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Full length article Effect of external stress on hydride reorientation in zirconium

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ABSTRACT

The usage and long-term storage of nuclear fuel cladding motivate efforts to understand the effect of external stress on hydride precipitation. Here, by using *in situ* bending device in electrolytic hydrogen charging, the nucleation and precipitation behaviors of subsurface hydrides under different degrees of tensile stress were obtained. The number density of surface hydride bumps increases with the elastic tensile stress and reaches a peak before plastic yielding. This is related to the statistical result that the reorientation of hydride bumps reaches maximum at the end of elastic stage. Morphologies of hydride bumps varies from needle- or circular-shape to faceted, indicating hydride reorientation. The faceted hydrides gradually transform from {0001} to {101i} (*i* = 1-7), even to the {1010} planes. Because of the local compressive stress, faceted hydrides growing along one <1120> direction are suppressed. External stress-stimulated tensile or compressive lattice stress on specific crystallographic planes in hydride precipitation, which plays an important role in the long-term performance of Zr cladding tubes.

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1. Introduction

Zirconium (Zr) alloys are widely used in nuclear reactors as pressure vessels and cladding tubes [1,2]. Due to low solid solubility of hydrogen in Zr [3], brittle hydrides are easy to form, leading to hydride embrittlement [4–8]. Besides, Zr cladding tubes experience multi-axial stress in service [2], among which the hoop stress in a range of 122–130 MPa is the largest. Even in the longterm storage for spent nuclear fuel cladding [9–11], residual tensile stress still exists. The external stress has a marked effect on the nucleation and precipitation of hydrides, causing hydride reorientation, which becomes the predominant culprit for the catastrophic reduction in the mechanical performance and the failure of Zr cladding tubes via delayed hydride cracking [12]. Therefore, the influence of external stress on hydride precipitation arises as an urgent issue in understanding the hydrogen embrittlement of Zr [13–17].

The effect of stress on hydride nucleation and characteristics has been explored [17–19]. Tensile stress increases the nucleation density of hydrides, whereas compressive stress suppresses it [17]. Notably, the external stress also causes hydride reorientation [12]. The threshold stress of hydride reorientation has been studied in details [20,21]. It was reported that hydrogen content [22], grain

* Corresponding author. *E-mail address:* wzhanxjtu@mail.xjtu.edu.cn (W.-Z. Han). size, degree of cold work [23] and stress state [24] are key factors affecting the threshold stress of hydride reorientation. Interestingly, hydride spacing also impacts on the threshold stress of hydride reorientation [25]. A threshold stress in the range of 75 and 80 MPa was reported for hydride reorientation in recrystallized Zr-2 and Zr-4 alloys [26,27]. Moreover, the reoriented hydrides significantly reduce the ductility and fracture toughness of Zr alloy [28–31].

Under external stress, hydrides show three different characteristics. First, external tensile stress alters the preferential nucleation sites of hydrides. With external tensile stress, the terminal solid solubility of hydrogen for hydride precipitation is significantly reduced at the sites where grain boundary (GB) planes and the basal planes of grains are near perpendicular to the tensile stress [32-37]. Thus, intergranular hydrides usually precipitate on the GBs that are perpendicular to the tensile axis [32]. Similarly, intragranular hydrides prefer to form in grains with a circumferential basal pole in cladding tubes [32]. Second, external tensile stress alters the alignment of hydrides. Mesoscale reoriented hydrides are related to the vertically stacking of microscale hydrides [12,27]. With external tensile stress, the precipitation sites of new hydrides shift from the diagonal corners of a pre-forming hydride to the middle point [38]. These hydrides still align along basal planes, but become thicker and shorter with the increase of external tensile stress. Third, external tensile stress alters the chosen of hydride variants and their habit planes. Under external stress, hy-









Fig. 1. Schematic showing the device for in-situ bending during hydrogen charging.

dride variants perpendicular to the normal of tensile stress are popular, while the formation of other hydride variants are suppressed [39–41]. Two out of three variants of hydrides form under tensile stress in simulation, and their staggered alignment turns the final mesoscale hydride near perpendicular to the tensile stress [41]. In addition, with external tensile stress, the habit plane of hydrides alters from original (0001) basal plane to {1011} pyramidal plane [42–44]. Reoriented hydrides with habit planes of {1012}, {1013}, {1017}, and {1010} were also reported [42,44]. Although the effect of external stress on hydrides reorientation has been explored in some aspects, how stress affects the crystallographic features of reoriented hydrides is still lacking a precise explanation. Therefore, revealing the detailed characteristics of microscale reoriented hydrides and their relationship with the external stress are needed [12].

