

Article

Influence of α Lamella Width on Hydrogen Embrittlement Behavior of Ti-6Al-4V Titanium Alloy

Ziye Zhang ^{1,2}, Yuanyuan Li ^{1,2}, Wenyu Yang ^{1,2}, Yinghua Liu ^{1,2} and Bin Miao ^{1,2,*} 

¹ State Key Laboratory of High Performance Roll Materials and Composite Forming, Hebei University of Technology, Tianjin 300401, China; 202321801093@stu.hebut.edu.cn (Z.Z.); 202411801019@stu.hebut.edu.cn (Y.L.); 202421801071@stu.hebut.edu.cn (W.Y.); 202531802011@stu.hebut.edu.cn (Y.L.)

² School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300401, China

* Correspondence: miaobin@hebut.edu.cn

Abstract

Titanium alloys are susceptible to hydrogen embrittlement (HE) failure when exposed to hydrogen-containing environments, and their microstructural characteristics significantly govern the HE susceptibility. In particular, the width of α lamella in α/β dual-phase titanium alloys is a critical microstructural parameter; however, its influence on hydrogen-induced damage behavior and the associated mechanisms remain to be systematically explored. In this study, the HE behavior of Ti-6Al-4V samples with coarse and fine α lamellar structures were systematically compared via electrochemical hydrogen charging, tensile testing, fracture observation, microhardness measurement, and microstructural characterization. The results show that the coarse lamellar structure exhibits high HE susceptibility, with extensive hydride precipitation. In contrast, benefiting from the dense α/β phase interfaces that modulate hydrogen partitioning and local stress states, the fine lamellar structure significantly suppresses hydride formation, demonstrating excellent HE resistance. This study provides experimental evidence for the microstructural optimization of titanium alloys for service in hydrogen-prone environments.

Keywords: titanium alloy; α lamella width; hydrogen embrittlement; hydride

1. Introduction

Owing to their high specific strength, excellent fatigue resistance, and superior corrosion resistance [1], titanium alloys are widely used in critical components in aerospace, petrochemical, and marine engineering, such as high-temperature oil well pipes and submarine pressure hulls [2–4]. In corrosive environments, titanium alloys in contact with more electronegative metals are subject to cathodic protection [5], which can lead to catastrophic failures [6–8]. The interaction of titanium alloys with hydrogen is closely related to their crystal structure, as titanium possesses two different crystal structures: the α phase with a hexagonal close-packed (HCP) structure [9] and the β phase with a body-centered cubic (BCC) structure [10]. At room temperature, the solid solubility of hydrogen in the α phase is 0.04 at.% and in the β phase is 50 at.% [11]. When the hydrogen content in α -titanium alloys exceeds the solubility limit, hydrides form within the α grains [12]. Typical hydrides include metastable γ -hydride (TiH) with a face-centered tetragonal (FCT, $c/a > 1$) structure and stable δ -hydride with a face-centered cubic (FCC) structure. The precipitation of hydrides reduces the plasticity and toughness of the material [13,14]. In $\alpha + \beta$ dual-phase



Academic Editor: Dariusz Rozumek

Received: 19 June 2026

Revised: 9 July 2026

Accepted: 11 July 2026

Published: 14 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

titanium alloys, since the hydrogen diffusion rate in the β phase is several orders of magnitude higher than that in the α phase [15] and the incoherent α/β phase interfaces provide a large number of hydrogen absorption sites [16], hydrides preferentially nucleate at these interfaces [17]; therefore, the morphology of the α and β phases and the density of phase boundaries significantly affect the hydrogen embrittlement resistance of the alloys.

Recent studies on the relationship between phase transformation behavior and microstructural evolution have provided a foundation basis for microstructure design in titanium alloys. The addition of alloying elements can tailor the microstructure by modifying the martensitic start temperature and phase stability [18,19]. For instance, Zr addition has been shown to significantly influence the martensitic transformation behavior and microstructural evolution of Ti-V-Al high-temperature shape memory alloys [18]. Similarly, variations in Zr content can modulate the transformation between the α'' martensite and β phases in Ti-V-Al-Zr alloys, while substantially enhancing their yield strength and ductility [19]. These studies demonstrate that precise control of α/β phase transformation and lamellar structure is feasible through appropriate heat treatment and compositional design. The lamellar structure is a typical microstructure formed in $\alpha + \beta$ titanium alloys after solution treatment in the β -phase region followed by slow cooling. Previous studies have shown that refining the lamellar structure generally improves the strength and fatigue performance of the material [20,21]. However, a consensus on its effect on hydrogen embrittlement behavior is currently lacking. How the width of α lamella governs the hydrogen embrittlement resistance of titanium alloys remains poorly understood due to a lack of systematic comparative studies. In particular, the differences in hydrogen embrittlement susceptibility, hydride distribution characteristics, and fracture mechanisms between lamellar structures with two distinct width scales are still unclear.

This study investigates Ti-6Al-4V dual-phase titanium alloy. Two samples with different α lamella widths were obtained by controlling the heat treatment process. The degradation of mechanical properties, fracture morphology, and hydrogen-induced phase transformation characteristics of the two samples under electrochemical hydrogen charging conditions were systematically compared. This study aims to investigate how lamella width affects hydrogen embrittlement resistance and the underlying micro-mechanisms, thereby providing an experimental basis for microstructure optimization and safe application of titanium alloys in hydrogen-prone environments.

2. Materials and Methods

The material used in this study was Ti-6Al-4V alloy, and its chemical composition is shown in Table 1. Two types of specimens with different lamellar widths, namely a coarse lamellar structure and a fine lamellar structure, were prepared by the heat treatment process illustrated in Figure 1a. The lamellar widths were measured by the linear intercept method, and the values obtained from multiple measurements were $7.25 \pm 3.41 \mu\text{m}$ and $1.86 \pm 0.41 \mu\text{m}$ (Figure 1b,c). According to the national standard GB/T 228.1-2021 standard tensile specimens were prepared from the samples by wire electrical discharge machining [22], as shown in Figure 1d. Electrochemical hydrogen charging of the specimens (Figure 1e) was performed with a platinum anode and the specimen as the cathode in an electrolyte consisting of 33 vol.% phosphoric acid and 67 vol.% glycerol. To simulate the service process of specimens in a hydrogen-containing environment, a current density of $10 \text{ mA}/\text{cm}^2$ was used for electrochemical hydrogen charging under moderate hydrogen permeation conditions. Subsequently, tensile tests were conducted to evaluate the mechanical properties of the two microstructures in both the uncharged and hydrogen-charged

states. All tensile tests were performed at room temperature with a constant strain rate of 0.001 s^{-1} . The I_δ index was used to quantify the hydrogen embrittlement susceptibility [23]:

$$I_\delta = \frac{\delta_0 - \delta_H}{\delta_0} \times 100\%$$

where δ is the elongation at fracture, and the subscripts 0 and H denote the uncharged and hydrogen-charged specimens, respectively. Fracture morphology was observed using a TESCAN GAIA3 field-emission scanning electron microscope (SEM) (TESCAN ORSAY HOLDING, a.s., Brno, Czech Republic) and the microstructure was examined using a JEOL JEM-F200 transmission electron microscope (TEM) (JEOL Ltd., Akishima, Tokyo, Japan).

Table 1. Composition of each alloying element in Ti-6Al-4V alloy (wt.%).

Elements	Al	V	O	Fe	C	N	H	Ti
Content	6.05	4.1	0.06	0.05	0.08	0.05	0.02	Bal.

