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Multi-dimensional morphology of hydride diffusion layer and associated sequential twinning in commercial pure titanium

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Abstract

The dominant hydride precipitates have been well demonstrated to follow two types of orientation relationships (ORs) with Ti matrix: OR1 with $\{0001\} // \{1\bar{1}1\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$, and OR2 with $\{0001\} // \{001\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$. Our previous work reveals the orientation dependence of the hydride nucleation with above two ORs. Within the grains with special orientations, the complicated interactions of different variants inside Ti-hydride diffusion layer are further characterized in this work. The orientations favorable for OR1 hydride layer are: $\{10\bar{1}3\}$ plane parallel to sample surface corresponding to the layer with one OR1 variant dominated and c -axis parallel to the surface normal with multiple OR1 variant layer preferred. As for OR2 hydride layer, the orientation of $\{10\bar{1}0\}$ plane parallel to the sample surface is favorable for three symmetrical OR2 variants, while a -axis parallel to the normal direction prefers two preferential OR2 variants. Furthermore, $\{10\bar{1}2\}$ extension twins and $\{11\bar{2}2\}$ contraction

twins are activated to accommodate the hydride-induced surface expansion and local misfit strain associated with the formation of OR1 hydride. The stimulation of these two twins is also orientation dependent: $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins can effectively accommodate the surface expansion of grains with c -axis parallel to and deviated from the surface normal of the sample, respectively. The further variant selection for each twin mode is performed through shear accommodation of hydride-twin pairs.

Keywords: Titanium; Hydride; Cross section; Twin; Variant selection;

1. Introduction

The combination of high corrosion resistance, strength-to-weight ratio, and exceptional biocompatibility of titanium and its alloys allows widespread applications especially in aerospace and biomedical industries[1]. When subjected to hydrogen-rich service conditions, nevertheless, the formation and transformation of hydride precipitations in Ti would induce high internal stress in the alloys, which is regarded as the origin of several important alloy properties decrease, such as ductility and toughness [2]. Indeed, the solubility of H in titanium is low, 0.15 wt. % in α -Ti at 300 °C [3], the consensus is that, even a small quantity of hydrogen will cause the formation of TiH_x hydrides in Ti and produce a considerable drop in alloy properties [4]. Accordingly, hydride precipitation has been considered as a major barrier for reliable applications of Ti alloys under hydrogen-rich conditions.

The phase structures of hydrides formed in Ti at room temperature are determined by hydrogen concentration: TiH with face-centered tetragonal (FCT) structure forms at relative low hydrogen concentration and transforms into the face-centered cubic (FCC) TiH_x (with x ranging between 1.5 and 2). The FCC phase (δ phase) is the most stable and prevalent hydride in titanium, which changes its lattice structure and transforms into the FCT TiH_2 with further increase of hydrogen concentration [5–9]. Another key factor that dominates the formation of hydride precipitations in titanium is crystallographic orientation. Four types of orientation relationships between the hexagonal close packed (HCP) Ti matrix and δ hydrides (FCC structured) have been reported in Refs [5–8], as shown in Table 1. OR1 (with $\{0001\} // \{1\bar{1}1\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$) and OR2 ($\{0001\} // \{001\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$) were the most common orientation relationships in pure titanium and referred to as B-type and P-type ORs respectively, according to their

nucleation mechanism [10]. While OR3 ($\{10\bar{1}0\} // \{1\bar{1}1\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$) and OR4 ($\{\bar{1}011\} // \{001\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$) were rarely observed, which were firstly reported in [5].

In our previous work [10], orientation dependence of hydride precipitation in commercially pure titanium has been investigated in detail. The formation of hydrides is significantly dependent on the matrix orientation for the reason of strain accommodation. The most favorable grain orientations for OR1 and OR2 hydride transformation are with $\{10\bar{1}3\}$ and $\{10\bar{1}0\}$ interface planes parallel to the diffusion surface, as the largest misfit strains along their interface plane normal can be accommodated by free surface relaxation. Besides, the interaction between hydride variants can also play a supportive role in accommodating the phase transformation-induced strain. OR1 hydride packets were observed under electron backscattered diffraction (EBSD) characterization in [11], the hydride grains inside the packet are in $\{111\} \langle 11\bar{2} \rangle$ twin relationships to relax the anisotropic misfit strain of hydride transformation. Conforto and Caillard [8] proposed that the hydride precipitates in different ORs prefer to form clusters to realize a more isotropic distribution of misfit strain produced by hydride transformation and decrease the total stored elastic energy. Indeed, hydride clusters formed by OR1 and OR2 hydrides were observed in [10], which can be energy favorable to accommodate the nearly perpendicular misfit strain of these two ORs transformation. However, the research efforts of [10] on orientation dependence and the interactions of hydride variants formed by electrolytic hydrogen charging were only carried out on 2D sample surface. Technically, a certain time of electropolishing on the post-charged sample surface is always necessary to achieve EBSD phase identification, that will inevitably, erase some valuable information of hydride diffusion

1 layer. It is therefore essential to conduct further investigations on the section
2 microstructure of hydride layer.

3 Owing to the large volume expansion of hydride transformation, dislocations are
4 necessary to accommodate the dilatation misfit between hydride and hexagonal matrix.
5 Carpenter [12] suggested that OR1 hydrides are formed by the dissociation of the normal
6 $1/3 \langle \bar{1}210 \rangle$ dislocations. Around the top and bottom ends of the hydride precipitate, shear
7 loop dislocations on the basal plane with $\mathbf{b} = 1/3 \langle \bar{1}210 \rangle$ are punched out and extending
8 in the direction of their Burgers vectors [7]. The formation of OR2 hydrides is related to
9 a ledge mechanism [6], including a shear component in $\langle \bar{1}210 \rangle$ and the normal dilatation
10 component in $\langle 10\bar{1}0 \rangle$ caused by volume variation. Conforto and Caillard [5] proposed
11 that the transition of OR2 produces two opposite prismatic loops along the interface,
12 contributing to the relaxation of misfit in the $\langle \bar{1}210 \rangle$ direction. Up to now, detailed study
13 on the formation mechanism and misfit dislocations related to the OR3 and OR4 hydrides
14 have not been reported. In addition, twins were also observed together with OR1 hydride
15 precipitates [10,11], but the hydride-twin accommodation mechanism is still not well
16 understood.

17 In the present work, multi-dimensional characterization of hydride layer in
18 commercial pure Ti (CP-Ti) formed by electrolytic hydrogen charging was performed.
19 The anisotropic section microstructure of hydride diffusion layer was examined in detail
20 for the first time via EBSD measurements, driving a further in-depth study on the
21 orientation dependence of hydride interaction. The associated plastic behaviors induced
22 by hydride transformation and corresponding accommodation mechanism were also
23 investigated.

24 **2. Methodology**

Commercially pure Ti rolled sheets (T40, ASTM grade 2) with thickness of 1.5 mm were used in the present work. The as-received sheets were firstly annealed in vacuum condition at 800 °C for 3 h to obtain a fully recrystallized microstructure with an average grain size of ~50 μm. The texture is a typical split basal texture with basal pole oriented $\pm 20^\circ$ away from normal direction (**ND**) of the sheet towards transverse direction (**TD**). Hydrogen charging was performed for the specimens by employing an electrolytic method [10] in an electrolyte consisting of 1/3 volume phosphoric acid and 2/3 volume glycerin under an applied current density of 2 kA/m². Sample was charged for 168 h to obtain stable δ -hydride (FCC) diffusion layer with a hydrogen concentration of 123 wt ppm, which is the same as that in [10].