In this study, we adopted subsurface hydrides as a model to investigate the nucleation, growth, distribution, and reorientation characteristics of hydrides in Zr under external stress. An in-situ bending device is used to apply elastic and plastic strain on pure Zr thin foils during electrochemical hydrogen charging, which favors the observations of hydride reorientation at room temperature. The influence of stress on the hydride nucleation and characteristics with different degrees of elastic or plastic deformation is revealed. Under external tensile stress, faceted subsurface hydrides form and their habit planes gradually transform from {0001} to {101i} (i = 1-7) and finally to {1010}. External stress-stimulated tensile or compressive local lattice stress on specific crystallographic planes impacts the choice of faceted/habit planes in hydride precipitation.

2. Experimental methods

2.1. In-situ bending under hydrogen charging

High-purity fully recrystallized Zr was used as a model material. Samples for hydrogen charging were ground and then pickled using a mixture of 3 vol.% hydrofluoric acid, 40 vol.% nitric acid and 57 vol.% distilled water. Fig. 1(a) shows the schematic of the

in-situ bending device. Two ends of thin foil samples were fixed at one side and movable at the other side for flexible bending. Central bending angle scale is marked on the outside of the device. The top view of the device and the approach to determine the bending angle are shown in Fig. 1(b). A hole is punched-out on the bottom of the device to allow the flow of electrolyte. The shape of thin foil samples used for hydrogen charging is shown in Fig. 1(c). To achieve a large elastic bending range, the final thickness of Zr samples was only 170 μ m. The L-shaped sample geometry was designed to connect the left part to an electrode. Hydrogen electrochemical charging was conducted in a solution of 0.5 mol/L sulfuric acid using a current density of 0.2 A/cm² at 30 °C for 1 h. Different bending angles of 0°, 5°, 10°, 15°, 20°, 25° and 30° were selected to achieve different degree of elastic and plastic deformation in thin Zr foils. During charging, the screws on both sides of the device were flexible, which enable the central part of the samples experiencing maximum stress.

2.2. Microstructural characterization

During charging, surface hydride bumps form. After taking the foil from the device, the surface hydride bumps were characterized using scanning electron microscope (SEM, SU6600). To survey the hydride bump number density inside grains or at GBs, more than two hundred 500 \times SEM micrographs were taken and involved in statistics. High-resolution micrographs of the central area $(1 \text{ mm} \times 5 \text{ mm})$ of each sample with different bending angles were obtained. All GBs and hydriding GB segments in the central area $(1 \text{ mm} \times 5 \text{ mm})$ were highlighted by Photoshop software, then the GB hydriding fraction of samples with different bending angles was calculated by Image-J software. To analyze the area fraction of hydriding in the central area (1 mm \times 1 mm), Photoshop software was used to increase the contrast between hydride bumps and Zr matrix, which partially decreases the hydriding area fraction. Thus, only a general trend can be obtained with this approach. Besides, to display the intragranular hydriding area fraction, a manual annotation method was used with less loss of the hydride area frac-



Fig. 2. Characteristics of surface hydride bumps in pure Zr after 1 h electrolytic hydrogen charging with different bending angles. (a) to (f) Morphologies of subsurface hydrides in Zr formed under different bending angles. The scale bar is 20 μ m for all figures.



Fig. 3. Variation of area fraction of hydriding with bending angle. (a) GB hydriding fraction vs. bending angle within the center of sample (1 mm \times 1 mm and 1 mm \times 5 mm) and area fraction of hydriding vs. bending angle within the center of sample (1 mm \times 1 mm). (b) Central Mises stress vs. bending angle obtained according to ABAQUS simulation. The inset is the Mises stress field in the tensile side of the sample with the bending angle of 15°.

tion. Then, the area fraction of hydriding and the intragranular hydriding area fraction were calculated by Image-J software.