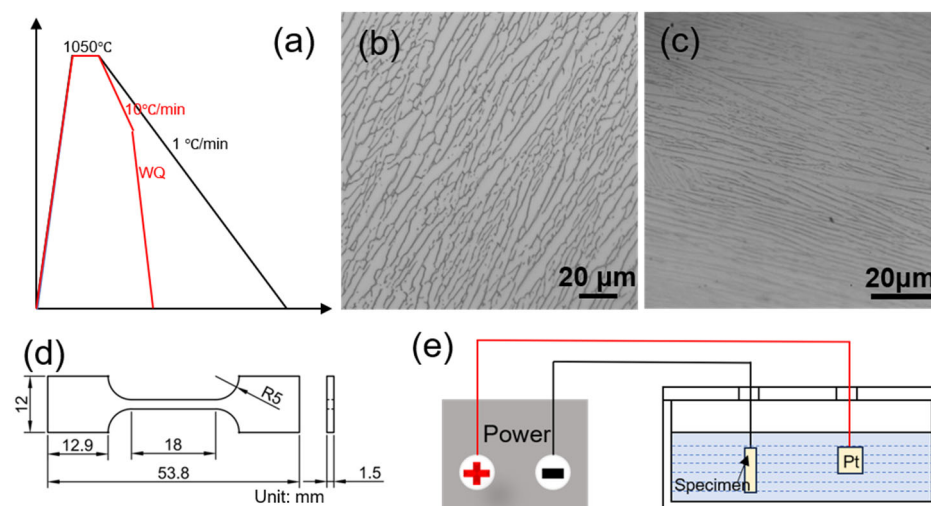


Figure 1. (a) Heat treatment process for preparing different microstructures. (b) Coarse lamellar structure. (c) Fine lamellar structure. (d) Dimensions and shape of tensile specimens. (e) Schematic diagram of electrochemical hydrogen charging.

Block-shaped specimens with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 4 \text{ mm}$ were prepared from the two microstructures for one-sided hydrogen charging experiments. During hydrogen charging, only the charging surface of each specimen was exposed to the electrolyte, while the other five surfaces were sealed with epoxy resin. A charging current density of 100 mA/cm^2 and a charging time of 30 h were adopted to accelerate hydrogen permeation into the matrix, achieve adequate diffusion depth within a short time. After charging, the cross-sections were polished and etched. The microstructural features were observed using Viyee Optics WYJ-910 upright microscope (OM) (Viyee Optics Co., Ltd., Tianjin, China). Based on the principle that the ingress of hydrogen atoms into the titanium alloy lattice induces solid-solution strengthening and lattice distortion, which in turn cause changes in microhardness, this study employed a Shimadzu HMV-G-XY-S Micro Vickers hardness tester (Shimadzu Corporation, Kyoto, Japan) to measure the hardness variation across the cross-section. At each depth, five indentations were made, the highest and lowest values were discarded, and the mean of the remaining three values was used as the hardness value, with the standard deviation used for the error bars.

3. Results and Discussion

3.1. Hydrogen Embrittlement Susceptibility of Specimens with Different Lamellar Widths

Figure 2 presents the room-temperature tensile stress-strain curves of Ti-6Al-4V alloys with two different lamellar widths, both before and after hydrogen charging. For each condition, at least three parallel specimens were tested. Figure 2a shows the changes in mechanical properties of the coarse lamellar structure. Compared with the uncharged specimen, which had a tensile strength of 808.3 MPa and an elongation of 12.1%, the tensile strength increased by 3.9% after 2 h of hydrogen charging, while the plasticity loss was as high as 38.0%, indicating a high susceptibility to hydrogen embrittlement. When the hydrogen charging time was extended to 5 h, the specimen fractured completely during the elastic stage during tensile testing, exhibiting a fully brittle fracture. Figure 2b shows that for the fine lamellar structure, compared with the uncharged specimen, the tensile strength increased by 1.4% after 2 h of hydrogen charging, while the plasticity loss was only 10.7%. After 5 h of charging, the tensile strength increased by 4.1% relative to the initial state, and the plasticity loss reached 41.7%. At this point, the plasticity loss was significantly lower than that of the coarse lamellar structure, exhibiting satisfactory overall mechanical stability. When the hydrogen charging time was further extended to 10 h, the fine lamellar structure still maintained a tensile strength higher than that of the initial state, with a plasticity loss of 63.1%. Compared with the coarse lamellar structure, it exhibited excellent hydrogen embrittlement resistance. Table 2 summarizes the tensile strength and elongation of the two microstructures before and after hydrogen charging, as well as the corresponding hydrogen embrittlement susceptibility index I_{δ} .

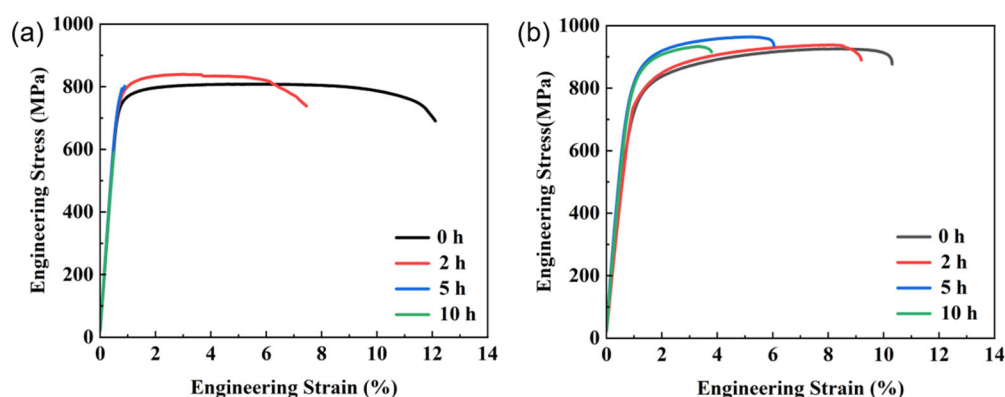


Figure 2. Engineering stress-strain curves of specimens with different microstructures after hydrogen charging. (a) Coarse lamellar structure. (b) Fine lamellar structure.

The increase in tensile strength at the initial stage of hydrogen charging mainly originates from the solid-solution strengthening effect of hydrogen atoms. Interstitial hydrogen atoms dissolve into the α -Ti lattice, inducing lattice distortion and generating an internal stress field, which impedes dislocation motion and thus enhances the material strength [24,25]. As the charging time is prolonged, the local hydrogen concentration continues to rise. Once it exceeds the solid solubility limit of α -Ti, hydrides nucleate and precipitate at phase interfaces. The incoherent interfaces formed between the precipitated hydrides and the matrix, which in turn promote microcrack initiation, at which point the tensile strength begins to decrease. Therefore, the tensile strength exhibits a trend of first increasing and then decreasing with increasing charging time, essentially reflecting a stage-wise transition in the dominant mechanism of hydrogen action from “solid-solution strengthening” to “hydride-induced embrittlement.”

The elongation of both microstructures gradually decreased with increasing charging time. This decrease is primarily attributed to the deformation incompatibility between hy-

drides and the matrix [26,27]. Previous studies have shown that the crack propagation rate in lamellar Ti-6Al-4V alloys during deformation is inversely proportional to the lamellar width [28]. However, in the present study, although the finer lamellar structure provided more hydrogen diffusion channels and trapping sites, the hydrogen embrittlement effect was not enhanced. This indicates that the beneficial effect of microstructural refinement on the initial properties of the material is not consistent with its effect on improving hydrogen embrittlement resistance, and that other intrinsic factors govern the hydrogen embrittlement behavior. The underlying mechanisms still require further in-depth investigation.

Table 2. Mechanical properties of Ti-6Al-4V alloy with different microstructures during tensile testing after various hydrogen charging times.

