Significance of mechanical twinning in hexagonal metals at high pressure

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Abstract

Diamond anvil cells (DAC) in radial synchrotron X-ray diffraction geometry were used to investigate texture development and identify deformation mechanisms in zinc and osmium at the Advanced Photon Source (APS) and the Advanced Light Source (ALS), respectively. Further experiments on cadmium and hafnium wires were carried out in the Deformation-DIA (D-DIA) multi-anvil press at APS to study the simultaneous effects of pressure, temperature and strain. At room temperature and increasing pressure the c-axis aligns near the compression direction in all hexagonal metals, but with considerable differences. Texture in zinc evolves gradually between 10 and 15 GPa and strengthens as pressure is increased to 25 GPa. In osmium, texture development starts very early (4 GPa). At ambient temperature cadmium and hafnium develop a similar textures as zinc and osmium, respectively. Texture in cadmium evolves gradually with axial shortening to 34%, whereas in hafnium texturing develops immediately after small strains. When hafnium is simultaneously heated to 700 K and deformed in compression, a texture develops with compression axes near (\(2\overline{1}10\)). Simulations from a visco-plastic self-consistent (VPSC) polycrystal plasticity model suggest that the gradual texture evolution observed in zinc and cadmium is controlled primarily by \(f_{0001}\) basal slip and later accompanied by \(f_{10\overline{1}2}\) tensile twinning when the \(c/a\) ratio is below \(\sqrt{3} \approx 1.732\). Conversely, early texture development in osmium and hafnium at room temperature is contributed mainly by \(f_{10\overline{1}2}\) tensile twinning. However, the \((2\overline{1}10)\) texture in hafnium at high temperature is attributed to basal and prismatic slip.

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1. Introduction

Relatively little is known about texture evolution of hexagonal close-packed (hcp) metals at high pressure. Texture development of hcp iron (\(\varepsilon\)-Fe) [1–3] and cobalt [4] has been studied at high pressure with diamond anvil cells (DAC). In general, hexagonal metals have been divided into two categories according to the \(c/a\) ratio: those with high \(c/a\) axial ratios (e.g. Zn, Cd) and those with low \(c/a\) ratios (e.g. Hf, Os). Here we add data for Zn, Cd, Hf and Os. Zn is considered to be weak and generally brittle [5]. On the other hand, Os is a dense and hard metal belonging to the platinum group, with very low compressibility [6] and a high bulk modulus (395–435 GPa [7–9]), second only to diamond. A recent report also suggests strong elastic anisotropy in Os at high pressure [10]. Interestingly, the \(c/a\) ratio of Zn shows an “anomalous effect” and decreases substantially with pressure [11,12].

We use the DAC in radial diffraction geometry to impose both hydrostatic pressure and deviatoric stresses on polycrystalline samples. This has become an important
method for \textit{in situ} rheological studies investigating deformation of materials under pressure conditions relevant to the deep Earth \cite{13}. It is generally believed that the solid inner core of the Earth is likely to be composed of hcp iron \cite{3,14–16}. The seismic anisotropy in the Earth’s inner core \cite{17} may be due to crystal alignment during deformation \cite{15,18,19}. In fact, hcp iron develops a strong crystallographic preferred orientation with the \textit{c}-axis parallel to the compression direction of the DAC \cite{1–3}. This has raised our interest in studying deformation mechanisms of other hcp metals at high pressure.

Texture development in polycrystals depends on the active deformation mechanisms. Much research has been devoted to model deformation of hexagonal metals using polycrystal plasticity theory. A visco-plastic self-consistent (VPSC) \cite{20} polycrystal model has been particularly useful, further developed by Molinari et al. \cite{21} and later refined by Lebensohn and Tomé \cite{22}. Comparing experimental texture patterns with VPSC simulations provides an insight into which slip and twinning mechanisms are consistent with the observed texture for a given deformation mode.

Studies of hexagonal metals have confirmed that mechanical twinning plays a major role \cite{23–26} in deformation and in texture evolution. By having different hcp metals tested at high pressure in DAC and Deformation-DIA (D-DIA) experiments, we aim to investigate the significance of twinning as a deformation mechanism by directly observing the \textit{in situ} elastic and plastic behaviors of Zn, Cd, Hf and Os.