Two sets of samples are prepared to observe the section microstructure of hydride diffusion layer (Sample A, Fig. 1a) and hydride-induced plastic deformation (Sample B, Fig. 1b). In order to examine the anisotropic section microstructures of OR1 and OR2 hydride diffusion layers, both the transverse direction (**TD**) and rolling direction (**RD**) surfaces of Sample A were ground with SiC papers of grits to 2000[#] and then charged as diffusion surface. The textures of **TD** and **RD** surfaces are favorable for respective OR1 and OR2 hydride transformations [10]. The hydrogenated sample were mounted with Struers Polyfast resin to protect the diffusion surface during the metallographic preparation process. After ground and chemical-mechanical polished with OPS (Struers), the diffusion layer section on **ND** surface was embellished by argon ion polishing using Gatan PECS II apparatus with 5kV for 2h. For the characterization of hydride nucleation inside hydride layer (Sample B), **ND** surface was chosen as the diffusion surface. The ground sample was hydrogen charged and then electrolytic polished at 5 °C for 1 s with voltage of 30 V in a solution of 10 vol% perchloric acid in methanol.

Microstructure characterization was performed through an interrupted in-situ method using a tungsten thermionic emission Jeol-6490 and field emission gun Jeol-6500F scanning electron microscopy (SEM), that are both equipped with EBSD detector and AZtec software package (Oxford Instruments) for data acquisition. To balance the characterization accuracy and efficiency, Jeol-6490 was used for high speed EBSD detection with the purpose of obtaining enough statistical information in large areas, while Jeol-6500F was employed to acquire detailed examination.

3. Results

3.1 Multi-dimensional morphology of hydride diffusion layer

The SEI – Secondary Electron Image showing the section microstructure of the hydride layer is presented in Fig. 2a. It can be seen that the sample and the resin are bonded tightly, with a stress-free area at the junction (the area between red dotted lines), which is ion polishing area obtainable under EBSD measurement. The higher-magnification SEI for the black box area in Fig. 2a is shown in Fig. 2b. In which, the interface between Ti matrix and hydride layer in light gray curve can be observed more clearly, highlighted by yellow dotted line. The thickness of hydride layer can be therefore measured around 7 μm . Besides, the section structures formed on **TD** or **RD** diffusion surface are indistinguishable under SEI.

Fig. 2c and d present the **TD**-IPF and **RD**-IPF maps of section microstructures of diffusion layers formed on respective **TD** and **RD** surfaces, that are colored by hydrogen diffusion directions. The IPF maps include two regions: FCC hydride layer (upper side) and HCP titanium matrix (lower side). It is obvious that the hydride layer has much lower indexing rates, especially at the junction area near titanium matrix, where Kikuchi patterns are too blur to be detected due to the large lattice distortion induced by hydride

transformation. Inside hydride layer, the hydride microstructures are dependent on the grain orientations of Ti matrix. According to Fig. 2c and d, some grains form homogeneous hydride layers with almost unique hydride variant, and some hydride layers contain complicated hydride interactions. Although with various hydride microstructures, the hydride layers are continuous and similar in thickness, as well as the hydride–matrix interfaces are approximately parallel to the diffusion surface.

The orientation dependent hydride nucleation on the diffusion surface has been investigated in our former work [10]. However, some valuable information inside hydride layer was lost when the surface prepared by electrolytic polishing. In this work, the anisotropic section microstructures of hydride layers are further investigated. According to the results in [10], there appear four typical titanium matrix orientations with multiple hydride platelet microstructures: (1) $\{10\bar{1}3\}$ planes parallel to the diffusion surface are favorable for the nucleation of single OR1 hydride variant; (2) c -axis oriented along diffusion direction prefers multiple OR1 variants; (3) $\{10\bar{1}0\}$ planes aligned to the diffusion surface refer to one dominant OR2 hydride variant; (4) OR1-OR2 hydride clusters are formed in the grain with a -axis along diffusion direction. In the present research, the section microstructures of hydride layers in the grains (G1-G4) corresponding to the above four typical orientations are characterized, as shown in Fig. 3. G1 and G2 (Fig. 3a and b) with dominant OR1 hydride layer are selected from **TD** diffusion surface (Fig. 2c), while G3 and G4 (in Fig. 3c and d) preferring OR2 hydride transformation are from **RD** surface (Fig. 2d). Interestingly, according to Fig. 3, no matter which type of grain orientation, more than one hydride variant is activated inside hydride layer. For convenience, B_i and P_j are employed to denote the six OR1 and three OR2 hydride variants ($i=1,2,3\dots6$ and $j=1,2,3$) as listed in Table 2. The OR1 hydride variants

are defined by the interface planes with corresponding shear of Shockley dislocation, while OR2 hydrides were defined by only interface planes. The different expression for OR1 and OR2 variants are determined by their transformation mechanism, which will be discussed in Section 4.1.

As mentioned above, the orientation of G1 ($\{10\bar{1}3\}$ interface plane parallel to diffusion surface is favorable for single OR1 hydride variant reported in [10]. Indeed, a major variant (B_4) almost occupy entire hydride layer in Fig. 3a. According to the pole figures, the $(\bar{1}013)$ interface plane of dominant B_4 is the closest to **TD** surface. This accords with the investigation of variant selection reported in [10], the hydride variant with its interface closest parallel to diffusion surface is selected because of its highest capacity to accommodate the misfit distortion through free surface. However, inside hydride layer, other hydride variants are also activated likely by the accumulated misfit strain of B_4 . Some B_5 variants with $(0\bar{1}13)$ interface slightly deviated from **TD** surface precipitate near the diffusion surface and embed into B_4 hydride layer. A few small OR2 particles are induced at the matrix-hydride junction, because the orientation of G1 is relatively unfavorable for OR2 transformation. It should be noticed that some OR3 hydrides appear along the upside sample edge. Normally, OR3 transformation is difficult in α -Ti matrix because of large misfit (around 15%) along c -axis, while the high density of dislocations on the free surface provides the possibility for the nucleation of OR3 hydrides.

Grain 2 has the orientation of c -axis close to **TD** (diffusion direction) preferring multiple OR1 variants. In Fig. 3b, four OR1 variants (B_1 , B_3 , B_4 and B_6) are formed inside hydride layer. According to the pole figures, B_1 and B_6 are the most favorable two variants and thus occupy a large proportion of hydride layer, while B_3 and B_4 are less favorable

processing lamellar shape. Noting that, B_1 - B_4 and B_3 - B_6 usually occur in pairs. The dislocation accumulation produced by the formation of B_6 and B_1 would induce the formation of B_3 and B_4 respectively, due to the fact that the Shockley dislocations are along opposite directions between B_i and B_{i+3} . The large distortion produced by the interactions of different variants results in a thicker non-indexed area at the hydride-matrix junction than G1. Besides, as investigated in the next section, $\{10\bar{1}2\}$ twins are always stimulated at the OR1 hydride interface in the grain with G2 orientation, but rarely detected on the cross section.

[Fig. 3c](#) shows the hydride layer in G3 with the orientation of $\{10\bar{1}0\}$ parallel to the **RD** surface (diffusion surface). Unlike the result in [\[10\]](#) that one dominant OR2 variant was activated, all the three OR2 hydride variants happen and interact in G3. Thus, the hydride layer in OR2 favorable grain is different from OR1 favorable grain dominated by the most favorable hydride variant, for an example B_4 in G1 ([Fig. 3a](#)). As shown in [Fig. 3c](#), in addition to the most favorable variant P_1 , both P_2 and P_3 variants with their $\{10\bar{1}0\}$ interfaces $\sim 60^\circ$ away from **RD** surface are also formed. The together nucleation of three symmetric OR2 hydride variants can be induced by the extremely anisotropic lattice dilatation of OR2 transformation: -6.0% along $\langle 0001 \rangle$, $+5.5\%$ along $\langle \bar{1}2\bar{1}0 \rangle$ and $+21.8\%$ along $\langle 10\bar{1}0 \rangle$ [\[10\]](#). During hydrogen diffusion, P_1 preferentially precipitates near the sample surface, partial misfit strain along $[10\bar{1}0]$ can be relaxed through free surface. Subsequently, symmetric P_2 and P_3 are formed interconnecting with P_1 to realize isotropic misfit strain inside hydride layer. In addition, a few OR1 hydrides are also activated inside the diffusion layer and/or at the hydride-matrix junction. Conforto and Caillard [\[8\]](#) suggested that, due to the nearly perpendicular misfit strain direction, the interconnection between OR1 and OR2 hydrides can decrease the total stored elastic energy.