Sample	Hydrogen/h	Tensile Strength/MPa	Elongation/%	I_{δ} /%
coarse lamellar structure	0	808.3	12.1	0
	2	839.8	7.5	38.0
	5	801.9	0.88	92.7
	10	590.3	0.47	96.1
fine lamellar structure.	0	925.8	10.3	0
	2	938.4	9.2	10.7
	5	964.0	6.0	41.7
	10	933.5	3.8	63.1

3.2. Fracture Characteristics Analysis of Specimens with Different Lamellar Widths After Hydrogen Charging

Figure 3 shows the fracture morphology evolution of the coarse lamellar structure under different hydrogen charging times. The low-magnification fracture surface of the uncharged specimen (Figure 3a) exhibits pronounced undulating features. The high-magnification images of three characteristic locations (Figure 3b–d) all show large and deep dimples. As shown in Figure 3f, after 2 h of hydrogen charging, the dimple size decreased, the dimples became shallower, and microcracks were observed along the α/β phase interfaces. After 5 h of charging, cleavage fracture occurred and necking was absent. After 10 h of charging, the specimen exhibited an interlamellar cleavage fracture morphology, with flat and uniformly oriented cleavage planes and distinct lamellar contours (indicated by yellow arrows). It can be clearly observed that cracks propagated along the α/β phase interfaces in the coarse lamellar structure. The coarse lamellar structure is highly sensitive to hydrogen, and with increasing charging time, the fracture mode transitions from ductile fracture to fully brittle cleavage fracture.

The fracture morphologies of the fine lamellar structure are shown in Figure 4. In the uncharged initial state, the fracture surfaces at the three observation locations exhibited pronounced tearing edges and ridges, showing typical ductile fracture features (Figure 4a–d). After 2 h of hydrogen charging (Figure 4e–h), the central part of the specimen (Figure 4f) still retained numerous dimple structures, indicating that the central region was less affected by hydrogen and did not embrittle. The upper and left regions also displayed large and deep dimples, and the overall features remained ductile fracture. When the charging time was further increased to 5 h, as shown in Figure 4i–l, dimples could still be observed in local areas of the central part, whereas the fracture morphology of the peripheral regions, especially the region in Figure 4l, had transformed into brittle fracture characteristics. The fracture mode was mixed ductile-brittle fracture. After 10 h of hydrogen charging, the fine lamellar structure maintained a mixed ductile-brittle fracture mode without undergoing complete embrittlement.

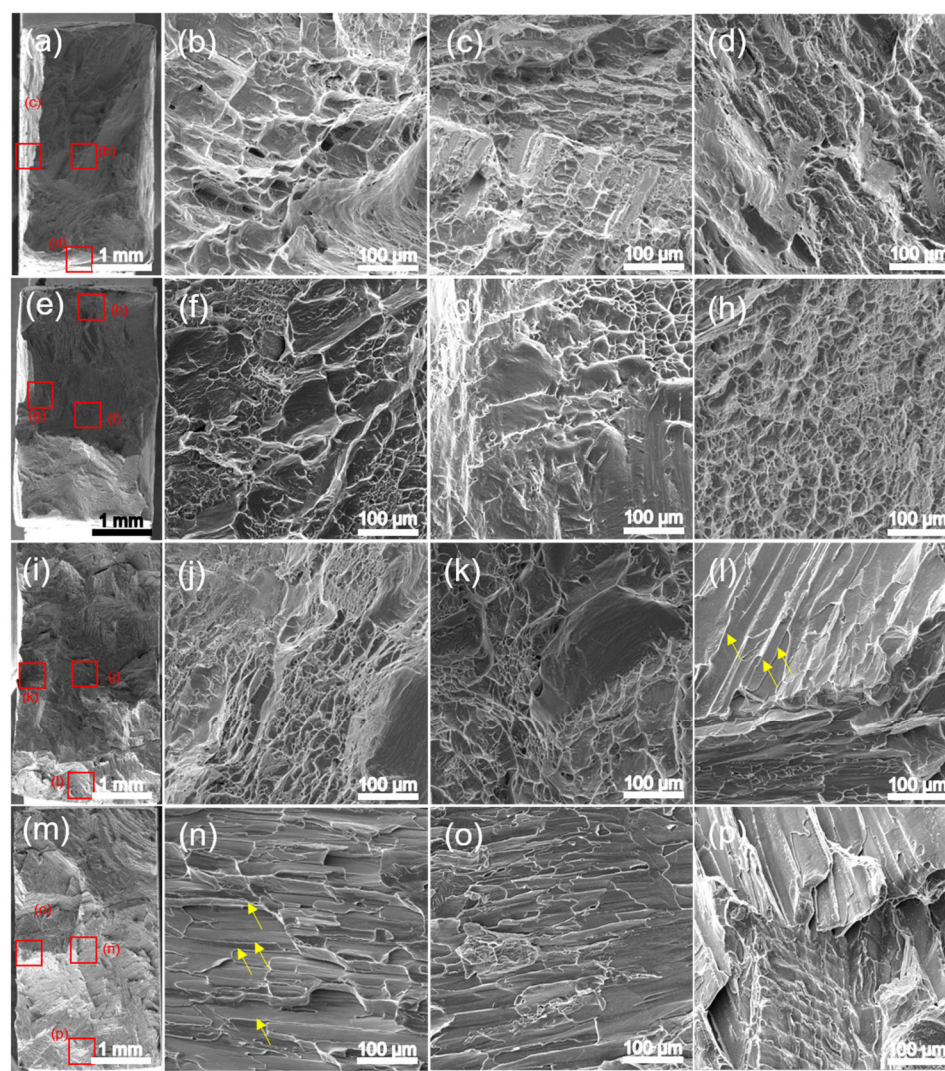


Figure 3. Fracture morphologies of the coarse lamellar structure with different hydrogen charging times. (a–d) Uncharged sample. (e–h) Sample charged for 2 h. (i–l) Sample charged for 5 h. (m–p) Sample charged for 10 h. (a,e,i,m) are the low-magnification SEM images. Enlarged SEM images are taken at the red boxes region, with the subscript letters denoted besides.

In the coarse lamellar structure, cracks propagated almost exclusively along the α/β phase interfaces, exhibiting interfacial decohesion fracture. The underlying mechanism is that under tensile stress, the hydrides precipitated at the phase interfaces become weak points and readily induce crack initiation and propagation, which is consistent with the findings of Kim et al. [16]. The spatial variation between the center and the edge regions of the fracture surface in the fine lamellar specimen after hydrogen charging can be attributed to the gradient distribution of hydrogen concentration. During electrochemical hydrogen charging, hydrogen atoms diffuse inward from the specimen surface, establishing a hydrogen concentration gradient from the surface to the interior [29]. The edge region (near the surface) has a higher hydrogen concentration and thus undergoes more severe hydrogen-induced damage, so the fracture morphology exhibits brittle features earlier. In contrast, the center region has a relatively lower hydrogen concentration and retains more dimple structures. As the charging time increases, hydrogen continuously penetrates inward, and the hydrogen concentration in the center region gradually rises, leading to increased damage, as evidenced by a progressive decrease in dimples and a gradual enhancement of brittle characteristics. In contrast, under the same conditions, the fine lamellar structure did not undergo complete brittle fracture, indicating better hydrogen embrittlement resistance.

This phenomenon has not been previously documented, and the underlying reasons for the superior hydrogen embrittlement resistance of the fine lamellar structure remain to be elucidated.