2. Experimental techniques

2.1. The diamond anvil cell (DAC)

In DAC experiments with radial diffraction geometry, the monochromatic X-ray beam penetrates an X-ray transparent gasket material and the sample orthogonal to the compression axis (Fig. 1a). Without inserting a pressure medium, diamond anvils impose a differential compressive stress in addition to hydrostatic pressure. The polycrystalline sample will deform ductily, activating intracrystalline deformation mechanisms, and thus lead to texture development.

The synchrotron X-ray diffraction experiment on Zn using the DAC was performed in the high pressure beamline 16-ID-B (HPCAT) of the Advanced Photon Source (APS) at Argonne National Laboratory. The modified Mao-Bell type DAC with large openings on two sides \cite{27} was set up in radial diffraction geometry and loaded in a holding frame for remote pressure control through a membrane of helium gas. The sample of Alfa Aesar Zn powder of 99.9%+ purity with spherical grains of <10 \(\mu\)m was packed into a kapton/boron–epoxy gasket \cite{28} in an 80 \(\mu\)m sample chamber. A small Pt flake (Alfa Aesar foil, 10 \(\mu\)m diameter, \sim 5 \(\mu\)m thickness) was imbedded in the Zn as an internal pressure standard to estimate pressure during the experiment using the equation of state of Pt \cite{29}. A monochromatic X-ray with a wavelength of 0.39853 Å, and 10 \(\times\) 10 \(\mu\)m in size, was collimated on the sample perpendicular to the loading axis to collect diffraction patterns for 300 s. Diffraction images were recorded in the \(2\theta\) range 0–31.5° with a Mar345 image plate detector, positioned about 348 mm from the sample.

An analogous experiment on Os was conducted at beamline 12.2.2 of the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. Os grains (Alfa Aesar Os 99.9%, <10 \(\mu\)m in size) and a small flake of Pt were loaded in the same gasket type and assembled in the same modified Mao-Bell DAC cell. Monochromatic X-rays with a wavelength 0.49594 Å were used and focused to 20 \(\times\) 20 \(\mu\)m to collect data in the \(2\theta\) range 0–38° for 300 s with a Mar345 image plate detector, 287 mm away from the sample.

2.2. The D-DIA multi-anvil press

Another set of experiments was performed with the D-DIA multi-anvil press. The D-DIA consists of three pairs of anvils, one pair of which can be controlled independently (Fig. 1b). This allows us to increase the pressure quasi-hydrostatically and impose axial differential stresses separately. The D-DIA is capable of reversing differential strain, and resistive heating can be applied to investigate the effects of temperature. Samples are much larger than for DAC experiments. The D-DIA thus has significant advantages but cannot reach the high pressures of the DAC apparatus.

The D-DIA experiments were performed in beamline 13-BM-D (GSECARS) of the APS. More details of the

![Fig. 1. Schematic diagrams of (a) the radial DAC diffraction geometry and (b) the D-DIA set-up for X-ray diffraction and radiography (from Wang et al. \cite{30}).](image-url)
D-DIA set-up have been described in Wang et al. [30]. The X-ray beam of wavelength 0.20663 Å was collimated to 200 × 200 μm and passed through the space between the anvil assembly (Fig. 1b). Cylindrical samples, 0.5 mm in diameter and 0.8 mm in length, were cut from high purity wires obtained from ESPI metals. These were loaded into a boron nitride sleeve and capped on both ends with densified alumina disks to serve as pistons then capped again with porous alumina to smoothly increase pressure. Diffraction patterns were recorded on a Mar165 charge-coupled device (CCD) (2048 × 2048 pixels) for 600 s. In addition, X-ray radiography recorded the changes in wire length providing a direct measure of macroscopic axial strain.

The experiment on Cd was carried out at ambient temperature to observe texture development upon compression. Cd was compressed quasi-hydrostatically to 20 tons (~4 GPa) and axial shortening was gradually applied to 52% strain, followed by axial lengthening back to 0% natural strain. Similar experiments were carried out on Hf under two different conditions. The first run was at ambient temperature; the sample was compressed quasi-hydrostatically to 15 tons (~4 GPa) and slowly deformed to 30% strain. Differential rams were then reversed to lengthen the wire to the initial length. The same method was repeated in the second run, except Hf was compressed to 5 tons (~1 GPa) and simultaneously heated to 700 K during deformation.