G4 represents the grain with $\langle \bar{1}2\bar{1}0 \rangle$ parallel to the hydrogen diffusion direction (**RD**), that hydrides nucleate in OR1-OR2 clusters [10]. However, in Fig. 3d, the majority of hydride layer is OR2 hydride indicating that G4 is also more favorable for OR2 than OR1 transformation. P_1 and P_3 variants are the relatively major components of hydride layer, as well as a small amount of P_2 variants occur at the junction of hydride layer and Ti matrix. According to the pole figures (Fig. 3d), P_2 variant is extremely unfavorable, presenting a large deviation $\sim 90^\circ$ of its $(01\bar{1}0)$ pole from the pole figure center, thus the formation of symmetric accommodation between three OR2 variants is restrained in G4.

In general, the section microstructure of hydride layer reveals more details of hydride interaction than the characterization of hydride nucleation in [10]. Among OR1-OR3 transformation, OR1 is determined in all the four typical grains, and thus the most likely to happen. While OR2 hydride did not precipitate in G2 indicating that c -axis parallel to diffusion direction is extremely unfavorable orientation for OR2 transformation. OR3 transformation is the most difficult, because it is only activated on the surface of OR1 hydride layer in G1. It can be speculated that the pre-existing OR1 hydrides play an important role on OR3 hydride nucleation, which will be discussed in Section 4.1.

3.2 Plastic accommodations stimulated by hydride transformation

Hydride nucleation has already been studied on diffusion surface to investigate the variant selection in our former work [10], where some micro twins were occasionally found near hydride platelets. In this section, the plastic deformation induced by hydride nucleation are further studied. For an explicit study of the hydrides and twins, two EBSD maps of post-charged surface are drawn: ND-IPF map (Fig. 4a) and phase map (Ti: silver, Hydride: white) with colored boundaries (Fig. 4b). The corresponding color definitions are presented under individual map. In Fig. 4b, the interface planes of OR1 hydrides are

colored by blue lines and OR2 hydride interfaces by pink lines. The fraction of OR1 hydrides is much higher than that of OR2 hydrides showing the favorable texture of **ND** surface for OR1 transformation.

Two types of twins are observed: majority of $\{10\bar{1}2\}$ extension twins (green lines) and a smaller quantity of $\{11\bar{2}2\}$ contraction twins (orange lines) as well. Some twins are activated inside grain matrix, while the others appear specially at the OR1 hydride interface regarded as hydride-induced twins. Twin variants are studied in detail by employing the same expression method in [13]: T_i^I ($i = 1, 2, \dots, 6$) denoted the six $\{10\bar{1}2\}$ (T_i^I) tension twin variants, while the six $\{11\bar{2}2\}$ twin variants are represented by C_i^I ($i = 1, 2, \dots, 6$), as presented in Table 2. Neither $\{11\bar{2}4\}\langle 22\bar{4}3\rangle$ or $\{11\bar{2}1\}\langle \bar{1}\bar{1}26\rangle$ twin appears in our experiments, they are usually activated when titanium is deformed at high strain rate [14]. Moreover, although no twin is activated, significant orientation change occurs in the grains with OR2 hydride.

To study the hydride-stimulated twinning, the OR1 hydride-twin pairs are examined in detail. Two specific grains (Grain I and Grain II) containing respective $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins are extracted from Fig. 4, their IPF maps (Fig. 5a and e) and corresponding phase maps (Fig. 5b and f) with the same color definition as Fig. 4 are shown in Fig. 5. In Fig. 5a and b, relatively large $\{10\bar{1}2\}$ twins are formed on both sides of OR1 hydride interfaces. According to the pole figures in Fig. 5c, inside the red circles, the hydride variant B_5 and twin variant T_2^I are selected. The $\{10\bar{1}2\}$ twin orientation existing a large deviation from OR1 favorable orientation ($\{10\bar{1}3\}$ plane parallel to diffusion surface), and restrains further thickening of hydride lamellas. For the grain containing $\{11\bar{2}2\}$ twins in Fig. 5e and f, smaller $\{11\bar{2}2\}$ twin plates are observed due to the larger shear

necessary for the formation of $\{11\bar{2}2\}$ twins than $\{10\bar{1}2\}$ extension twins. The hydride platelets gradually become thinner or/and break off when $\{11\bar{2}2\}$ twins are stimulated near the hydride tips. The growth of intragranular hydrides can be explained via the autocatalytic nucleation mechanism [15,16]. The chemical potential wells produced by the misfit strain at the growth front attract the hydrogen atoms and then control the path for further nucleation and growth of hydride. However, the local strain can be relaxed by the activation $\{10\bar{1}2\}$ or $\{11\bar{2}2\}$ twins, which decrease the chemical potential wells and also relative hydrogen affinities. Therefore, when a hydride stimulates the twinning process or intersects with an impinging twin, further growth will be restrained or changed.

The grains containing hydride-twin pairs are selected from Fig. 4, their orientations are projected into IPFs, as shown in form of IPF contouring maps in Fig. 5d and h, where the red points represent the most favorable orientations for OR1 and OR2 transformations. According to Fig. 5d, $\{10\bar{1}2\}$ twins prefer to be stimulated in the grains with c -axis close to hydrogen diffusion direction (**ND**). The grain with c -axis aligned to diffusion direction involve large distortion produced by complex interactions between multiple hydride variants, as reported in [10]. Thus, the local stress of hydride interaction can be also partially relaxed by the stimulation of $\{10\bar{1}2\}$ twin. For $\{11\bar{2}2\}$ twins, the grain orientations locate between the orientations favorable for OR1 and OR2, as shown in Fig. 5h, which prefer unique hydride variant, such as Fig. 5e. $\{11\bar{2}2\}$ twin-hydride pair is rarely observed in the grain with more than one hydride variant showing that the hydride interaction restrains the $\{11\bar{2}2\}$ twin nucleation. Furthermore, 10 hydride- $\{10\bar{1}2\}$ twin pairs and 10 hydride- $\{11\bar{2}2\}$ twin pairs are detected on the observe surface of Fig. 4, they can be described unanimously by $B_i-T_{i+3}^I$ and $B_i-C_i^I$, respectively. The reason for the orientation dependent twin nucleation and the accommodation mechanism of $\{10\bar{1}2\}$ and

$\{11\bar{2}2\}$ twins on OR1 transformation resulting in the special twin variant selection can be found in Section 4.2.

Fig. 6a shows the IPF map of a typical grain (Grain III) with OR2 hydride nucleation at grain boundary. The $\{10\bar{1}0\}$ interfaces of OR2 hydrides are less straight than the $\{10\bar{1}3\}$ interfaces of OR1 hydrides. The preferential grain boundary nucleation and curved interface can relax the large misfit dilatation of OR2 transformation along $\langle 10\bar{1}0 \rangle$ (about 20%). Furthermore, according to the identified grain boundaries ($>5^\circ$, black lines) inside Grain III, the intragranular orientation changes are more significant in the OR2 favorable grains due to a high density of geometrically necessary dislocation produced by hydrogen diffusion, which will be the favorable positions for subsequent nucleation of OR2 hydride in the grain interior.