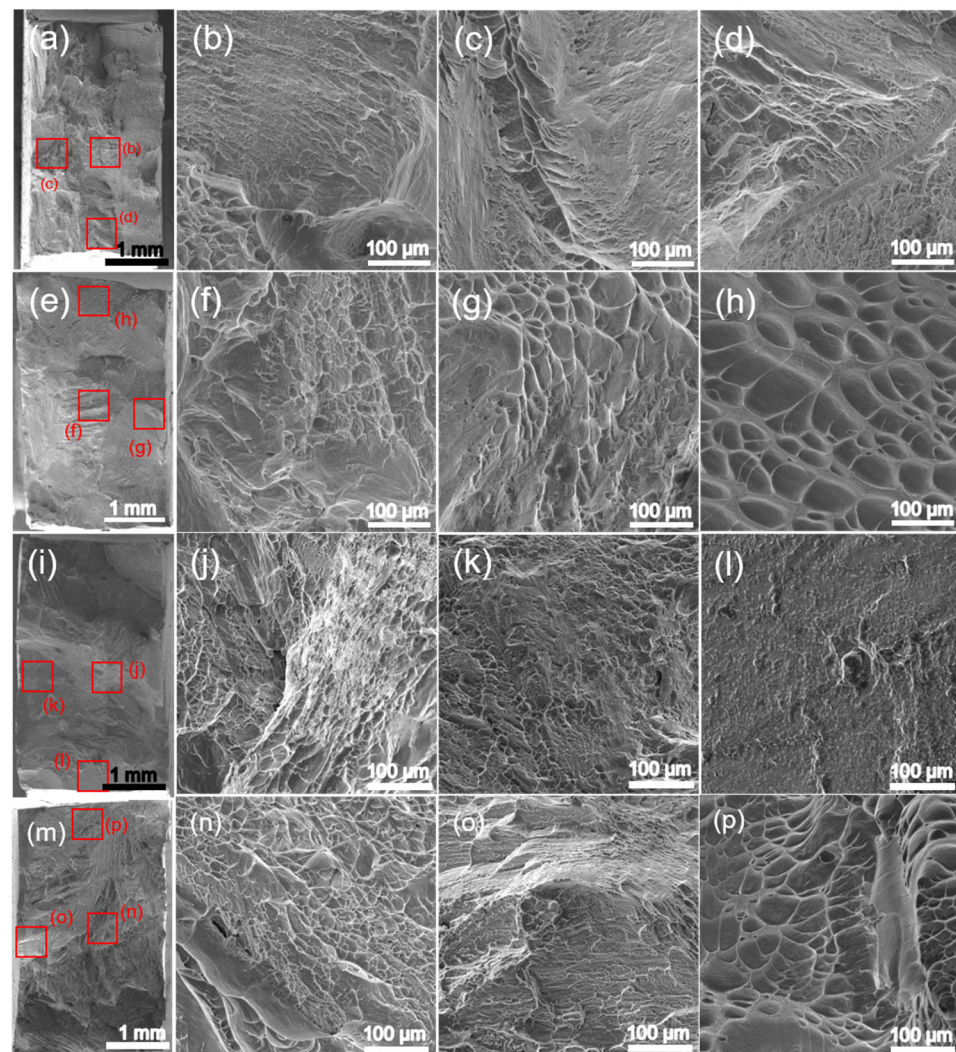


Figure 4. Fracture morphologies of the fine lamellar structure under different hydrogen charging times. (a–d) Uncharged sample. (e–h) Sample charged for 2 h. (i–l) Sample charged for 5 h. (m–p) Sample charged for 10 h. (a,e,i,m) are the low-magnification SEM image. Enlarged SEM images are taken at the red boxes region, with the subscript letters denoted besides.

3.3. Hydrogen Diffusion Depth in Specimens with Different Lamellar Widths

To investigate the hydrogen diffusion depth in specimens with two different lamellar widths, one-sided hydrogen charging experiments were conducted. To clearly reveal the actual morphology and distribution characteristics of hydrides in the specimens, the same region was analyzed by electron backscattered (EBSD), SEM, and OM (Figure 5). The morphology of hydrides under the optical microscope was confirmed. The phase identified as hydride appears as a blue region in the phase map (Figure 5a), corresponding to the gray-white precipitates with acicular geometry at the α/β phase interfaces observed under SEM (Figure 5b). In the optical micrograph (Figure 5c), these regions exhibit clearly distinguishable gray-black acicular or clustered structures after etching.

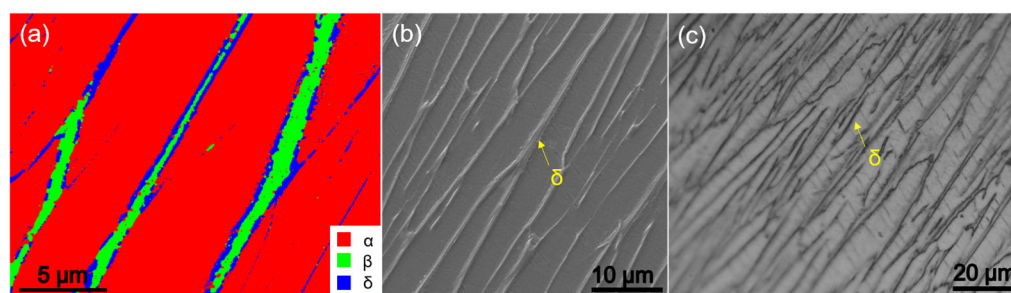


Figure 5. The microstructure morphology of Ti-6Al-4V after hydrogen charging. (a) EBSD phase diagram. (b) SEM diagram. (c) OM diagram. The hydride precipitates are indicated by yellow arrows and annotated as δ .

Figure 6 shows the cross-sectional microstructural changes in Ti-6Al-4V specimens with two different microstructures after one-sided hydrogen charging for 30 h. In the coarse lamellar structure, numerous microcracks formed in the surface layer, propagating mainly along the α/β phase interfaces. Hydrides were present over an extensive depth range in the coarse lamellar structure, and pronounced hydride precipitation could still be observed at a depth of 2300 μm from the surface (Figure 6b–d). In contrast, for the fine lamellar structure, hydrides formed only in the surface layer within several hundred micrometers (Figure 6f). To investigate the distribution range of hydrides (the region where hydride precipitation is observable under optical microscopy), microstructural observations were performed at distances of 850 μm and 1350 μm from the charging surface (Figure 6g,h). The results showed that no hydrides were observed at these two depths, indicating that the hydride precipitation range in the fine lamellar structure was limited to the surface layer and confined to the surface layer.

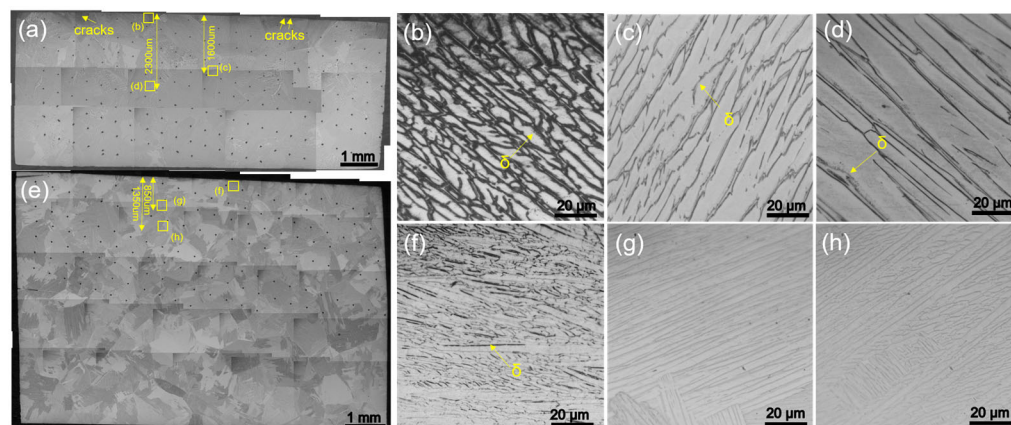


Figure 6. Microstructural evolution with two different microstructures after hydrogen charging at a current density of 100 mA/cm^2 for 30 h. (a–d) Coarse lamellar structure. (e–h) Fine lamellar structure. (a,e) are the low-magnification OM images. Enlarged OM images are taken at the yellow boxes region at different positions, with the subscript letters denoted besides. The hydride precipitates are indicated by yellow arrows and annotated as δ .