3. Data analysis

3.1. Rietveld refinement

Diffraction data analysis relies on the Rietveld refinement [31], which uses a least squares approach to minimize the difference between experimental diffraction data (dotted) and a calculated model (solid) (Fig. 2a and c). First, the diffraction images were integrated from 0° to 360° azimuth over 10° sectors to produce 36 spectra with the MAUD software [32]. Fig. 2b and d (bottom) displays a stack of these spectra for Zn and Hf, respectively. Note that we express spectra as a function of \(Q = 2\pi/d\). The instrument geometry in the DAC experiment (wavelength, sample to detector distance, beam center and image plate tilt) was calibrated with a standard (CeO₂ for Zn, Cd and Hf and LaB₆ for Os). Volume fractions, orientation distributions and lattice parameters for Zn, Cd, Hf and Os at different pressures were refined. The diffraction spectra of the refined model (top) were compared with experimental spectra (bottom) (Fig. 2b and d), which indicate a close similarity indicative of an excellent fit, both in intensities as well as the position of diffraction peaks.

3.2. Stress and strain analysis

Sinusoidal variations in peak positions are a result of deviatoric stress imposed by DAC or the D-DIA on the sample. The pressure was determined by fitting unit cell parameters (corrected for non-hydrostatic stresses) with a third order Birch–Murnaghan equation of state (EOS) [33]. The initial volume at atmospheric pressure \(V₀\) of Zn is 30.24 Å³, and values for the bulk modulus \(K₀\) and its pressure derivative \(K′\) are 65 and 4.6 GPa, respectively [11]. The pressures of the other metals were calculated by the same approach (Os, \(V₀ = 27.98\) Å³, \(K₀ = 411\) GPa, \(K′ = 4.0\) [8]; Cd, \(V₀ = 43.17\) Å³, \(K₀ = 42\) GPa, \(K′ = 6.5\) [11]; Hf, \(V₀ = 43.36\) Å³, \(K₀ = 105\) GPa, \(K′ = 3.95\) [34]).

The variation in peak positions (or lattice \(d\) spacings) along the azimuth of diffraction rings clearly indicates that the sample was under deviatoric stress and experiencing elastic lattice distortion. If the single crystal elastic constants, the texture and, the lattice spacings in the diffracting subsets of grains are known, an elastic averaging model (Moment Pole Stress model [35,36]) can be applied to calculate the macroscopic deviatoric stress that superimposes on the hydrostatic pressure. The single crystal elastic constants \(Cᵢⱼ\) of Zn [37] and Hf [38] at ambient pressure and of Os [39] and Cd [40] at various pressures were used to determine the deviatoric stress component. According to the geometry of axial compression and axially symmetric textures we assume that the deviatoric stress component \(Sᵢⱼ\) in the DAC and the D-DIA [44,45] is

\[
Sᵢⱼ = \begin{bmatrix}
-t/3 & 0 & 0 \\
0 & -t/3 & 0 \\
0 & 0 & 2t/3
\end{bmatrix}
\]

where \(t\) is the differential stress and provides a lower bound of yield strength such that compressive stresses are negative. Table 1 summarizes the changes in lattice parameters and axial stress values with pressure. Lattice parameters refer to the hydrostatic condition, i.e. at an azimuth of 54.7° to the compression direction [41,42].

Axial plastic strain is more difficult to estimate and to distinguish from elastic strain (lattice distortion) for radial DAC experiments. This is due to the small sample size, the effect of the confining gasket material, compaction of the original powder and the geometry of the DAC and gasket. Judging from texture development in previous DAC experiments on a wide range of materials, it is estimated that an axial strain of 20–25% may be reached at 20 GPa [1,4]. At higher pressures strain continues to increase, but at a diminishing rate. For D-DIA experiments X-ray radiographs can be used to calculate the macroscopic strain \(ε\), which is defined as \(ε = 100 \times \ln(l₀/l)\), where \(l₀\) is the initial sample length after quasi-hydrostatic compression [43].