Using the method of Chun et al. [17], IGMA (In-Grain Misorientation Axes) analysis of EBSD data is performed to explore the activated slip mode. The lower cutoff misorientation angle in IGMA analysis is taken as 1.2° , because of the limited angular resolution of the EBSD analysis. Actually, the IGMA distributions of material-point pairs between 1.2° and 2° is enough to investigate active slip mode, which is plotted for Grain III as shown in Fig. 6c, showing strong intensities around $\langle 0001 \rangle$. By matching the Taylor axis, such IGMA distributions are attributed to the predominant activation of prismatic $\langle a \rangle$ slip. According to Weatherly et al. [18], the HCP-FCC transformation of OR2 hydrides was formed by the partial dislocations on prismatic plane. Thus, it can be inferred that the accumulation of prismatic $\langle a \rangle$ dislocations is produced for the nucleation of intragranular OR2 hydrides.

4. Discussion

4.1 HCP-FCC structure transformation of OR1-OR3 hydrides

In addition to the anisotropic lattice misfit strain, the mechanisms of HCP-FCC structure transformation for OR1 and OR2 hydrides are also different [18], as illustrated in Fig. 7, which leads to the multiple plastic accommodation modes: twins are commonly induced by OR1 hydrides (Fig. 5) and prismatic dislocations are found in OR2 favorable grains (Fig. 6). The HCP-FCC transformation of OR1 hydride is shown in Fig. 7a, a simple shear introduced by the slip of Shockley dislocation along $[10\bar{1}0]$ on (0001) plane converts the hexagonal lattice (black circle) into cubic structure (blue circle). The angle α produced by $\mathbf{b} = 1/3[10\bar{1}0]$ is around 20.0° :

$$\alpha = \arctan\left(\frac{|\mathbf{b}|}{c}\right) = \arctan\frac{a}{\sqrt{3}c} \quad (1)$$

where $a = 0.295$ nm and $c = 0.468$ nm are the lattice parameters of α -Ti. The OR1 hydride will be formed by the HCP-FCC transformation combined with lattice dilatation, of which the energy favorable habit plane $\{10\bar{1}3\}$ is around 31° from (0001) shear plane. Dislocations and/or twins are required to accommodate the shear and lattice misfit of hydride transformation.

As for OR2 hydride transformation, there also exists a shear of 30° along $[1\bar{2}10]$ on prismatic plane in Fig. 7b produced by prismatic partial dislocations, which bring the hexagonal atoms into face-centered arrangement [18]. Besides, atom rearrangements (shuffles) are needed along the $[10\bar{1}0]$ invariant plane normal. Prismatic dislocations are attributed to the originating of HCP-FCC structure transformation of OR2 hydride, which is consistent with our experimental results in Fig. 6. Furthermore, a sample shear deformation is always accompanied by a rigid body rotation, which should destroy the undistorted $\{10\bar{1}0\}$ interface plane. Internal deformation mechanisms (like slip, twinning

or shuffling) are necessary to accommodate the shear on $\{10\bar{1}0\}$ plane and achieve the experimental orientation relationship of OR2. Indeed, internal twins and dislocations were observed by TEM at hydride-matrix interfaces [18], but not detected by EBSD measurement in our work.

The activation of OR3 transformation is hard in α -Ti due to the large misfit strain along c -axis, while it was observed at the edge of OR1 hydride layer, as mentioned before in Fig. 3a. It was speculated that the surface defects and B_4 hydride layer can stimulate the OR3 hydride nucleation. The activated B_4 and OR3 variants have respective habit planes of $(\bar{1}013)//(1\bar{1}0)$ and $(\bar{1}010)//(\bar{1}11)$ with the same zone axis $\langle\bar{1}2\bar{1}0\rangle//\langle\bar{1}\bar{1}0\rangle$. Their HCP-FCC transformations are illustrated in Fig. 8, where the black to blue refers to OR1 and black to red represents OR3 transformation. If not considering lattice dilatation, the difference between FCC structures of OR1 and OR3 hydrides is only a simple lattice rotation $\sim 20.0^\circ$ around $\langle\bar{1}2\bar{1}0\rangle//\langle\bar{1}\bar{1}0\rangle$ (the same as α in Fig. 7a). Thus, it could be derived that the OR3 precipitates are induced from the pre-existing OR1 variant B_4 to accommodate the accumulated distortion inside hydride layer. Indeed, the experimental misorientation between them is $\sim 26.6^\circ/\langle\bar{1}\bar{1}0\rangle$. The deviation of misorientation angles between 20.0° and $26.6^\circ/\langle\bar{1}\bar{1}0\rangle$ is due to the anisotropic lattice dilatation during phase transformation.

4.2 Variant selection of $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins

During plastic deformation at room temperature, $\{10\bar{1}2\}$ extension twins and $\{11\bar{2}2\}$ contraction twins are commonly observed in α -Ti [19]. OR1 hydride transformation includes both lattice expansion and shear of $1/3 \langle 10\bar{1}0 \rangle$ Shockley partial dislocation. Only dislocation slip is not enough to accommodate such complicated misfit strain, but

also twinning is always induced. $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins induced by OR1 hydride nucleation were observed in our work, which are orientation dependent, as shown in Fig. 5. $\{10\bar{1}2\}$ twin prefers the orientation with c -axis parallel to diffusion direction and $\{11\bar{2}2\}$ is easier to be activated in the grain located between the orientations favorable for OR1 and OR2.

In the current work, we use DGA (deformation gradient accommodation) criterion to explore the accommodative twin nucleation which can relax the local distortion at the interface of hydrides. The original DGA criterion was employed to predict the secondary twinning in magnesium alloys [20] and also extended for the exploration of the accommodation between different twin variants in titanium alloys [19]. According to the transformation mechanism, the OR1 hydriding frame is set up by: $\boldsymbol{\eta}$ // gliding direction of partial dislocation $\langle 10\bar{1}0 \rangle$, $\boldsymbol{\gamma}$ // normal of basal plane and $\boldsymbol{\lambda}$ // the zone axis ($\boldsymbol{\lambda} = \boldsymbol{\gamma} \times \boldsymbol{\eta}$). The twin frame is set up by: \boldsymbol{n} // twinning shear direction, \boldsymbol{m} // normal of twin habit plane and \boldsymbol{p} // normal of shear plane. The calculated displacement gradient tensors \mathbf{D} of OR1 hydride \mathbf{D}_H and twins \mathbf{D}_T in their defined reference frames are summarized in Table 3. The method of calculating \mathbf{D}_H and \mathbf{D}_T can be found in [10] and [20], respectively. The different shear values of twin modes are obtained from classical twinning theory [21].

At first, the accommodation of twinning on the hydride-induced surface expansion is considered as a constraint for the selection between $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twin modes. The contribution of hydrides and twin variants in Grain I and Grain II (see Fig. 5) to the expansion along surface normal is evaluated by transforming their displacement gradient tensor \mathbf{D} into sample frame \mathbf{D}^s :

$$\mathbf{D}^s = \mathbf{R}_{cs}^{-1} \cdot \mathbf{D} \cdot \mathbf{R}_{cs} \quad (2)$$

where \mathbf{R}_{cs} is Bunge rotation matrix [22]. The D_{33}^S values of B₅ hydride +0.228 in Grain I is larger than that of B₂ hydride +0.220 in Grain II. The D_{33}^S values of $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins in these two grains are summarized in Table 4. The twin variants with larger D_{33}^S values have higher capacity to accommodate the expansion along sample surface. As for Grain I with *c*-axis close to surface normal, the surface expansion coincides with *c*-axis extension, thus all the D_{33}^S of $\{10\bar{1}2\}$ tension twin T^I is positive (bold in Table 4) but negative for $\{11\bar{2}2\}$ twin C^I, indicating all the six $\{10\bar{1}2\}$ twin variants are favorable to accommodate the surface expansion of B₅ hydride. In contrast, only one $\{10\bar{1}2\}$ twin variant has positive D_{33}^S in Grain II, while three $\{11\bar{2}2\}$ twin variants are more preferred with larger D_{33}^S (C₂^I, C₄^I and C₅^I). The basal plane of Grain II is oriented away from diffusion surface, thus the surface expansion of B₂ hydride trends to perpendicular to *c*-axis equivalent to a *c*-axis compression, which is favorable to be accommodated by $\{11\bar{2}2\}$ contraction twinning.