Electron backscatter diffraction (EBSD) was used to measure the orientation of grains. EBSD scans were conducted with a voltage of 20 kV and a probe current of 2.7 nA using a step size of 0.5 μ m. The EBSD data was further analyzed using MTEX software [45]. Transmission electron microscope (TEM, JEOL 2100F) was employed to characterize the microstructures of subsurface hydrides. TEM thin foils with the dimensions of 12 μ m × 6 μ m × 100 nm were cut by focus ion beam (FIB) on specific hydride bumps. To mitigate the ion-beam damage, an 8 μ m Pt layer was deposited on the top of chosen hydride bumps before cutting. The raw TEM foils were further polished using a gentle Ga⁺ beam with a voltage of 5 kV and a beam current of 48 pA to reduce hydride formation during FIB thinning.

2.3. Estimation of bending stress

To estimate the value and distribution of tensile stress in each sample with different bending angles, a model of three-point bending was created by using ABAQUS software. The deflection used in each calculation was fitted with the corresponding experiment. Tensile tests were performed on the pure Zr to obtain input data for simulation [46]. One average stress-strain curve was chosen with E = 116 GPa and $\sigma_{true} = 146$ MPa for plastic yielding ($\varepsilon_{pl} = 0$). The yield stress-plastic strain curve was inputted as the plastic deformation data of Zr in ABAQUS. Considering the applicability of the simulation model, the ABAQUS/Standard solver was chosen and an eight-node brick element (C3D8) was used. After calculation, the central Misses stress and the corresponding strain of each bending test were extracted.

3. Results

3.1. Effect of bending angle on the number density of subsurface hydride bumps

Fig. 2 shows the morphology of hydride bumps formed on Zr thin foil with different bending angles after hydrogen charging for 1 h. For the sample without bending, hydride bumps are sparse, as



Fig. 4. Faceted hydride bumps. (a) Morphologies of needle and circular hydride bumps formed under stress-free hydrogen charging. (b) and (e) Faceted hydride bumps formed in grain with basal plane bearing a tensile stress. (c) and (f) Faceted hydride bumps formed in grain with basal plane bearing a compressive stress. (d) Intragranular area fraction of faceted hydride bumps and needle hydride bumps vs. bending angle average over five grains with grain size of 80 μ m. The unit cell in each image marks the orientation of the grain.



Fig. 5. Characteristics of faceted planes in surface hydride bumps for grains with basal plane bearing a tensile stress. (a) to (c) SEM images of faceted hydrides. The faceted planes are highlighted by colored dash lines. (d) to (f) are pole figures for (a) to (c), respectively. Facet planes of $\{10\overline{1}i\}$ (i = 1, 2, 3, 4, 5, 6, 7) can be determined according to the pole figures.



Fig. 6. Faceted hydrides in Zr grains with basal plane bearing a compressive stress. The bending angle of each case is labeled in the right top corner of the image. Faceted hydride bumps are along two preferred $<11\overline{2}0>$ directions and shrunken in one $<11\overline{2}0>$ direction in (a), (c), (e), (g) according to the pole figures in (b), (d), (f) and (h), respectively.

displayed in Fig. 2(a). With bending deformation, the number density of hydride bumps generally increases as shown in Fig. 2(b) to (f). Thin foil Zr can be fully recovered after deformation within the bending angle of 20°, thus the sample only has elastic deformation in this case. For the elastic bending range, both the area density of intergranular and intragranular subsurface hydride bumps increases with bending angle, as shown in Fig. 2(b) to (d). Once the bending angle is larger than 20°, the Zr thin foil undergoes plastic deformation. For the plastic bent samples, the area density of hydrides decreases with further increase of bending angle from 25° to 30°, as shown in Fig. 2(e) and (f). Morphologies of hydrides are similar for samples with and without bending, both circular-like and needle-like hydrides are observed.

Fig. 3(a) displays the evolution of GB hydriding fraction and the area fraction of hydriding at the central area of samples with increasing of bending angle. The area density of both intergranular and intragranular hydrides is continuously increasing in the elastic bending stage, whereas a turning point appears slightly before the plastic yielding; once the sample bent into the plastic stage, the area density of hydrides decreases with the further increase of bending angle. The highest area density of hydrides appears in the range of 15° to 20°. A variation of the statistics area does not alter this trend, as shown in the statistics for the central area of 1 mm $\times 1$ mm and 1 mm $\times 5$ mm in Fig. 3(a). Fig. 3(b) plots the increase of central Misses stress with bending angle. The stress distribution on Zr thin foil with the bending angle of 15° is also displayed in Fig. 3(b) as an inset. The central stress is highest in the bent Zr thin foil, corresponding to the maximum area density of hydrides in the central region. Comparing the central Misses stress with the $\sigma_{
m true}$ (146 MPa) at $\varepsilon_{\rm pl}$ = 0, the elastic and plastic deformation stages of the whole Zr thin foil can be distinguished. According to this criteria, Zr thin foil sample remains in elastic deformation for the bending angle of 20°, then gradually transitions into plastic deformation.