3.3. Texture analysis

The variation in intensity along the diffraction rings immediately indicates a crystallographic preferred orientation attained during plastic deformation (insets to Fig. 2). Texture analysis was computed by the EWIMV algorithm [44] to produce an orientation distribution function (ODF). A cylindrical symmetry was imposed, as we assume axial symmetry around the compression direction. The ODF from MAUD was exported to the BEARTEX software.
Fig. 2. Diffraction patterns of (a, b) Zn at 25 GPa and (c, d) Hf at 1 GPa with 20% strain. Stacks of “unrolled” diffraction rings (b, d) show the variation in intensity and lattice spacing for a 360° azimuth angle, indicating texture development and stress imposed on the sample. The bottom frame are experimental data and the top frame the Rietveld fit. Inserted on the right side are diffraction images for DAC and D-DIA, as well as D-DIA radiographs.
and smoothed with a 7.5°C176 filter to minimize artifacts due to OD cell structures. Inverse pole figures (IPF), which describe the orientation of the compression axis relative to the crystal coordinates, are used for representation. Fig. 3 illustrates the lattice geometry of hcp metals, including major slip systems, in crystal coordinates and equal area projection. Due to the hexagonal crystal symmetry, a 30°C176 partial IPF is sufficient to represent the complete texture information (shaded area in Fig. 3). Pole densities are expressed as multiples of a random distribution (m.r.d.), where 1 m.r.d. corresponds to a random texture. Fig. 4 displays IPF for Zn, Os, Cd and Hf, using the same scale for all.

### 4. Results

Data analysis was performed on selected diffraction images and the details of pressure, differential stress, lattice parameters and texture strength are summarized in Table 1. Here we define “texture strength” as the maximum density in the measured IPF. In general, lattice parameters and the c/a ratio of hcp metals decrease as a function of pressure (Fig. 5). However, while the changes in c/a ratio of Os and Hf are minimal over the pressure ranges explored in this study, the axial ratios of Zn and Cd deviate strongly from their initial values at atmospheric pressure.

#### 4.1. Stress

The evolution of differential stress (t) with pressure or strain varies for different experiments (Table 1). For Zn, Cd and Hf differential stresses are relatively low (≤1 GPa) due to the low yield strength of plastic systems
for these metals. In contrast, the differential stress of Os is high and reached 6.31 GPa at a pressure of 58 GPa. This is lower than the results reported in Weinberger et al. [10] (t = 9 GPa at a pressure of 25 GPa), but it confirms the high strength of Os. The differences between the results could be related to the gasket materials used in the experiments. Boron–kapton epoxy was used in this study, while beryllium was used by Weinberger et al. [10].

4.2. Texture

4.2.1. Zinc

Diffraction images at ambient pressure show that both Zn and Os crystals are initially randomly oriented in the aggregate, since the intensity is uniform along the diffraction rings. As compression and deformation proceed, a systematic variation in diffraction intensity and lattice spacings with azimuthal angle is observed in the samples (inset in Fig. 2a). In Zn, only a very weak (0001) maximum develops (1.27 m.r.d.) at 10 GPa (Fig. 4a, no. 2). It gradually strengthens at 15 GPa to 2.57 m.r.d. and reaches 5.18 m.r.d. at 25 GPa (Fig. 4a, no. 5). The texture of Zn at 25 GPa is four times stronger than that at 10 GPa, suggesting a different mechanism of texture development at high pressure. As will be shown later, this behavior is consistent with the activation of (1 0 1 2) twins, and their transition from compressive to tensile as the c/a ratio decreases with pressure.

4.2.2. Osmium

Os behaves very differently. At pressures as low as 4 GPa a weak texture starts to develop with a 1.89 m.r.d.
maximum near (0001) (Fig. 4b, no. 2). The texture strength increases with pressure to 2.33 m.r.d. at 10 GPa, and then reaches 2.99 m.r.d. at 58 GPa (Fig. 4b, no. 5). The IPF maximum remains near (0001), although it is always slightly displaced.