In addition to microstructural observations, hardness tests at different depths were performed on both specimens. Figure 7 shows the variation in hardness along the depth direction for the two specimens with different lamellar widths after one-sided hydrogen charging. The initial hardness values of the uncharged specimens were determined to be 292.2 HV for the coarse lamellar structure and 317.5 HV for the fine lamellar structure. These values increase as the lamellar width decreases, which is consistent with the hardness variation reported for lamellar structures with different widths obtained by varying the cooling rate [30]. These two values are indicated by the horizontal blue dashed lines in

Figure 7. For lamellar structures, refinement increases the density of interfaces between adjacent secondary α phases. As crystal defects, these interfaces significantly hinder dislocation motion, making dislocation slip difficult. Therefore, the fine lamellar structure of the Ti-6Al-4V alloy exhibits higher hardness. For the coarse lamellar structure after hydrogen charging, the surface hardness increased by 60 HV compared with the uncharged state, and the hardness across the entire thickness (0–3800 μm) remained higher than the baseline value, indicating reaching a hydrogen diffusion depth of up to 3800 μm in the coarse lamellar structure. For the fine lamellar structure, the hardness in the near-surface region was approximately 340 HV, representing an increase of 20 HV compared with the uncharged state. As the depth increased, the hardness gradually fell below the uncharged state. When the depth reached approximately 4000 μm , the hardness gradually returned to the original level. For the fine lamellar structure, in the depth range of 850–3500 μm , the hardness was significantly lower than that of the uncharged specimen, suggesting that hydrogen-induced effects extended to approximately 4000 μm below the surface.

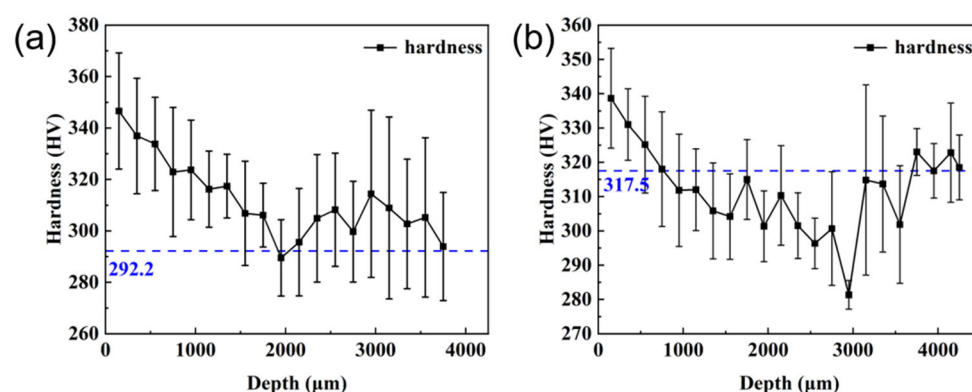


Figure 7. Hardness variation trends of two microstructures after unidirectional hydrogen charging. (a) Coarse lamellar structure. (b) Fine lamellar structure.

The hydrogen-affected region (the permeation depth of hydrogen atoms detected) appeared comparable based on hardness variation, the hydrogen-affected depth in both the coarse and fine lamellar structures was approximately 4 mm. The change in microhardness after hydrogen charging results from the synergistic action of multiple factors, mainly including: (1) the solid-solution strengthening effect of hydrogen atoms; (2) changes in the microscopic stress field caused by hydrogen-induced lattice distortion; (3) second-phase strengthening due to hydride precipitation [31]; and (4) the modulation of dislocation behavior by hydrogen [32,33]. In this study, the hardness of the fine lamellar structure in the depth range of 850–3500 μm was lower than the initial value, combined with the optical microscopy images in Figure 6, where no hydrides were visible. This phenomenon can be attributed to the lattice softening effect caused by dissolved hydrogen, which results from the reduction in the dislocation source activation stress and the dislocation line tension due to hydrogen [32,33]. As the hydrogen content increases, solid-solution strengthening occurs. When the local hydrogen concentration exceeds the solid solubility, hydrides precipitate, and precipitation hardening dominates. Compared with the coarse lamellar structure, the hydrogen-induced surface hardening rate in the fine lamellar structure is lower than that in the coarse lamellar structure, suggesting that the fine lamellar structure exhibits a lower local hydrogen concentration than its coarse counterpart [34]. It should be noted that techniques such as Thermal Desorption Spectroscopy (TDS), and Secondary Ion Mass Spectrometry (SIMS) can more directly characterize the distribution and content of hydrogen. It worth to further characterize the hydrogen distribution in the one-sided hydrogen charged specimen in the future and confirm the discussion here.

3.4. Deformation Behavior Characteristics of Hydrogen-Charged Specimens with Different Lamellar Widths

Figure 8 shows TEM images of the coarse lamellar structure after different hydrogen charging times, taken from the same location near the tensile fracture surface (approximately 50 μm from the surface). In the specimen charged for 2 h (Figure 8a,b), no hydrides were observed. Plastic deformation was mainly characterized by planar dislocation slip, and dislocations were able to pass through and shear the β phase. After 10 h of charging (Figure 8c–f), the SAED patterns taken at the α/β phase interfaces revealed the α phase with a hexagonal close-packed (HCP) structure, the β phase with a body-centered cubic (BCC) structure, and characteristic diffraction spots of a face-centered cubic structure, which are consistent with the standard diffraction pattern of $\delta\text{-TiH}_x$. To further elucidate the formation mechanism of the δ -hydride, a more detailed crystallographic analysis of the SAED pattern in Figure 8c was performed. Detailed indexing of the SAED pattern revealed a well-defined crystallographic orientation relationship between the δ -hydride and the α matrix, namely: $[0001]_\alpha \parallel [001]_\delta$ and $(01\bar{1}0)_\alpha \parallel (\bar{2}20)_\delta$ [35]. The existence of this specific orientation relationship confirms that the additional diffraction spots originate from the δ -hydride phase rather than from double diffraction or thickness effects. The observed crystallographic correspondence further indicates that the hydride precipitates maintain a strong crystallographic constraint with the surrounding α matrix during precipitation. This orientation relationship indicates that the δ -hydride nucleates preferentially at the α/β phase interfaces with a specific crystallographic alignment, which is consistent with the mechanism by which hydrogen diffusion along the α/β interfaces leads to local supersaturation [16]. In addition, careful examination of the β -phase diffraction spots in the SAED patterns reveals slight diffuse scattering or elongation in some cases, suggesting a certain degree of lattice distortion in the β phase. This phenomenon is most likely attributed to the lattice expansion caused by the interstitial incorporation of hydrogen atoms into the β -phase lattice [36]. However, since the diffuse scattering is relatively weak and does not reach the level that could be definitively indexed as a strain-induced new phase (e.g., β' or β''), this observation is attributed to hydrogen-induced lattice distortion rather than a distinct structural transformation of the β phase.

Under the present experimental conditions, no characteristic diffraction spots of martensite (α' or α'') were identified in the SAED patterns, nor were typical lath-like or acicular morphologies observed in the bright-field TEM images. This is also consistent with the well-established kinetic condition that martensitic transformation in titanium alloys typically requires rapid cooling ($>410^\circ\text{C/s}$) or high strain rates [37], conditions not met in the present room-temperature charging process. The high-resolution images in Figure 8e–f further confirm that the phase observed at the α/β interface is the δ -hydride. This result is consistent with earlier reports on hydride precipitation at the interfaces of dual-phase titanium alloys after hydrogen charging [16]. To further clarify the distribution characteristics of the δ -hydride, dark-field imaging was performed using the (200) diffraction spot of the δ -hydride, and the results are shown in Figure 8d. A hydride with a width of approximately 90 nm formed at the α/β phase interface.

Figure 9 shows TEM images of the deformed fine lamellar structure after hydrogen charging for 2 h and 10 h. The specimens were taken from the same location near the tensile fracture surface (approximately 50 μm from the surface). In the specimen charged for 2 h (Figure 9a,b), no hydride precipitation was observed. Dislocations were accumulated at the phase interfaces, and plastic deformation occurred mainly via dislocation slip. After 10 h of charging (Figure 9c,d), only α and β phases were present in the specimen, and no hydride precipitation was observed.