A general prediction of orientation for each twin mode is carried out using D_{33}^S values. Fig. 9 plot the maximum D_{33}^S values associated with respective six $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twin variants in the full IPFs with the shown color bar. The crystal orientations with maximum D_{33}^S values around +0.08 are colored by red and less than zero are white. As shown in Fig. 9a, the maximum D_{33}^S (red domain) of $\{10\bar{1}2\}$ twins focuses on the center of IPF, which shows that the $\{10\bar{1}2\}$ twin is more favorable to accommodate the surface expansion in the grain with *c*-axis close to sample normal, coinciding with the experimental results in Fig. 5d. In Fig. 9b, the D_{33}^S value is increase with the larger deviation angle of *c*-axis from IPF center, and $\{11\bar{2}2\}$ twin is preferentially selected in the grain with *c*-axis deviated from sample normal. However, no twin was observed in

the OR2 favorable orientation with c -axis fully oriented from **ND**. Thus, as shown in Fig. 5h, the orientations of grain with $\{11\bar{2}2\}$ twin-hydride pairs are between the OR1 and OR2 favorable positions.

To further explore the variant selection among six twin variants of respective $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins, the displacement gradient tensor of OR1 hydride are transformed into different twin frames. The coordinate rotation matrix from OR1 hydride system and twinning system to crystal frame are shown as follows:

$$\mathbf{R}_{hc} = \begin{bmatrix} \eta_1 & \eta_2 & \eta_3 \\ \lambda_1 & \lambda_2 & \lambda_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{bmatrix} \text{ and } \mathbf{R}_{tc} = \begin{bmatrix} n_1 & n_2 & n_3 \\ p_1 & p_2 & p_3 \\ m_1 & m_2 & m_3 \end{bmatrix} \quad (3)$$

where η - λ - γ and n - m - p are OR1 hydriding frame and twinning frames. The transformed displacement gradient tensor (\mathbf{D}^{H-T}) from OR1 frame to twinning frame can be expressed as:

$$\mathbf{D}^{H-T} = \mathbf{R}_{tc} \cdot \mathbf{R}_{hc}^{-1} \cdot \mathbf{D}_H \cdot \mathbf{R}_{hc} \cdot \mathbf{R}_{tc}^{-1} \quad (4)$$

The D_{13}^{H-T} component of transformed tensor indicates the displacement gradient of hydride transformation happens along the shear direction on the twin plane. The twin variants with larger D_{13}^{H-T} corresponding to higher capability to accommodate the resultant strain of hydrides are preferentially selected.

The D_{13}^{H-T} transformed from activated OR1 hydride variants (B5 and B2 in Fig. 5) into corresponding twin variants of T^I and C^I are shown in Table 5. The bold variants have largest D_{13}^{H-T} values among six variants of each twin mode and thus are most capable for hydride accommodation. In Grain I, the most favorable hydride-twin pair B5- T_2^I is consistent with the experimental result. Indeed, in the grains with $\{10\bar{1}2\}$ twin like Grain I with c -axis close to diffusion direction, the accommodative hydride-twin pairs always

follow $B_i-T_{i+3}^I$. Furthermore, both C_1^I and C_2^I have the same largest D_{13}^{H-T} (+0.080) in Grain II, while the larger D_{33}^S of C_2^I (+0.008) than C_1^I (0.000) results in the final activation of $B_2-C_2^I$ pair. Thus, in the grains with orientation between OR1 and OR2 favorable ones like Grain II, the $B_i-C_i^I$ hydride-twin pair can be determined by the combination of surface expansion and twin shear accommodation.

5. Conclusion

The interactions of different hydride variants are for the first time investigated by section characterization of hydride diffusion layer through EBSD measurement. The section microstructure of hydrogen diffusion layer is dependent on Ti matrix orientation. The grains with $\{10\bar{1}3\}$ and basal plane parallel to the diffusion surface are favorable for the OR1 hydride layer with one dominant variant and multiple variants, respectively. OR3 hydrides are sometimes stimulated as well near diffusion surface of the grain with former orientation. The hydride layers in the grains with the orientations of $\langle 10\bar{1}0 \rangle$ and $\langle \bar{1}2\bar{1}0 \rangle$ aligned to the diffusion direction mainly encourage OR2 hydrides of three symmetric variants and two preferential variants, respectively.

Two types of deformation twins, $\{10\bar{1}2\}$ extension and $\{11\bar{2}2\}$ contraction twins, are observed at hydride interface to accommodate the misfit strain induced by OR1 hydride nucleation. $\{10\bar{1}2\}$ twins prefer to be formed in the grains with c -axis parallel to the diffusion direction and $\{11\bar{2}2\}$ twins in the grains located between the orientations favorable for OR1 and OR2. The orientation dependence of the stimulated twins is due to the accommodation capacity of $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twins on the hydride-induced surface expansion. The further variant selection among the six variants of each twin mode is determined via displacement gradient accommodation and denoted as $B_i-T_{i+3}^I$ and B_i-

C_i^I . Moreover, the OR2 transformation prefers to take place at grain boundary due to the larger distortion, while the accumulated prismatic dislocations in the grain interior provide favorable nucleation positions for intragranular hydride.

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Table 1
Four orientation relationships of α -Ti / δ -hydride (FCC structured) transition.

	Orientation relationship	Interface plane
OR1	$\{0001\} // \{1\bar{1}1\}$ (angle of 4°), $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$	$\{10\bar{1}3\} // \{1\bar{1}0\}$
OR2	$\{0001\} // \{001\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$	$\{10\bar{1}0\} // \{1\bar{1}0\}$
OR3	$\{10\bar{1}0\} // \{1\bar{1}1\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$	$\{0001\} // \{1\bar{1}2\}$
OR4	$\{1011\} // \{001\}$, $\langle 1\bar{2}10 \rangle // \langle 110 \rangle$	$\{10\bar{1}1\} // \{1\bar{1}\bar{1}\}$

Table 2
Variants of hydride and twin

	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5	Variant 6
OR1 hydride (B_i)	$(10\bar{1}3)[10\bar{1}0]$	$(01\bar{1}3)[01\bar{1}0]$	$(\bar{1}103)[\bar{1}100]$	$(\bar{1}013)[\bar{1}010]$	$(0\bar{1}13)[0\bar{1}10]$	$(1\bar{1}03)[1\bar{1}00]$
OR2 hydride (P_i)	$(10\bar{1}0)$	$(01\bar{1}0)$	$(\bar{1}100)$			
$\{10\bar{1}2\}$ twin (T_i^I)	$(10\bar{1}2)[\bar{1}011]$	$(01\bar{1}2)[0\bar{1}11]$	$(\bar{1}102)[\bar{1}101]$	$(\bar{1}012)[10\bar{1}1]$	$(0\bar{1}12)[01\bar{1}1]$	$(1\bar{1}02)[\bar{1}101]$
$\{11\bar{2}2\}$ twin (C_i^I)	$(11\bar{2}2)[11\bar{2}3]$	$(\bar{1}2\bar{1}2)[\bar{1}2\bar{1}3]$	$(\bar{2}112)[\bar{2}113]$	$(\bar{1}\bar{1}22)[\bar{1}\bar{1}23]$	$(1\bar{2}12)[1\bar{2}13]$	$(2\bar{1}\bar{1}2)[2\bar{1}\bar{1}3]$

Table 3
Displacement gradient tensor of OR1 hydriding and twinning in α -titanium ($c/a=1.587$).