4.2.3. Cadmium

Cd shows a spotty diffraction pattern at ambient pressure, indicating large crystals and poor grain statistics. The crystallite size decreases as compression proceeds, allowing a regular texture to develop. As we apply quasi-hydrostatic pressure to 4 GPa and impose axial shortening to 34% strain, a weak texture (2.04 m.r.d.) is observed near (0001), but slightly displaced (Fig. 4c, no. 2). The texture in Cd becomes strongest (2.53 m.r.d.) when deformed to 52% strain (Fig. 4c, no. 2), but the maximum shifts ~30° from (0001). The maximum reverses back to near (0001) during decompression and strain reversal (Fig. 4c, no. 3), and eventually becomes weak under ambient conditions.

4.2.4. Hafnium

The diffraction image of the starting Hf wire shows a strong texture (7.72 m.r.d.), with an IPF maximum near (2 1 1 0) and (1 0 1 0) (Fig. 4d, no. 1), corresponding to a typical hcp extruded wire texture [46,47]. In a first run at ambient temperature, an IPF maximum near (0001) starts to develop as soon as quasi-hydrostatic pressure is applied to 4 GPa (Fig. 4d, no. 2). Simultaneously, depletion around the (1 0 1 0) orientation takes place, which is consistent with tensile twinning reorientation. Upon further compression the strength of the (0001) maximum quickly increases and then saturates. As deformation proceeds to 29% strain, the maximum near (0001) reaches 6.91 m.r.d., while the initial maxima near (2 1 1 0) and (1 0 1 0) become depleted (Fig. 4d, no. 3). An IPF maximum evolves near (1 0 1 0) during strain reversal and decompression (Fig. 4d, no. 5). In a second run at 700 K, the starting Hf crystals are also preferentially oriented with the IPF maximum of 3.30 m.r.d. near (2 1 1 0) and (1 0 1 0) (Fig. 4e, no. 1). As hydrostatic pressure is applied to 4 GPa and an axial shortening of 15% strain imposed, the texture shifts from (1 0 1 0) to near (2 1 1 0) (4.36 m.r.d.) (Fig. 3e, no. 2). During decompression and strain reversal the IPF maximum gradually decreases, but remains near (2 1 1 0) (Fig. 3e, no. 5). These observations are different from the first run, suggesting that temperature has a significant effect on the deformation mechanisms in Hf.

5. Discussion

In DAC and D-DIA experiments, high pressure conditions and axial shortening induce both plastic deformation and elastic lattice distortion. Elastic strains are small compared with plastic strains and are only used to infer stress conditions. Plastic strains produce texture development. An interpretation of the texture patterns relies on a comparison of experimental observations with simulations of the VPSC polycrystal code [22], which neglects elasticity and accommodates deformation by slip and twin shear. VPSC can generate deformation textures for different combinations of active systems and different strains by treating each crystal as a visco-plastic inclusion in a homogeneous but anisotropic medium with the average properties of the polycrystal. Two thousand initially randomly oriented crystals were used to simulate the Zn, Cd and Os aggregates. However, the experimentally measured texture of the extruded Hf wire was introduced as the starting distribution for the Hf plasticity simulations. The ODF of the Hf wire at ambient temperature was quantified, exported from MAUD, and used to assign weights to the initial 2000 orientations in the routine ODFW of Beartex [45]. As we applied compressive strain in 20 steps of 1% strain crystals deform plastically and preferentially reorient.

Deformation mechanisms for hcp metals are well established [5], and here we investigate dominant basal and prismatic slip and tensile and compressive twinning. Different values of critical resolved shear stress (CRSS) (Table 2) for the deformation modes generate distinctive texture patterns. They were chosen to explore the importance of slip and twinning on texture patterns and are kept constant throughout the simulation. Work hardening is not taken into account here due to a lack of accurate measurements of the macroscopic stress–strain response. To conform with estimated strains in the DAC experiments, simulated IPF for 5% and 20% compressive strain are shown.