3.2. Faceted surface hydride bumps

3.2.1. Crystallographic features of faceted hydride bumps

Under stress-free hydrogen charging condition, the angle between basal habit plane and hydriding surface determines the choice of two types of hydride bumps [47]. Fig. 4(a) shows that circular bumps form in grains with basal plane near parallel to the sample surface, whereas needle-shaped bumps precipitate in grains with basal plane near perpendicular to the sample surface. However, under stress condition, the morphology of hydride bumps shows faceted features, indicating the altering of hydride habit/faceted plane. Fig. 4(b), (c), (e) and (f) display the morphology of faceted hydride bumps formed under the bending angle of 10° in the sample central area (1 mm \times 5 mm). Some circular hydride bumps also form in the grains with basal plane near perpendicular to the sample surface in Fig. 4(b) and (c), indicating the altering of hydride habit plane. Besides, the basal plane of the grain in Fig. 4(b) is near perpendicular to the loading axis, indicating that the basal plane underwent tensile stress. In contrast, the basal plane in the grain in Fig. 4(c) is near parallel to the loading axis, thus the basal plane bears a compressive stress. Therefore, all grains with faceted hydrides forming can be categorized into these two cases. Fig. 4(d) reveals that the intragranular area fraction of faceted hydride bumps continuously increases with the bending angle from 0° to 15°, and then decreases with further increasing of the bending angle from 20° to 30°. This trend is similar to the variation of hydride bump number density with increasing bending angle (Fig. 3(a)), implying that the formation of faceted hydride is related to the external stress.

Fig. 5 displays the crystallographic characteristics of faceted hydride bumps in *case I* with basal plane experiencing tensile stress. Fig. 5(a) to (c) show the details of some faceted hydride bumps formed with different bending angles. Fig. 5(d) to (f) are corresponding pole figures showing their facet planes. Faceted planes of $\{10\bar{1}i\}$ (i = 1-7) were observed. The faceted planes have a twin character and the twinned $\{10\bar{1}i\}$ plane has a mirror symmetry with the original $\{10\bar{1}i\}$ plane. Faceted hydrides prefer to form on the coupled $\{10\bar{1}i\}$ planes near perpendicular to the loading axis (Fig. 5(d), (e) and (f)). As the value of i in $\{10\bar{1}i\}$ plane increases, the angle between the two coupled $\{10\bar{1}i\}$ plane increases toward 180°.

Fig. 6 reflects the relationship between $<11\overline{2}0>$ directions and the macroscopic faceted directions of faceted hydride bumps with different bending angles in *case II* with basal plane experiencing compressive stress. The faceted hydrides extend in two pre-



Fig. 7. Microstructures of the subsurface hydrides in Zr thin foil with the bending angle of 15°. (a) Lift-out area chosen in the sample. (b) and (c) Low magnification TEM images showing the microstructures of subsurface hydrides underneath hydride bump I, II and III marked in (a). The loading directions are marked in (a) to (d). (e) The selected area diffraction pattern (SADP) of the region marked by the white dash circle in (d). (f) and (g) Dark-field TEM images of α -Zr matrix and γ -ZrH hydrides, respectively. Red dash lines mark the faceted planes of the hydrides.



Fig. 8. Microstructures of the subsurface hydrides in Zr with the bending angle of 25°. (a) Lift-out area chosen in the sample. (b) and (c) Low magnification TEM images showing the microstructures of subsurface hydrides underneath the hydride bump I, II and III marked in (a). The loading directions are marked in (a), (b) and (d). (e) SADP of the region marked in (d). (f) and (g) Dark-field TEM images showing the twinned γ -ZrH hydrides using $(1\overline{1}1)_{\gamma}$ and $(00\overline{2})_{\gamma}$ diffraction spots. Red dash lines mark the faceted planes of hydrides.

ferred <1120> directions and shrink in one <1120> direction, as shown in Fig. 6(a), (c), (e) and (g). The angle between the shrunken <1120> direction and the loading axis is near 90°, much larger than the others, as illustrated in Fig. 6(b), (d), (f) and (h). Therefore, the angle between the special crystallographic directions and the loading axis also affects the morphology of hydride bumps under stress condition.