OR1 hydride (D_H)	Twinning (D_T)	
	T^I	C^I
	$\{10\bar{1}2\} \langle \bar{1}011 \rangle$	$\{11\bar{2}2\} \langle 11\bar{2}3 \rangle$
$\begin{bmatrix} 0.055 & 0 & 0.384 \\ 0 & 0.055 & 0 \\ 0 & 0 & 0.086 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0.173 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0.218 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

Table 4
The values D_{33}^S obtained by transforming displacement gradient tensors from $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twinning frames into sample frame. The bold variants are more favorable.

	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5	Variant 6
B_5 (Grain I)	$T_1^I + \mathbf{+0.071}$	$T_2^I + \mathbf{+0.063}$	$T_3^I + \mathbf{+0.071}$	$T_4^I + \mathbf{+0.066}$	$T_5^I + \mathbf{+0.052}$	$T_6^I + \mathbf{+0.065}$
	$C_1^I -0.038$	$C_2^I -0.038$	$C_3^I -0.081$	$C_4^I -0.100$	$C_5^I -0.100$	$C_6^I -0.082$
B_2 (Grain II)	$T_1^I + \mathbf{+0.004}$	$T_2^I -0.056$	$T_3^I -0.008$	$T_4^I -0.009$	$T_5^I -0.044$	$T_6^I -0.001$
	$C_1^I 0.000$	$C_2^I + \mathbf{+0.008}$	$C_3^I -0.024$	$C_4^I + \mathbf{+0.063}$	$C_5^I + \mathbf{+0.078}$	$C_6^I -0.017$

Table 5
The values D_{13}^{H-T} obtained by transforming displacement gradient tensors from hydriding frame into the twinning frames. The bold variants are more favorable.

	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5	Variant 6
B ₅ (Grain I)	T ₁ ^I +0.120	T₂^I +0.224	T ₃ ^I +0.120	T ₄ ^I +0.089	T ₅ ^I -0.193	T ₆ ^I -0.089
B ₂ (Grain II)	C₁^I +0.080	C₂^I +0.080	C ₃ ^I -0.014	C ₄ ^I -0.108	C ₅ ^I -0.108	C ₆ ^I -0.014

1
2

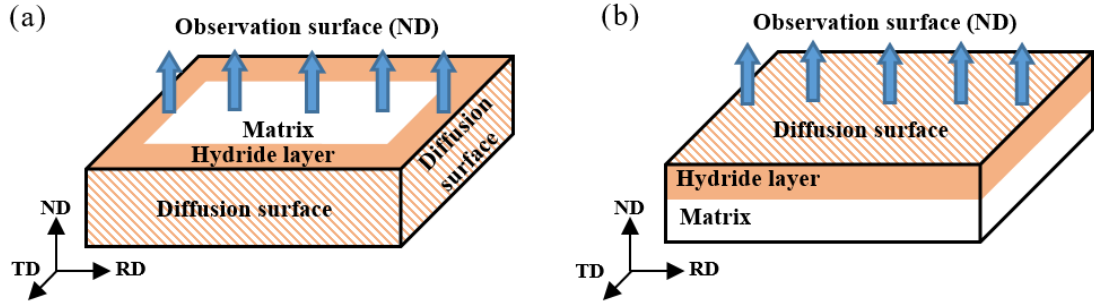


Fig. 1. Illustration of sample preparation (a) Sample A used to observe section microstructure of hydride layer and (b) Sample B for characterization of hydride induced plastic deformation.

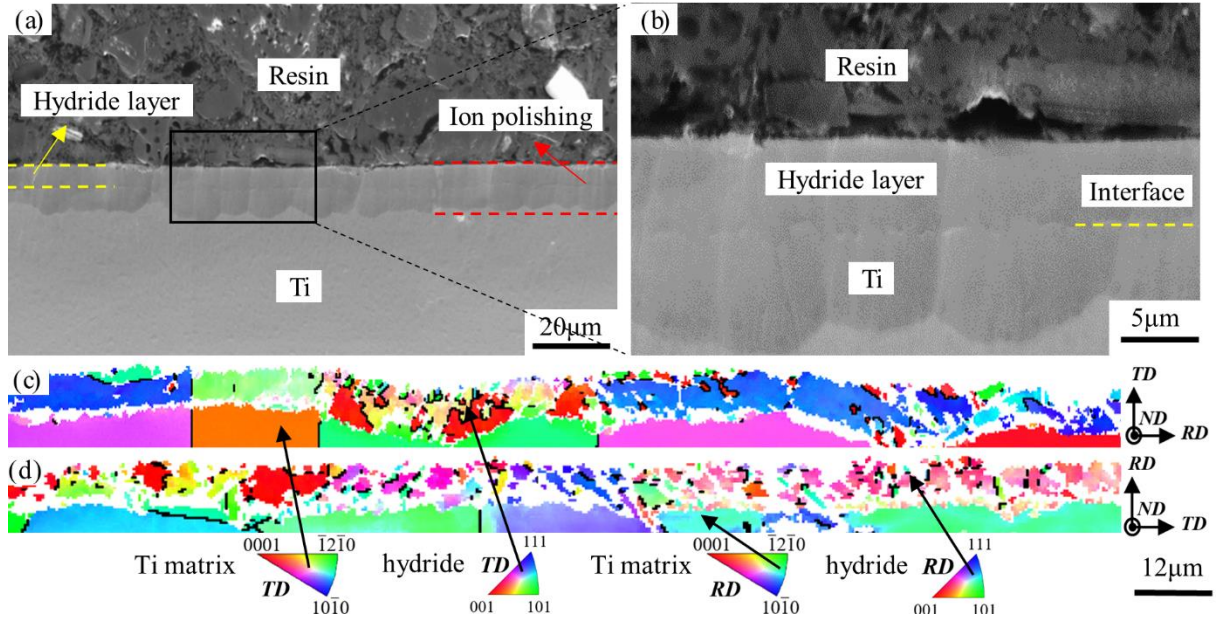


Fig. 2. (a) SEI showing section microstructure of hydride layer. (b) The higher-magnification SEM of the area in the black box. (c) **TD**-IPF maps of hydride layer formed on **TD** surface. (d) **RD**-IPF maps of hydride layer formed on **RD** surface. Grain boundaries are indicated by black lines in the IPF maps.