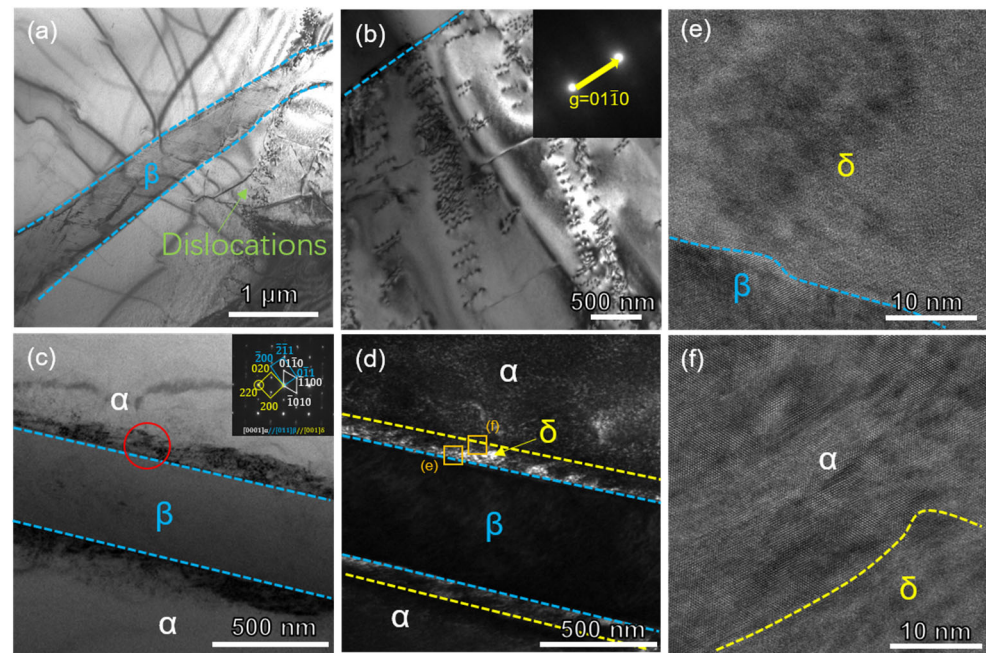


Figure 8. TEM observations of the coarse lamellar structure after hydrogen charging. (a) Bright-field TEM image of the specimen charged for 2 h. The blue dashed lines delineate the boundaries of β phase. (b) Dislocation distribution in the specimen charged for 2 h shown at two beam condition, the g value of which is given as the inset. (c) Bright-field TEM morphology of β lamellae in the specimen charged for 10 h, with the inset showing the selected area electron diffraction (SAED) pattern near the phase interfaces (red circle region). (d) Dark-field TEM image of hydrides. The yellow dashed lines delineate the boundaries of hydrides. (e,f) High-resolution TEM images of the interface of hydrides as indicated by orange boxes region in (d).

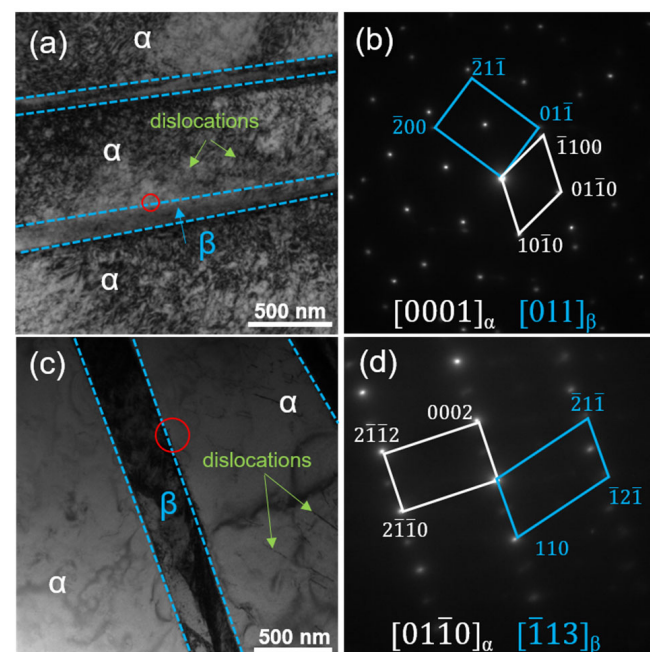


Figure 9. TEM observations of the fine lamellar structure after hydrogen charging. (a) Bright-field TEM image of the fine lamellar structure in the sample hydrogen-charged for 2 h. The blue dashed lines delineate the boundaries of β phase. (b) Diffraction pattern of the region marked by the red circle in (a). (c) Bright-field TEM image of the fine lamellar structure in the sample hydrogen-charged for 10 h. (d) Diffraction pattern of the region marked by the red circle in (c).

Combined with the optical microscopy observations in Figure 6, hydrides were observed only within a few hundred micrometers from the surface in the fine lamellar structure, whereas in the coarse lamellar structure, the hydride distribution extended over a much broader region. This spatial difference indicates that the refined α lamellae significantly impede hydride formation. Figure 8 provide crystallographic evidence for hydride precipitation at the α/β phase interfaces. In contrast, in the fine lamellar structure (Figure 9), no hydrides were detected, also suggesting that their formation is limited. This is consistent with the findings of Lulu-Bitton et al. [38], who demonstrated that α/β phase interfaces can act as uniformly distributed hydrogen traps that promote hydrogen dispersion, thereby delaying the accumulation of local hydrogen concentration to the solubility limit. Collectively, these observations indicate that the refined lamellar structure can effectively inhibit the formation of hydrides, which is the key to its excellent hydrogen embrittlement resistance.

3.5. Discussion

The poor hydrogen embrittlement resistance of lamellar structures has been widely attributed to their continuous β network and higher hydrogen uptake capacity to other microstructural types [38–40]. In this study, by comparing the changes in mechanical properties of two lamellar specimens with different widths under the same hydrogen charging conditions, the significant influence of α lamella width on hydrogen embrittlement susceptibility was identified, and refining the lamellar structure was found to effectively improve hydrogen embrittlement resistance. Microstructural observations (Figures 7–9) show that the α lamella width plays an obvious regulatory role in hydrogen diffusion, hydride precipitation, and hydrogen-induced crack initiation, and that the fine lamellar structure effectively suppresses the formation of hydrides.

The principle by which the refined lamellar structure enhances the hydrogen embrittlement resistance of Ti-6Al-4V titanium alloy is illustrated in Figure 10. Figure 10a illustrates the initial state of the two lamellar structures before hydrogen charging. The fine lamellar structure possesses a significantly higher density of α/β phase interfaces compared with the coarse lamellar structure, whereas the coarse structure has relatively fewer phase interfaces. When the material is exposed to a hydrogen-rich environment, hydrogen atoms penetrate from the surface, diffuse along the β phase toward the α phase, and accumulate at the α/β phase interfaces. As shown in Figure 10b, the densely distributed α/β phase interfaces in the fine lamellar structure serve as numerous uniformly dispersed trapping sites for hydrogen atoms [38]. These interfaces effectively promote the spatial dispersion of hydrogen, thereby retarding the build-up of local hydrogen concentration and delaying the onset of hydride nucleation. In contrast, in the coarse lamellar structure, the lower density of phase interfaces allows hydrogen atoms to segregate more readily at limited interfacial sites, leading to faster local supersaturation.

With prolonged hydrogen charging time (Figure 10c), the α phase in the coarse lamellar structure reaches the solid solubility limit for hydrogen, resulting in the nucleation and precipitation of hydrides at phase interfaces and within the grains. The precipitated hydrides form incoherent interfaces with the matrix, accompanied by volume expansion, which induces local stress concentration and microcrack initiation, ultimately causing a sharp decline in tensile performance. In the fine lamellar structure, however, the abundant phase interfaces effectively disperse the hydrogen atoms, so that the local hydrogen concentration is less likely to exceed the critical concentration required for hydride nucleation. Consequently, hydrogen stays predominantly in interstitial solid solution, and hydride formation is substantially suppressed. Furthermore, the narrower β lamellae in the fine structure undergo smaller volume expansion upon hydrogen charging, giving rise to a

lower degree of localized stress concentration at the interfaces [16], which further alleviates the embrittlement effect. Therefore, the fine lamellar structure exhibits excellent hydrogen embrittlement resistance during tensile testing, primarily attributed to the synergistic actions of dense phase interfaces as hydrogen traps and strain homogenization via reduced volume expansion.