3.2.2. Microstructures of faceted subsurface hydrides

To further investigate the effect of elastic and plastic stress on the chosen of hydride faceted planes for *case I*, TEM characterization was performed on hydrogen charged samples with the bending angles of 15° and 25°, as shown in Figs. 7(a) and 8(a), respectively. Because of all $\{10\overline{1}i\}$ (i = 1-7) planes are likely faceted/habit planes of hydrides formed under external stress, EBSD was used to find the unique $<11\overline{2}0>_{\alpha}$ zone axes as an edge-on viewing direction to characterize those hydride facet planes. The stacking structure of hydrides is hard to be determined underneath the surface bumps, thus here we focused on the variation of hydride faceted/habit plane.

Fig. 7 shows the microstructures of subsurface hydrides with bending angle of 15°. One side of three faceted hydride bumps is selected (Fig. 7(a)), and the typical TEM microstructures of subsurface hydrides underneath these bumps are shown in Fig. 7(b) and (c). The depth of subsurface hydride region under hydride bumps is proportional to the width of surface hydride bumps. Fig. 7(d) to (g) display the detailed morphologies of subsurface hydrides underneath bump I. Fig. 7(e) shows the selected area diffraction pattern (SADP) taken from the region marked with (e) in Fig. 7(d). Since the appearance of {110} spot, the subsurface hydrides are typical γ

hydrides, and the orientation relationship (OR) between Zr matrix and γ hydrides is $(0001)_{\alpha} || (001)_{\gamma}$ and $[2\overline{11}0]_{\alpha} || [110]_{\gamma}$. Fig. 7(f) and (g) are dark field images of Zr matrix and γ hydrides by selecting $(000\bar{1})_{\alpha}$ and $(2\bar{2}0)_{\nu}$ spots, respectively. Fig. 7(f) displays some smaller lenticular-shaped hydrides beneath the major subsurface hydrides precipitate along the typical {0001} faceted/habit plane, as highlighted by red dash lines. For convenience, these hydrides are named basal hydrides. Fig. 7(g) shows that several downward triangle shape hydrides compose a major subsurface hydride region. The closer to the sample surface, the wider the hydrides, because of the tensile stress gradient from sample surface to sample interior. As marked by the red dash lines in Fig. 7(g), several $\{10\overline{1}i\}$ (i = 0, 1, 4, 5) faceted planes are observed around the hydrides. These hydrides are named pyramidal hydrides. Thus, a surface faceted hydride bump is a gathering of several subsurface pyramidal hydrides formed under external elastic bending.

Fig. 8 shows the microstructures of subsurface hydrides in the sample with bending angle of 25°. The chosen bumps are shown in Fig. 8(a). Fig. 8(b) shows the typical morphology of subsurface hydrides. The ratio of width-depth for current subsurface hydride region is nearly same as the sample under the bending angle of 15°. According to the SADP in Fig. 8(c), the subsurface hydride underneath bump II is also a γ hydride with the OR of $(0001)_{\alpha} ||(001)_{\gamma}$ and $[2\overline{11}0]_{\alpha} || [110]_{\gamma}$. Since the hydride having a {1011} faceted plane, it is also a pyramidal hydride. Detailed characterization of the subsurface hydrides underneath bump I is shown in Fig. 8(d) to (g). Different from the γ hydride mentioned above, twinned γ hydrides form with OR of $(0001)_{\alpha} || (\bar{1}11)_{\gamma}$ and $[2\bar{1}10]_{\alpha} || [110]_{\gamma}$, according to the SADP in Fig. 8(e). The dark filed TEM images of twinned hydrides using diffraction spots of $(1\overline{1}1)_{\gamma}$ and $(00\overline{2})_{\gamma}$ are shown in Fig. 8(f) and (g). The stacking of twinned hydrides forms a subsurface hydride cluster. These twinned hydrides have a lath shape rather than a downward triangle shape, indicating the decrease of hydride nucleation density with further increasing of bending angle from 20° to 25° (Fig. 3(a)). Nevertheless, the external tensile stress also alters hydride faceted planes from {0001} to $\{10\overline{1}i\}$ (*i* = 1, 3, 7), as marked with red dash lines in Fig. 8(f) and (g). These hydrides are pyramidal hydrides as well. Therefore, the faceted hydride bump is a result of stacking of several subsurface pyramidal hydrides.