Many studies of hcp metals [23–26] have shown that mechanical twinning plays a major role in texture development. The characteristic twinning shear (g) for a particular twin system depends on the c/a axial ratio [5, Table IV]. It relates the amount of shear contributed by the twin system \( \Delta \gamma^{tw} \) to the volume fraction of the grain that reorients by twinning \( f^{tw} \) as: \( \Delta \gamma^{tw} = g f^{tw} \). Because \( g \) has values lower than 0.2 for the cases considered here it turns out that even small amounts of twin shear activity require large volume fractions to reorient by twinning. We explored the most common observed twinning modes, i.e. \{1 0 1 2\}(1 0 1 1) tensile twinning and \{2 1 1 2\}(2 1 1 3) compressive twinning in the models, but only selected simulations that were compatible with the experimental results displayed are in Fig. 6. Mechanical twinning is unidirectional and is characterized by the ability to produce either compressive or tensile strain parallel to the c-axis [29]. Thus, the conventional use of “tensile twinning” and “compressive twinning” refers to the c-axis strain and not the deformation experiment.

In model A, basal slip on (0 0 0 1)(2 1 1 0) is the dominant deformation mechanism. Basal slip was combined with \{1 0 1 2\}(1 0 1 1) tensile twinning in model B, and with compressive twinning on \{2 1 1 2\}(2 1 1 3) in model C. Model D considered basal slip and \{1 0 1 0\}(1 2 1 0) prismatic slip. Two sets of simulations were performed, first with an initial random orientation distribution (Fig. 6a) and then with the same conditions but an initial
extruded wire texture (Fig. 6b) based on Hf (Fig. 4d, no. 1). The output of the simulations also includes the relative activity of deformation mechanisms as a function of applied strain (Fig. 7).

For the random initial texture (Figs. 6a and 7a), basal slip (model A) produces a maximum at (0001) and, indeed, basal slip is the only significantly active system. Tensile twinning (model B) also produces a maximum near (0001), although slightly displaced. This texture develops immediately at low strains. In this case twinning is active initially, but when favorable orientations are twinned, deformation proceeds by pyramidal and basal slip. For compressive twinning (model C), a maximum near (1010) develops. Again, twinning is initially active, followed by pyramidal and prismatic slip. If both basal and prismatic slips are active and twinning is suppressed (model D), a relatively weak bimodal texture develops with concentrations near (0001) as well as near (2110). Orientations closer to (0001) deform mainly by basal slip and rotate towards (0001), while orientations at high angles to (0001) deform by prismatic slip and rotate towards (2110).

For an initial wire texture (Figs. 6b and 7b), most grains are unfavorably oriented for basal slip (model A). A few grains rotate towards (0001), but most remain at high angles. Many slip systems are active. For tensile twinning (model B), there is a spike in twinning activity that rotates grains with c-axes at high angles to the compression direction, towards (0001). This is followed by pyramidal slip. Pyramidal slip is active because most grains are unfavorably oriented, and thus strain is accommodated by other systems. Finally, for basal and prismatic slip (model D) these two

<table>
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systems dominate and compete. Rotations do not proceed towards (0001) but converge at \( \left( \frac{2}{3} \right) \) \( \frac{1}{2} \) \( \frac{10}{12} \). This shows the importance of the original orientation distribution, especially for cases where twinning is subordinate. The texture patterns for model A and model D are entirely different. Basal and prismatic slip favor grains with \( c \)-axes inclined at intermediate angles \( (\sim 45^\circ) \), and if these orientations do not exist, texture evolution is impeded. These simulations are now compared with the experimental results for different hcp metals.

5.1. Osmium

Model B (Fig. 6a) agrees best with the low pressure texture for Os at 4 GPa (Fig. 4b, no. 2), and resembles the high pressure texture at 58 GPa (Fig. 4b, no. 5). At as little as 4 GPa mechanical twinning on \( \{10\bar{1}2\}\{10\bar{1}1\} \) produces tensile strain parallel to the \( c \)-axis and yields a texture maximum near (0001). It can be concluded that \( \{10\bar{1}2\}\{10\bar{1}1\} \) tensile twinning is a significant mechanism in Os, accommodating plastic deformation even at low pressure/low strain. With increasing strain the texture does not significantly strengthen.