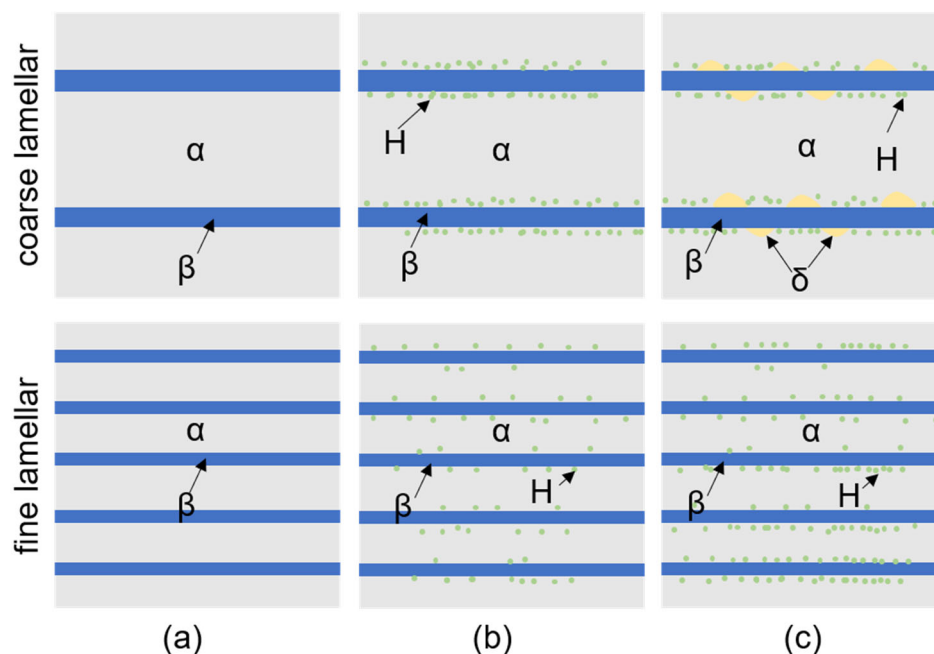


Figure 10. Schematic diagram illustrating the mechanism by which the refined lamellar structure improves the hydrogen embrittlement resistance of Ti-6Al-4V titanium alloy. (a) Before hydrogen charging. The blue rectangles outline the β -phase regions, the white rectangles outline the α -phase regions. (b) After a short period of hydrogen charging. Bullets mark the positions of hydrogen atoms. (c) After prolonged hydrogen charging. The yellow areas indicate hydride precipitates.

4. Conclusions

Electrochemical hydrogen charging experiments and microstructural characterization were performed on Ti-6Al-4V titanium alloys with two different lamellar widths to investigate their hydrogen embrittlement susceptibility. The main findings are as follows:

1. After hydrogen charging under the same conditions, the coarse lamellar structure exhibited severe plasticity loss, with complete plastic loss after 5 h of charging, indicating high hydrogen embrittlement susceptibility. In contrast, the fine lamellar structure showed a smaller plasticity loss, reaching 63.1% after 10 h of charging, while demonstrating superior hydrogen embrittlement resistance.
2. Despite comparable hydrogen-affected depths in both structures, the hydride formation characteristics were markedly different. The coarse lamellar structure exhibited extensive hydride precipitation over a wide range, with hydride-induced embrittlement as the dominant damage mechanism. In contrast, the fine lamellar structure showed only limited hydride precipitation within a restricted region, where hydrogen-induced plasticity damage prevailed.
3. For the lamellar Ti-6Al-4V titanium alloy, appropriately refining the α lamella width can modify hydrogen distribution and hydride precipitation behavior, thereby suppressing hydride-induced embrittlement. This represents an effective microstructural design strategy for improving the hydrogen embrittlement resistance of titanium alloys.

In addition, it is worth noting that this work does not involve numerical modeling; hence, a quantitative analysis of stress-affected hydrogen diffusion is yet to be achieved. In the future, we will adopt multi-scale simulation approaches to systematically investigate the synergistic effects of phase-interface density, lamellar width, and residual stress on hydrogen-induced crack initiation, aiming to deepen the mechanistic understanding from a computational perspective.

Author Contributions: Conceptualization, B.M.; formal analysis, Z.Z., Y.L. (Yuanyuan Li), W.Y. and Y.L. (Yinghua Liu); methodology, Z.Z. and Y.L. (Yuanyuan Li); investigation, Z.Z., Y.L. (Yuanyuan Li), W.Y. and Y.L. (Yinghua Liu); writing—original draft, Z.Z.; writing—review and editing, Y.L. (Yuanyuan Li), W.Y., Y.L. (Yinghua Liu) and B.M.; visualization, Z.Z.; project administration, B.M.; funding acquisition, B.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the financial support from the Hebei Natural Science Foundation (No. E2025202231), the Tianjin Natural Science Foundation (No. 25JCYBJC00980), the Hebei Major Science and Technology Special Project (No. 252G1003D), and the Hebei Yanzhao Talent Program (No. B2025003). The authors also thank the support of instruments from the Advanced Materials Testing and Analysis Center of Hebei University of Technology.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Li, W.; Zhu, S.; Wang, C.; Chen, M.; Shen, M.; Wang, F. SiO₂-Al₂O₃-glass composite coating on Ti-6Al-4V alloy: Oxidation and interfacial reaction behavior. *Corros. Sci.* **2013**, *74*, 367–378. [\[CrossRef\]](#)
2. Williams, J.; Boyer, R. Opportunities and Issues in the Application of Titanium Alloys for Aerospace Components. *Metals* **2020**, *10*, 705. [\[CrossRef\]](#)
3. Sun, Z.; Hou, H.; Zhou, W.; Wang, Y.; Li, Z. The effect of hydrogen on microstructures evolution and deformation behaviors of Ti-6Al-4V alloys. *J. Alloys Compd.* **2009**, *476*, 550–555. [\[CrossRef\]](#)
4. Liu, H.; Zhou, L.; Liu, P.; Liu, Q. Microstructural evolution and hydride precipitation mechanism in hydrogenated Ti-6Al-4V alloy. *Int. J. Hydrogen Energy* **2009**, *34*, 9596–9602. [\[CrossRef\]](#)
5. Li, J.; Oudriss, A.; Metsue, A.; Bouhattate, J.; Feaugas, X. Anisotropy of hydrogen diffusion in nickel single crystals: The effects of self-stress and hydrogen concentration on diffusion. *Sci. Rep.* **2017**, *7*, 45041. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Nguyen, T.-D.; Singh, C.; Lee, D.-H.; Kim, Y.S.; Lee, T.; Lee, S.Y. Deciphering Hydrogen Embrittlement Mechanisms in Ti6Al4V Alloy: Role of Solute Hydrogen and Hydride Phase. *Materials* **2024**, *17*, 1178. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Hardie, D.; Charles, E.; Lopez, A. Hydrogen embrittlement of high strength pipeline steels. *Corros. Sci.* **2006**, *48*, 4378–4385. [\[CrossRef\]](#)
8. Sinha, V.; Schwarz, R.; Mills, M.; Williams, J. Influence of hydrogen on dwell-fatigue response of near-alpha titanium alloys. *Acta Mater.* **2020**, *188*, 315–327. [\[CrossRef\]](#)
9. Chapman, T.; Dye, D.; Rugg, D. Hydrogen in Ti and Zr alloys: Industrial perspective, failure modes and mechanistic understanding. *Philos. Trans. R. Soc. A* **2017**, *375*, 20160418. [\[CrossRef\]](#)
10. Ouyang, P.; Mi, G.; Li, P.; He, L.; Cao, J.; Huang, X. Non-Isothermal Oxidation Behavior and Mechanism of a High Temperature Near- α Titanium Alloy. *Materials* **2018**, *11*, 2141. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Alvarez, A.; Robertson, I.; Birnbaum, H. Hydrogen embrittlement of a metastable β -titanium alloy. *Acta Mater.* **2004**, *52*, 4161–4175. [\[CrossRef\]](#)
12. Chen, C.; Li, S.; Lu, K. The deformation behaviors of gamma hydrides in titanium under cyclic straining. *Acta Mater.* **2003**, *51*, 931–942. [\[CrossRef\]](#)
13. Madina, V.; Azkarate, I. Compatibility of materials with hydrogen. Particular case: Hydrogen embrittlement of titanium alloys. *Int. J. Hydrogen Energy* **2009**, *34*, 5976–5980. [\[CrossRef\]](#)
14. He, X.; Shen, B.; Cao, J.; Qiu, S.; Zou, H. Effects of Hydrogen on Strength and Plasticity of Two Types of New Titanium Alloys. *Rare Met. Mater. Eng.* **2003**, *32*, 390–393.