In addition, the effect of tensile stress on the formation of single hydride is obtained. Beneath the subsurface hydride region, some single hydrides aligned perpendicular to the *basal hydrides* are observed, as shown in Fig. 9(a). According to the SADP in Fig. 9(b), it is a γ -ZrH with the OR of $(0001)_{\alpha}||(001)_{\gamma}$ and $[2\overline{110}]_{\alpha}||[110]_{\gamma}$. Notably, the faceted/habit plane is $\{10\overline{10}\}$ according to Fig. 9(c), which is different from the common basal habit plane [48], thus this type of hydride is called *prismatic hydride*. Statistics in Fig. 9(d) demonstrates that the area fraction of single *pyramidal* and *prismatic hydride* increases with the increasing of central stress according to Fig. 3(b). These observations indicate that the external stress alters the hydride faceted/habit planes from {0001} to {10\overline{1}} and even to {10\overline{10}}.

4. Discussion

4.1. Effect of external tensile stress on hydride nucleation density

According to Fig. 3(a), tensile stress can increase the nucleation density of hydrides. However, the maximum hydride nucleation achieves just before the plastic yielding. Such observation was explained by the strain most-matching theory for single hydride reorientation in Gd[18], which means the nucleation density of hydrides reaches maximum as the tensile strain of matrix matching the dilatation misfit between matrix and the single hydride. By

Table 1

Central Misses stress and true strain in the bent samples with different bending angles.

Bending angle	Misses Stress in central area (MPa)	True Strain (%)
0°	0	0
5°	70.56	0.07479
10°	85.29	0.08746
15°	114.7	0.1189
20°	145	0.2592
25°	164.1	0.4035
30°	172.2	0.4894

comparing the central strain in Table 1 and the dilatational misfit strain in Table 2 for single Zr hydrides, it can be found that these two types of strain have huge difference. The dilatational misfit strain is almost 25 times of the central strain achieved in the thin foil sample with the bending angle of 20°. Therefore, the strain compatibly theory cannot explain the hydride clusters reorientation observed in this study.

Fig. 10 shows variation of the area fraction of needle/circularshaped bumps (without reorientation) and the faceted bumps (with reorientation) with the bending angle. The area fraction of faceted bumps drastically increases before plastic yielding and decreases with plastic deformation, however, the area fraction of needle/circular hydrides only has a gentle variation with the bending angle (Fig. 10). Thus, the formation of faceted hydride bumps causes the marked increase of hydride bump area fraction before plastic yielding in Fig. 3(a). The decreasing of needle/circular hydride bump area fraction within the plastic bent stage is related to the plastic deformation-induced dislocations, which enhance hydrogen solubility and suppress hydride precipitation [50–52].

According to Figs. 4 to 6, the formation of faceted hydride bump is a cluster of reoriented hydrides. Microscale hydride clusters can stack and combine to elongate perpendicular to the loading axis [25,38,41], thus it requires a lower threshold stress. The threshold stress for hydride cluster reorientation is usually smaller than the yield stress of Zr alloys [24,53]. As a results, the appearance of faceted hydrides occurs under the bending angle of 5°, and the peak density of faceted hydride bumps achieves at the bending angle between 15° and 20° (before plastic yielding), as shown in Fig. 10. According to the calculated stress in Fig. 3, the critical threshold stress for hydride clusters reorientation locates between 114 and 145 MPa. For such a tensile stress, the produced matrix strain is likely just meeting the misfit between Zr matrix and the reoriented hydride clusters. Therefore, the threshold stress bestmatching is a relatively reasonable explanation for the achieving peak area fraction of faceted hydride bumps before plastic yielding [12]. Besides, some experiments demonstrated that once the applied stress is higher than the threshold stress for hydride cluster reorientation, the number of reoriented hydrides continues to increases under a constant hydrogen concentration [24], which is different from the current continuous hydrogen charging.

In contrast to the hydride clusters, the area fraction of single *pyramidal* and *prismatic* hydride continuously increases with bending angle, as shown in Fig. 9(d), which manifests that the threshold stress for a single hydride reorientation is much higher than the yield stress. This observation consistent with a recent multiphase filed modeling [25], in which the threshold stress of a single hydride reorientation is 28 times larger than that of a hydride cluster.