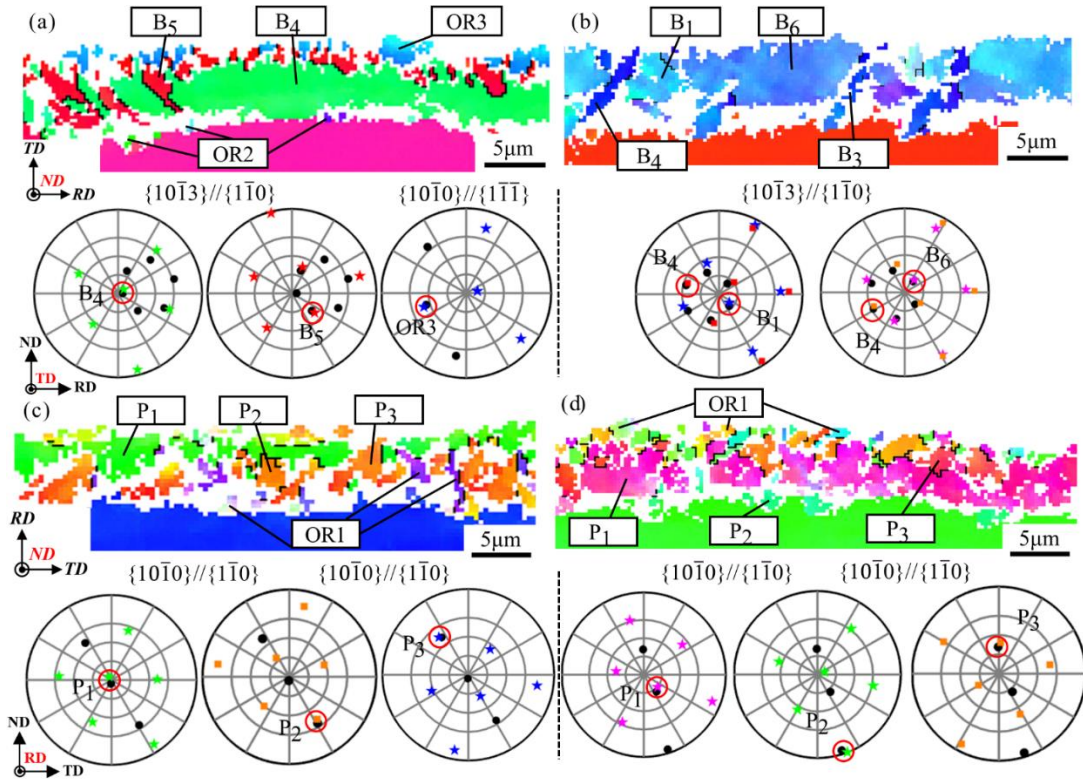


Fig. 3. IPF maps of hydride layer and corresponding pole figures of hydride variants in (a) Grain 1, Euler angle: 37.9°, 82.5°, 13.3°, (b) Grain 2, Euler angle: 166.2°, 87.1°, 26.3°, (c) Grain 3, Euler angle: 101.1°, 73.3°, 22.9° and (d) Grain 4, Euler angle: 86.7°, 57.1°, 5.2°. The IPF maps are colored with hydrogen diffusion direction. Grain boundaries are indicated by black line. The black dots in pole figures represent the $\{10\bar{1}3\}$ or $\{10\bar{1}0\}$ interface planes of Ti matrix and the color dots refer to the $\{1\bar{1}0\}$ or $\{1\bar{1}\bar{1}\}$ planes of hydrides.

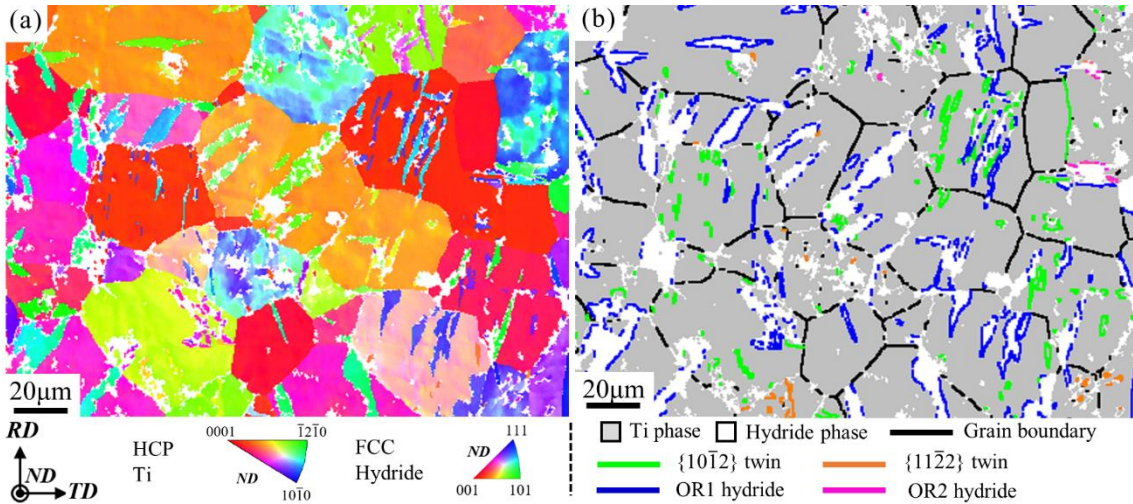


Fig. 4. (a) ND-IPF map of Ti matrix and hydride precipitates with corresponding color code. (b) Phase map with Ti matrix in silver and white hydride. The hydride and twin boundaries are highlighted by color lines: $\{10\bar{1}2\}$ extension twins (green), $\{11\bar{2}2\}$ contraction twins (orange), interface planes of OR1 hydrides (blue) and OR2 hydrides (pink). Black lines refer to grain boundaries ($>5^\circ$).

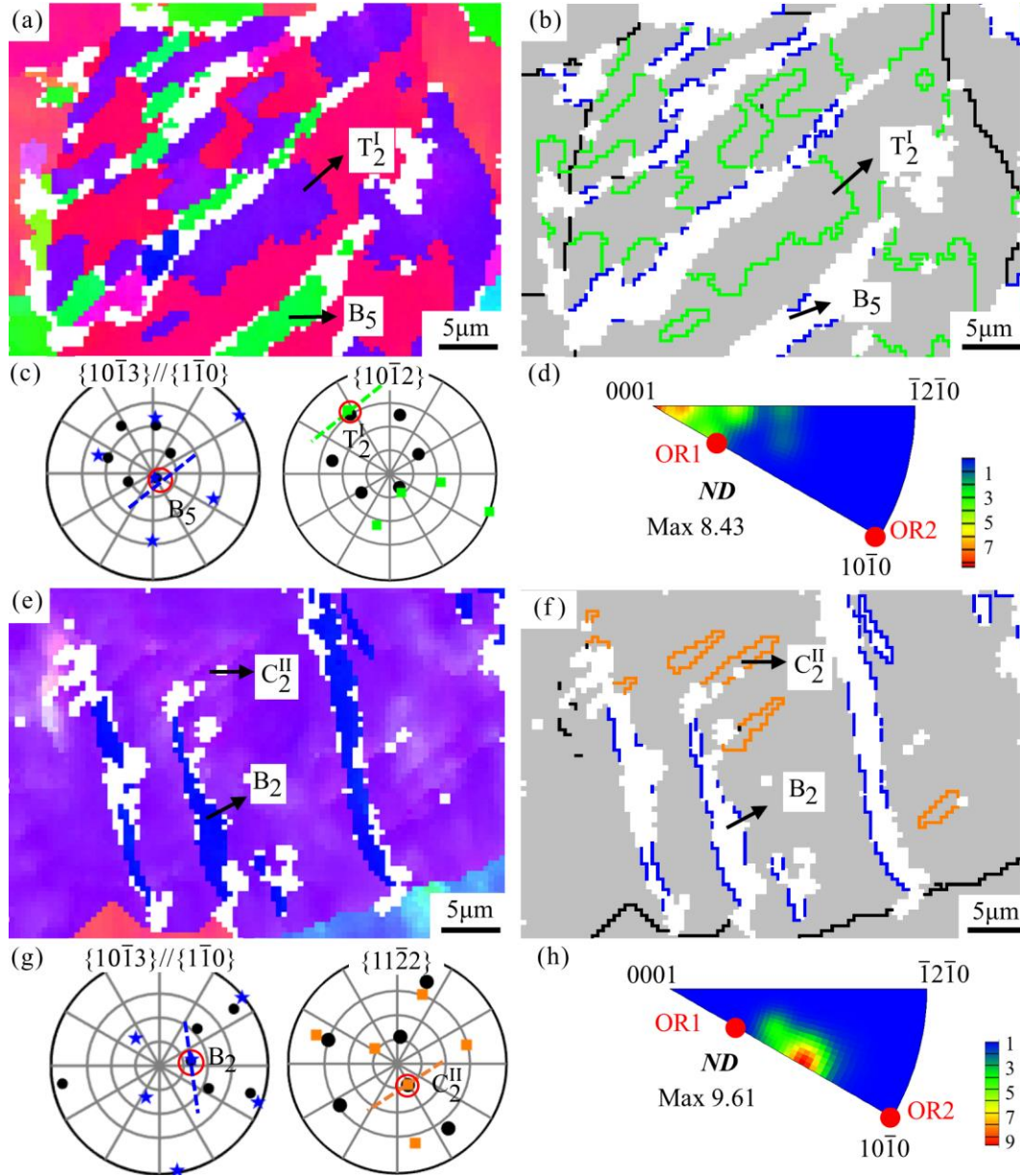


Fig. 5. (a) and (e) ND-IPF map of Grain I (Euler angles: 33.2°, 155.5°, 29.2°) containing $\{10\bar{1}2\}$ twin-hydrate pairs and Grain II (Euler angles: 100.2°, 62.6°, 25.1°) containing $\{11\bar{2}2\}$ twin-hydrate pairs. (b) and (f) Phase maps of Grain I and Grain II. The color code for the EBSD maps is the same as Fig. 4. (c) and (g) Pole figures of $\{10\bar{1}3\}$, $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ planes. The black dots represent the planes of Ti matrix and the color ones are the planes of hydrides or twins. The dotted lines represent the traces of corresponding interface planes of hydrides. (d) and (h) IPF contouring maps of all the grains with respective $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ twin-hydrate pairs. The OR1 and OR2 favorable orientations are indicated by red points.