15. Nelson, H.; Williams, D.; Stein, J. Environmental hydrogen embrittlement of an α - β titanium alloy: Effect of microstructure. *Metall. Trans. A* **1972**, *3*, 473–479. [[CrossRef](#)]
16. Kim, J.; Plancher, E.; Tasan, C. Hydrogenation-induced lattice expansion and its effects on hydrogen diffusion and damage in Ti–6Al–4V. *Acta Mater.* **2020**, *188*, 686–696. [[CrossRef](#)]
17. Wen, J.; Allain, N.; Fleury, E. Hydrogen evolution and its effects on cold rolling behavior in commercial pure titanium. *Mater. Charact.* **2016**, *121*, 139–148. [[CrossRef](#)]
18. Bağ, Ö.; Yilmaz, F.; Kölemen, U. Transformational, microstructural and superelasticity characteristics of Ti–V–Al high temperature shape memory alloys with Zr addition. *Phys. Scr.* **2021**, *96*, 085702. [[CrossRef](#)]
19. Zhao, J.; Zhang, Q.; Dong, Z. Microstructure, strain recovery characteristics and corrosion resistance of Ti–V–Al–Zr lightweight shape memory alloy. *Met. Sci. Heat Treat.* **2025**, *66*, 611–617. [[CrossRef](#)]
20. Zeng, Z.; Kang, R.; Zhang, Y. Effect of Deformation Amount in Near-Isothermal β Forging on the Microstructure and Properties of TC17 Titanium Alloy. *Heat Treat. Technol. Equip.* **2025**, *46*, 5–8.
21. Yuan, T.; Zhang, X.; Jing, J.; Wu, X.; Fan, Y.; Lai, M.; Li, J. Research Progress on Fatigue Behavior of Ultra-High Strength Titanium Alloys. *Dev. Appl. Mater.* **2024**, *39*, 110–122. [[CrossRef](#)]
22. GB/T 228.1-2021; Metallic Materials—Tensile Testing—Part 1: Method of Test at Room Temperature. Standards Press of China: Beijing, China, 2021.
23. Lu, X.; Wang, D.; Wan, D.; Zhang, Z.; Kheradmand, N.; Barnoush, A. Effect of electrochemical charging on the hydrogen embrittlement susceptibility of alloy 718. *Acta Mater.* **2019**, *179*, 36–48. [[CrossRef](#)]
24. Liu, Q.; Long, W.; Fu, L.; Zhong, S.; Li, X. Tensile properties evolution of hydrogen-induced TA10 titanium alloy welded joints. *Trans. China Weld. Inst.* **2020**, *41*, 20–24.
25. Liu, Y.; Huang, X.; Qiu, S.; Zu, X.; Kang, P. Study of hydrogen induced embrittlement of Ti–Al–Zr alloys. *Nucl. Power Eng.* **2005**, *26*, 456–460.
26. Chen, Y.; Wang, S.; Meng, J.; Mitsuzaki, N.; Chen, Z. Effects of hydrogen on microstructure evolution and mechanical properties of TB8 titanium alloy. *PLoS ONE* **2025**, *20*, e0297528. [[CrossRef](#)] [[PubMed](#)]
27. Wasz, M.; Brotzen, F.; McLellan, R.; Griffin, A. Effect of oxygen and hydrogen on mechanical properties of commercial purity titanium. *Int. Mater. Rev.* **1996**, *41*, 1–12. [[CrossRef](#)]
28. Nelson, H. A film-rupture model of hydrogen-induced, slow crack growth in acicular alpha-beta titanium. *Metall. Trans. A* **1976**, *7*, 621–627.
29. Lulu-Bitton, N.; Navi, N.; Eliaz, N. Tensile Properties of Electrochemically Hydrogenated As-Built, Hot Isostatic Pressed and Heat-Treated Electron Beam Melted Ti–6Al–4V Alloys. *Acta Metall. Sin. Engl. Lett.* **2025**, *38*, 1711–1718.
30. Teixeira, J.; Maréchal, D.; Wimpory, R.C.; Denis, S.; Lefebvre, F.; Frappier, R. Formation of residual stresses during quenching of Ti17 and Ti–6Al–4V alloys: Influence of phase transformations. *Mater. Sci. Eng. A* **2022**, *832*, 142456.
31. Wang, B.; Xu, D.; Xu, T. Effect of electrochemical hydrogen charging in corrosion medium on microstructural evolution and mechanical behavior of an as-forged Ti–6Al–4V (in wt.%) alloy. *J. Iron Steel Res. Int.* **2025**, *32*, 1371–1381.
32. Huang, L.; Chen, D.; Xie, D.; Li, S.; Zhang, Y.; Zhu, T.; Raabe, D.; Ma, E.; Li, J.; Shan, Z. Quantitative tests revealing hydrogen-enhanced dislocation motion in α -iron. *Nat. Mater.* **2023**, *22*, 710–716. [[CrossRef](#)] [[PubMed](#)]
33. Gavriljuk, V.; Shyvaniuk, V.; Teus, S. Hydrogen-dislocation interaction in relation to hydrogen embrittlement and enhanced plasticity of metals. *Int. J. Hydrogen Energy* **2024**, *50*, 352–360. [[CrossRef](#)]
34. Wang, X.; Zhou, J.; Huang, S.; Sheng, J.; Zheng, Y. Effect of laser peening on Hydrogen Embrittlement Resistance of TC4 Titanium Alloys. *Acta Opt. Sin.* **2017**, *37*, 175–183. [[CrossRef](#)]
35. Deconinck, L.; Depover, T.; Verbeken, K. Characterisation of hydride formation in as-built and heat-treated laser powder bed fused Ti–6Al–4V. *J. Alloys Compd.* **2024**, *972*, 172859. [[CrossRef](#)]
36. Li, M. Lattice variations of Ti–6Al–4V alloy with hydrogen content. *Mater. Charact.* **2011**, *62*, 7. [[CrossRef](#)]
37. Ahmed, T.; Rack, H. Phase transformations during cooling in α + β titanium alloys. *Mater. Sci. Eng. A* **1998**, *243*, 206–211. [[CrossRef](#)]
38. Lulu-Bitton, N.; Navi, N.; Haroush, S. The Effects of Hot Isostatic Pressing (HIP) and Heat Treatment on the Microstructure and Mechanical Behavior of Electron Beam-Melted (EBM) Ti–6Al–4V Alloy and Its Susceptibility to Hydrogen. *Materials* **2024**, *17*, 2846. [[CrossRef](#)] [[PubMed](#)]
39. Tal-Gutelmacher, E.; Eliezer, D. The hydrogen embrittlement of titanium-based alloys. *JOM* **2005**, *57*, 46–49. [[CrossRef](#)]
40. Liu, S.; Wang, Y. Effect of microstructure on room-temperature hydrogen absorption behavior of Ti–6Al–4V alloy. *Rare Met. Mater. Eng.* **2017**, *46*, 2240–2243.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.