4.2. Preferential formation of γ hydride under tensile stress

The preferential formation of γ hydride under tensile stress is obvious, as shown in Figs. 7 to 9. It is interesting that all the hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure Zr and Zr-2.5Nb alloy are γ hydrides formed at crack-tip in pure



Fig. 9. Hydrides with orientation relationship of $(0001)_{\alpha} ||(001)_{\gamma}$ and $[2\overline{110}]_{\alpha} ||[110]_{\gamma}$. (a) TEM image showing hydrides interacting an angle of 90°, which are the prismatic hydrides. The loading direction is marked in (a). (b) SADP of the region marked with circle in (a). (c) Dark-field images displaying the γ -ZrH hydrides using diffraction spots in (b). (d) The area fraction of single pyramidal and prismatic hydride vs. bending angle.

Table 2

Dilatational misfit of hydride in Zr with two different orientation relationships.

Orientation relationship	[uvtw] _{\alpha}	[uvw] _{hydride}	The misfit between γ and α (%)	The misfit between δ and α (%)
{0001} {111}	[0001]	[111]	5.69	7.25
<1120> <110>	[1120]	[110]	0.54	4.60
	[1100]	[112]	5.64 [49]	4.58 [49]
{0001} {001}	[0001]	[001]	-3.48	-7.09
<1120> <110>	[1120]	[110]	0.54	4.60
	[1100]	[101]	20.58	20.82

drides as well [54]. Similarly, under a tensile creep test on a Zr single crystals with 10 ppm hydrogen, all observed hydrides are γ phases either [55]. On the contrary, the formation of δ hydrides is preferred in a stress-free sample under a slow cooling rate [56]. The preferential formation of γ hydride under external stress is likely due to the increasing of heterogeneous nucleation density [57]. For both elastic and plastic bending, the nucleation density of surface bumps increases markedly than that of samples with a stress-free charging condition (Fig. 3(a)), which promotes the formation of dispersed subsurface hydrides. Therefore, under external stress, the heterogeneous nucleation site for hydride increases and the hydrogen diffusion distance decreases, thus the allocated hydrogen concentration for each hydride decreases, which favor the formation of γ hydride. This phenomenon is similar to the prefer-

ential formation of γ hydride in quenched samples [56,57,48] and cold-worked Zircaloy-2 [58].

4.3. Stress-stimulated hydride reorientation

Clarifying the mechanism of hydride reorientation requires a deep understanding of the effect of external stress on the preferential formation condition of *basal hydride*, *pyramidal hydride* and *prismatic hydride*. Notably, the applied external stress plays a key role to promote the reorientation of hydride during precipitation, which is also similar for hydride reorientation in Zr alloy during slow cooling [20,42].

Figs. 4 to 9 show that the formation of *pyramidal* and *prismatic hydride* increases compared with the stress-free charging



Fig. 10. Comparison of the intragranular area fraction of needle/circular bumps (without reorientation) and faceted bumps (with reorientation) vs. bending angle within the central region of sample (1 mm × 5 mm). The area fraction of faceted hydrides increase markedly with bending angle from 0° to 15°.



Fig. 11. Effect of stress on hydride characteristics. Pole figures of grains where the faceted hydride forms. (a) to (d) shows grains with basal plane near perpendicular to the loading axis. (e) to (h) shows grains with basal plane near parallel to the loading axis. The symbols in (b) to (d) and (e) to (h) indicate the different crystallographic planes bearing a compressive or tensile local stress.

[47], no matter which types of ORs, {0001}]|[111] or {0001}]. The preferential formation of *pyramidal hydride* is also observed in Zircaloy-4 cladding under hoop tensile stress [42] and in Zr-2 alloy with pre-deformation [43]. Similarly, *prismatic hydride* was frequently formed at the crack-tip and under high-temperature tensile creep test condition [54,55]. On the contrary, *basal hydride* was usually observed in a stress-free sample after annealing [56,48]. To unveil the influence of external stress, pole figures with the projections of {0001}, {1010}, {1011}, {1120} poles and the loading axis are plotted in Fig. 11. A dash line is plotted at an interacting angle of 45° between the pole and the loading axis in each pole figure to mark the type of external stress, such as tensile (red region) or compressive stress (blue region) on the specific planes.