5.2. Zinc

Zn, for which \( c/a \) decreases rapidly with increasing pressure [11,12], provides a dramatic example of the significance of twinning in hcp metal deformation at high pressures. The prevalent twin system goes from being compressive \( \{10\bar{1}2\}\{10\bar{1}1\} \) to tensile \( \{10\bar{1}2\}\{10\bar{1}1\} \) as \( c/a \) becomes smaller than the critical value of \( \sqrt{3} \) (see [5] and Fig. 8). Model A (Fig. 6a) most closely resembles the experimental texture of Zn at 10 GPa (Fig. 4a, no. 2), indicating that basal slip is dominant (Fig. 7a). As the \( c/a \) ratio crosses below the critical value at a pressure of 15 GPa, \( \{10\bar{1}2\}\{10\bar{1}1\} \) tensile twinning (model B, Fig. 6a) reorients the crystals and strengthens the (0001) texture (Fig. 4a, no. 3). Additional models with different \( c/a \) ratios were generated to explore the effect of tensile twinning on Zn texture evolution (Fig. 8). We modified the parameters used in model B of Fig. 6 for different \( c/a \) ratios of Zn obtained from DAC experiments and updated their corresponding characteristic shear \( (g) \). Note that \( c/a = 1.856 \) for model B1, \( c/a = 1.741 \) for model B2, \( c/a = 1.710 \) for model B3, and \( c/a = 1.641 \) for model B4 (Fig. 8). A new set of CRSS parameters was also employed (CRSS for basal slip is 2, CRSS for tensile twinning is 1, the rest are 6). At \( c/a > 1.732 \) models B1 and B2 show a maximum in the distribution of compression axes near \( (2\bar{1}10) \) and \( (10\bar{1}0) \). This texture pattern is controlled by compressive twinning on \( \{10\bar{1}2\}\{10\bar{1}1\} \). As the \( c/a \) ratio crosses below 1.732, \( \{10\bar{1}2\}\{10\bar{1}1\} \) twinning reverses the shear direction to \( \{10\bar{1}1\} \) and becomes tensile twinning, which leads to a maximum near (0001) (models B3 and B4 in Fig. 8). Model B4 (Fig. 8) corresponds to the strongest texture of Zn at 25 GPa (Fig. 4e, no. 5). These observations confirm the role of \( \{10\bar{1}2\}\{10\bar{1}1\} \) tensile twinning in Zn texture development at high pressure.
5.3. Cadmium

Cd behaves similarly to Zn, as they both have high c/a ratios (Fig. 5). Model A in Fig. 6a most closely resembles the (0001) texture in Cd during compression and axial shortening to 52% strain (Fig. 4c, nos. 1 and 2). As decompression and strain reversal proceed the texture weakens slightly, but remains near (0001) (Fig. 4c, no. 3). The simulations infer that the texture in Cd is mainly controlled by \( \{0001\}\_{\text{h}} \) tensile slip. Tensile twinning might not be active in Cd at low pressure, as the c/a ratio obtained from the D-DIA experiment did not cross below the 1.732 threshold, contrary to Zn.

5.4. Hafnium

Since Hf initially had a wire texture, we introduced the experimentally measured wire texture as the starting distribution for the plasticity simulations (Figs. 6b and 7b). Hf crystals reorient and immediately develop an IPF maximum near (0001) (Fig. 4d, no. 2) when we apply a quasi-hydrostatic pressure of 4 GPa and axial shortening to 8%. This texture is activated by \( \{10\overline{1}2\}\{101\overline{1}\} \) tensile twinning (model B in Fig. 6b), which produces a (0001) maximum parallel to the compression direction. Our simulations confirm that \( \{10\overline{1}2\}\{101\overline{1}\} \) tensile twinning is the main deformation mechanism in Hf at high pressure. Upon decompression and strain reversal to ambient conditions the texture remains strong, but developed an IPF maximum near \( \{1010\} \) (Fig. 4d, no. 5). As Hf crystals detwin, their c-axes rotate away from the compression direction.

In the second run of the Hf experiment, we incorporated resistive heating to examine texture development at high temperature. The starting Hf wire had a relatively weaker texture (3.00 m.r.d.) than that in the first run (7.72 m.r.d.).