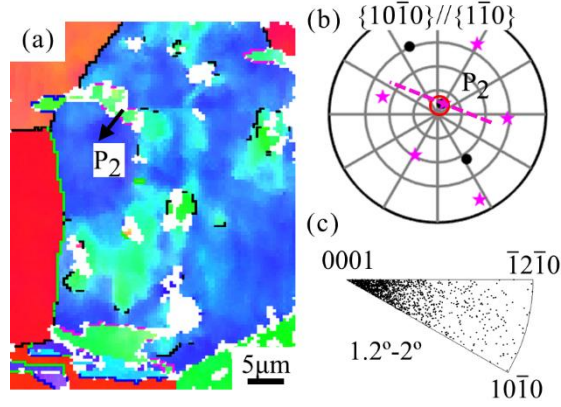


Fig. 6. (a) IPF map of Grain III (Euler angles: 116.0°, 98.2°, 21.1°) containing OR2 hydrides. The color code for the IPF maps is the same as Fig. 4. (b) {10 $\bar{1}$ 0} pole figure, the black dots represent the planes of Ti matrix and the color ones represent the hydride planes. The dotted lines represent the traces of corresponding interface planes of hydrides. (c) IGMA distributions obtained from the misorientation angles of Grain III.

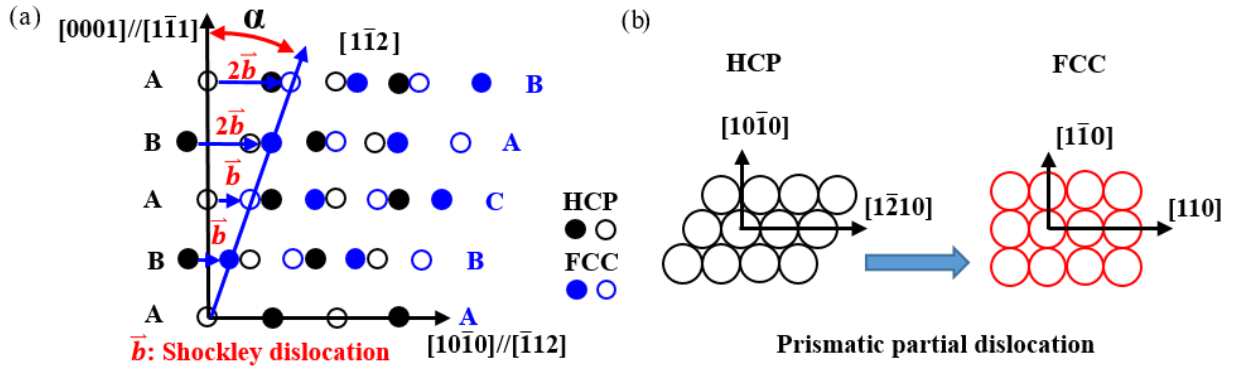


Fig. 7. Illustration of HCP-FCC structure transformation of (a) OR1 and (b) OR2 hydride. The filled and open circles are in the different atom layers.

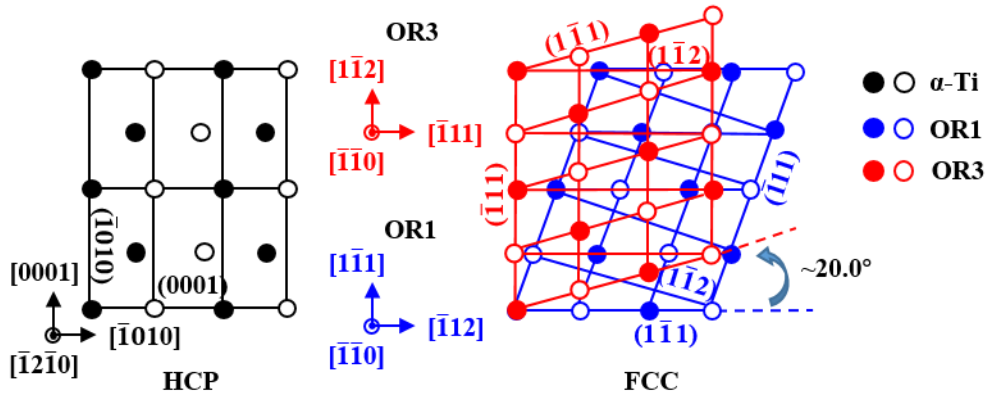


Fig. 8. The relationship of HCP-FCC structure transformations between OR1 and OR3 hydrides. The filled and open circles are in the different atom layers.

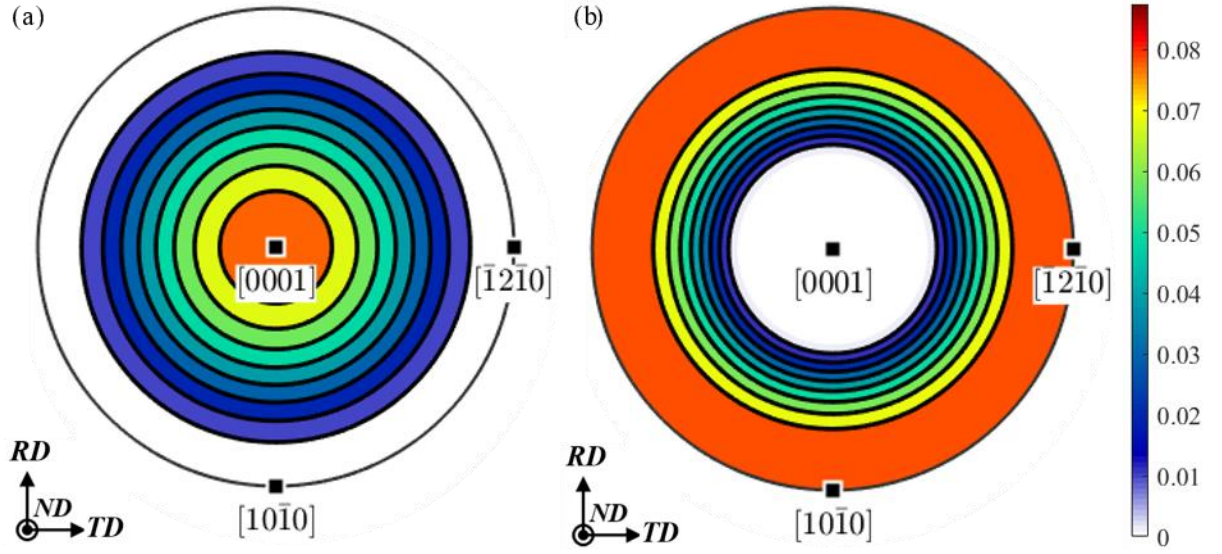


Fig. 9. Full inverse pole figure of D_{33}^S value for (a) six $\{10\bar{1}2\}$ twin variants and (b) $\{11\bar{2}2\}$ twin variants