely operated. For hydrostatic high pressure experiments, small Zr chips of size $20\mu m$, obtained through diamond filing Zr sheet, were loaded in symmetric type DAC with He as a pressure transmitting medium and ruby balls as a pressure marker.

Several experimental runs, prescribing different complex compression/torsion paths to plastically pre-deformed and annealed Zr samples, were performed as described in section 6. In situ x-ray diffraction (XRD) experiments were performed at 16-BM-D and 16-ID-B beamlines at HPCAT sector at Advanced Photon Source employing monochromatic x-rays of wavelength 0.3108 Å and 0.4056 Å respectively. At each load - rotation angle condition, the sample was radially scanned over the entire culet diameter (500 μm) in steps of 10 μm and 2D diffraction images were recorded at Perkin Elmer flat panel detector at 16-BM-D beamline and by the PILATUS 1MF detector at 16-ID-B beamline.



Figure S2: Contour plots of XRD patterns across scanning position at various loads (a)150 N;(b) 200 N;(c) 220 N;(d)240 N;(e)260 N;(f)280 N;(g) 300 N;(h) 350 N;(i) 500 N;

2D diffraction images were converted to a 1D diffraction pattern using FIT2D software [9, 10] and subsequently analyzed through Rietveld refinement [11, 12] using GSAS II [13] software for obtaining lattice parameters, phase fractions and texture parameters of both α and ω phases of Zr. Fig. S2 shows some representative contour plots of XRD patterns across scan position at various loads in one of the unconstrained compression runs. Diffraction peaks of ω -Zr first emerge at the center of culet, as can be clearly seen in Fig. S2, and then spread across culet diameter. The systematic shift of α and ω -Zr diffraction peaks across

the culet is indicative of heterogeneous pressure distribution.

Pressures in each phase at each scanning position was determined using third order Birch-Murnaghan equation of state of α and ω phases of Zr obtained from hydrostatic experiment (see Table S2). Total pressure at each scanning position was estimated based on mixture theory.

Table S2: Parameters in the third order Birch-Murnaghan equation of state of Zr phases obtained from hydrostatic experiments

Zr phase	V_{\circ} (per formula unit)	Ko	K'_{\circ}
α -Zr	23.272(2) Å ³	92.2 GPa	3.43
$\omega\text{-}\mathrm{Zr}$	$22.870(8) \text{ Å}^3$	$102.4 \mathrm{GPa}$	2.93

4 Texture analysis

As the sample was highly textured due to substantial preliminary plastic deformation, the Rietveld refinement was performed with refinement of Marsh Dollase ratio (r) [14, 15], for (001) plane for each phase, in order to obtain correct phase fraction. Fig. S3 shows the refined r values for both α and ω - Zr. Initially α -Zr is highly textured along c axis parallel



Figure S3: Surface plot of Marsh Dollase ratio r for (001) plane of both α and ω -Zr across the culet diameter and at various loads

to the load axis and uniform across the culet diameter. At higher loads the r slightly reduces at the edges of culet. This is due to rotation of Zr grains while they move around the anvil edges due to plastic deformation of Zr. For ω -Zr, the *r* parameter implies texturing of *c* axis away from load direction, which is consistent with earlier reported orientation relationship between α and ω -Zr phases after transition under high pressure [16].

5 Thickness estimation

For sample thickness estimation, 2D/1D x-ray absorption scans were recorded. X-ray absorption was estimated using the current measured at the reference ionization chamber, (I_{\circ}) (before sample), and at photo diode at beam stop, (I) (after sample). These current values were corrected for absorption in diamond anvils.



Figure S4: Thickness profile of Zr sample at various loads estimated using absorption law

Subsequently, thickness at each scanning position was estimated using the absorption law equation, $I/I_{\circ} = exp(-\mu\rho x)$, like in [17]. Here I, I_{\circ}, μ, ρ and x represent the X-ray intensity after the sample, incident X-ray intensity before the sample, mass attenuation coefficient, density, and thickness of the sample. For correct thickness estimation at each scanning position, density was calculated using lattice parameters of Zr at each position. Fig. S4 shows thickness profile of sample across culet at a few representative loads.

6 Experimental runs

Three experimental runs, designated as run \sharp 1, 2, and 3, were performed on plastically pre-deformed Zr sample in RDAC, prescribing different complex compression/torsion paths. One similar compression/torsion RDAC experiment was performed on annealed sample to study the effect of initial micro-structure. In addition to this, one constrained compression run was performed on an annealed Zr sample with a steel gasket. As mentioned above, at each load/rotation angle state, sample was radially scanned over the entire culet diameter (500 μ m) in steps of 10 μ m and XRD images were recorded at each scanning point. In runs \sharp 1 to \sharp 3, 3 mm disk of ~ 140 μ m thick plastically pre-deformed Zr sample was loaded in RDAC.

In run $\sharp 1$, the sample was subjected to the axial loads of 100N, 150N, 220N, 300N, 350N, and subsequently to the rotation of 20° and 40° at the fixed load of 350N. After this, the load was released to 100N and subsequently 50N and rotation of 180° was performed before complete release to check the reverse $\omega \to \alpha$ transition.

In run $\sharp 2$, the sample was subjected to the axial loads of 160N, 190N, 220N, and subsequently to the rotation of 10°, 20°, 30°, and 40° at the fixed load of 220N.

In run $\sharp 3$, sample was loaded along with gold powder, with particle size 1 to 5 μm , sprinkled over sample. The sample was subjected to axial loads of 100*N*, 150*N*, 180*N*, 190*N*, 210*N*, 230*N*, 250*N*, 270*N*, 300*N*, 320*N*, 350*N*, 370*N*, 400*N*, 430*N*, 450*N*, 500*N*, 550*N* and 600*N*. Presence of relatively soft gold particles reduced friction at sample-anvil contact surface in this run. This led to different p-q loading paths in runs $\sharp 3$ and $\sharp 1$, despite prescribing nearly similar axial loads, as can be seen in Fig. 2 of the main text.

For compression/torsion run on the annealed sample, a ~ $90\mu m$ thick 3 mm disk of annealed Zr sample was loaded in RDAC. The sample was subjected to loads of 150N, 180N, 220N, 250N, 280N, and then rotation up to 80° in steps of 10°. Subsequently, load was released in steps of 200N, 150N, 100N, 50N, and then completely released.

In the constrained compression/torsion run, a ~295 μm diameter disk of annealed Zr sample with thickness ~ 90 μm was loaded in ~ 300 μm hole, drilled in steel gasket preindented from 250 μm to ~ 90 μm . The sample was subjected to loads of 100N, 200N, 250N, 300N, 350N, 410N, 500N, 550N, 610N, 700N, and subsequently rotation of 10°, 20°, 40°, 100°. After this treatment, the sample was completely transformed to ω phase. The sample was subsequently subjected to further higher loads of 800N, 960N, 1060N, 1150N, and 1250N.

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