Fig. 7. Relative activity (%) of different deformation mechanisms are plotted as a function of percentage axial strain for simulations using models A–D (Table 2) for (a) a random initial orientation distribution and (b) an initial wire texture.
As we simultaneously heated the sample to 700 K and applied compression as well as axial shortening, the IPF maximum developed near \( (\overline{2} \overline{2} 1) / (\overline{2} \overline{2} 1) \) (Fig. 3e, nos. 2–4), indicating that the \( c \)-axes are inclined at intermediate angles to the compression direction. The \( (\overline{2} \overline{2} 1) / (\overline{2} \overline{2} 1) \) texture agrees with model D in Fig. 6b, which is mainly controlled by \( \{0001\}(2\overline{1}1\overline{0}) \) basal slip and \( \{1\overline{0}1\overline{0}\}(\overline{1}2\overline{1}0) \) prismatic slip (Fig. 7b). Interestingly, the IPF maximum remains near \( (\overline{2} \overline{2} 1) \) during decompression and strain reversal (Fig. 3e, no. 5). These observations suggest that mechanical twinning is inactive at high temperature.

The maximum texture in Zn (Fig. 4a), Os (Fig. 4b) and Cd (Fig. 4c) is slightly displaced from \( \{0001\} \), which can be characteristic of tensile twinning, as we document in model B at 20% strain (Fig. 6a). Clausen et al. [24] and Agnew et al. [48] suggested that displacement of the IPF maximum after dominant basal slip and tensile twinning of hcp metals is influenced by pyramidal slip \( (a+c) \), rotating the \( c \)-axis away from the compression axis. Twinning causes a large number of grains to reorient the \( c \)-axis and align it with the compression axis, which is a plastically hard orientation. The presence of twin boundaries may also serve to inhibit the movement of dislocations and increase the yield strength. This is supported by high differential stresses observed in the Os samples. However, at high temperature the texture in Hf is controlled by \( \{0001\}(2\overline{1}1\overline{0}) \) basal slip and \( \{1\overline{0}1\overline{0}\}(\overline{1}2\overline{1}0) \) prismatic slip systems. It is evident that tensile twinning is an unfavorable mechanism to accommodate plastic strain at high temperature.

There was very little change during decompression of both Zn and Os due to the fact that in DAC experiments, even if hydrostatic pressure is released, differential stress remains compressive. This differs in multi-anvil press experiments. Fig. 9 shows the changes in differential stresses during axial shortening and lengthening cycles of Hf at ambient temperature, which illustrates an immediate switch from compression (negative \( t \)) to tension (positive \( t \)) during strain reversal (Table 1) and corresponding detwinning.

Transmission electron microscopy (TEM) would be necessary to further characterize the microstructure, particularly the penetration of twin boundaries by dislocations and the misorientation angle between the twinned crystals and surrounding grains. Dislocation and twin interactions in Zr and Hf have been observed by TEM [25], as the twinned regions produce strong contrast variations. If prismatic and pyramidal slips are significantly activated, i.e. the CRSS are around 3, the texture pattern does not conform to the experimental data. It is revealing to look at the different deformation system activities (Fig. 7). For slip activities remain fairly constant, at least at moderate strains, and activities correspond to the CRSS inputs. If twinning is active it dominates at low strains and immediately reorients favorably oriented crystals. However, once crystals are twinned, twinning activities decline rapidly (Figs. 7 and 8, models B and C). Twinning produces a rapid but moderate and stable preferred orientation. Slip, on the other hand, steadily increases the texture strength. In addition, the fact that a relatively large volume fraction of crystals needs to reorient in order to accommodate a rather modest amount of shear strain means that slip is always a player, in the parent and in the twin, to accommodate the remaining imposed deformation.
6. Conclusion

Hcp metals deformed in axial compression at ambient temperature and high pressure develop an alignment of c-axes near the compression axis. The textures in Zn and Cd initially develop by \{0001\}/\{2110\} basal slip, while at higher pressure slip may be accompanied by \{10\{2\}/\{1011\} tensile twinning when the c/a ratio decreases below a critical value (c/a = 1.732). In contrast, the texture in Os and Hf at ambient temperature develops early due to a dominant role of \{10\{2\}/\{1011\} tensile twinning, with some degree of basal slip. At elevated temperatures (700 K), tensile twinning is suppressed and the texturing in Hf is due to combined basal and prismatic slip. Twinning is activated as soon as compression is applied, with rapid changes in texture pattern. However, once twinning of favorably oriented grains has occurred the mechanism stops and subsequent deformation takes place by slip. Under all conditions basal slip appears to be the main slip mechanism in hcp metals at high pressure.

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