For *case I*, the loading axis is near perpendicular to the basal plane, which undergoes a tensile stress (Fig. 11(a)). However, for the two coupled $\{10\overline{1}1\}$ planes (Fig. 5), their interacting angles with the loading axis are also less than 45°. In particular, at least two of $\{10\overline{1}1\}$ pole in Fig. 11(c) is closer to the loading axis poles, thus tensile stress is higher on these first pyramidal planes, and these $\{10\overline{1}1\}$ planes become the faceted planes of hydrides. Simi-



Fig. 12. Schematic showing the gradual transition of hydride faceted/habit plane from $\{0001\}_{\alpha}$ to $\{01\overline{1}0\}_{\alpha}$ plane under external tensile stress.

larly, for all other $\{10\overline{1}i\}$ planes, their interacting angles with the loading axis are also smaller than that of the $\{0001\}$ and $\{10\overline{1}1\}$ poles (Fig. 5(d), (e) and (f)), favoring the formation of *pyramidal hydride*, as shown in Figs. 5, 7 and 8.

The gradual transition of faceted/habit plane with external stress is illustrated in Fig. 12. Under tensile stress, for the plane nearly perpendicular to the loading axis, hydrogen diffusion becomes easier and the misfit between hydride and matrix reduces, which enable the transformation of habit/faceted plane from original basal to the "opened plane" (Fig. 12). Besides, all the three {1010} planes are under compressive stress in *case I*, as shown in Fig. 11(b). Because of the large positive misfit along [1100] according to Table 2, the formation of {1010} faceted/habit plane is suppressed, thus {1011} plane becomes the predominant habit plane (Figs. 5, 7 and 8), similar to the formation of *pyramidal hydride* in real service situation [42,59].

For *case II*, the loading axis is near parallel to the basal plane, which bears a compressive stress (Fig. 11(e)). One of the three {1010} poles in Fig. 11(f) bears tensile stress whose interacting angle with loading axis is less than 45° . Thus, the formation of *prismatic hydride* increases, assisting the hydride bumps extend along the {1010} plane. Since the projection of the chosen {1010} pole, the original needle-shaped hydride bumps formed under stress-free condition are now turn into circular hydride bumps under an external tensile stress (Fig. 4(c)). As for Fig. 4(b) in *case I*, the gradual shifting of "opened plane" in Fig. 12 promotes the formation of circular hydride. Almost all {1011} poles are under compressive stress for *case II*, which are unfavorable for the formation of *pyramidal hydride*, as shown in Fig. 11(g).

In contrast, the formation of faceted hydride in Fig. 6 is caused by the effect of external stress on growth directions rather than on habit planes. The interacting angles between one of $<11\overline{2}0>$ direction and the loading axis is near 90°, while interacting angles of the other two $<11\overline{2}0>$ directions with loading axis are less than 45° according to Fig. 11(h). For the two types of ORs, the misfit along $<11\overline{2}0>$ direction is positive according to Table 2. Therefore, the hydride bumps extend along the two tensile $<11\overline{2}0>$ directions and shrink along the compressed $<11\overline{2}0>$ direction in Fig. 6. However, the effect of external stress on the transformation of faceted/habit planes is more obvious than the choice of growth directions [39].

5. Conclusions

In this study, the effect of external stress on hydride nucleation density and precipitation characteristics is investigated. The following findings can be drawn.

- 1 The maximum nucleation density of hydride bumps achieves before plastic yielding, which is because of the formation of high fraction of faceted hydrides owing to best matching between the threshold stress of hydride clusters reorientation and the external tensile stress just before plastic yielding.
- 2 Under tensile stress, the heterogeneous nucleation sites increase, while the hydrogen concentration for each site decreases, which promote the formation of γ hydride.
- 3 Under tensile stress, faceted hydride bumps form accompanied with the formation of irregular circular hydrides. The macroscale and the microscale hydrides show faceted features with faceted/habit planes transforming from {0001} to {101i} (i = 1-7), or extending in two <1120> directions.
- 4 Tensile stress-simulated hydride reorientation is the reason for the formation of *pyramidal hydride* and *prismatic hydride*. The angle between the normal axis of $\{10\overline{1}i\}$ plane and the loading axis is the predominant factor that determines the selecting of faceted/habit planes during hydride precipitation.

Declaration of Competing Interest

The authors declare that there is no competing financial interests.

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