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Exploration on the Effect of Pretreatment Conditions on Hydrogen-Induced Defects in Pure Titanium by Positron Annihilation Spectroscopy

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Abstract: Electrolytic hydrogen charging experiments on cold-deformed and well-annealed (annealing at 700 °C for 2 h) pure titanium samples were carried out, respectively. Positron annihilation spectroscopy and X-ray diffraction were used to characterize all experimental samples to explore the formation of vacancy defects and the storage form of hydrogen in pure titanium after charging. Results showed that hydrides formed in well-annealed samples after electrolytic hydrogen charging, but a new phase in the cold-deformed samples was not observed. The annealed samples formed vacancy-type defects in the process of electrolytic hydrogen charging, and the excess hydrogen atoms were easily trapped by vacancies to form a hydrogen vacancy complex ($H_m V_n$). The defects formed in the cold-deformed hindered the diffusion of hydrogen atoms and inhibited the formation of vacancies. Compared with the well-annealed electrolytic hydrogen charging samples, the S parameters of the deformed electrolytic hydrogen charging samples hardly changed. The coincidence Doppler broadening spectrum results showed that wide peaks related to hydrogen vacancy complexes were found in electrolytic hydrogen charging samples. The formation of hydride in titanium affected the positron annihilation environment in the low-momentum region. The hydride-related peak was observed only in the electrolytic hydrogen-charged samples after being well annealed.

Keywords: pure titanium; electrolytic hydrogen charging; positron annihilation spectroscopy; vacancy defect



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1. Introduction

Hydrogen is one of the most common elements that cause thermal stability, toughness, and corrosion resistance of metal materials to decrease [1,2]. In extreme environments, hydrogen molecules are easily decomposed into hydrogen atoms on a metal surface. Whether the hydrogen atoms enter the interior of the material, whether in the interstitial position of the lattice or existing in the form of hydrides, mainly depends on the properties of the metal material and the electrolytic hydrogen charging conditions [3–5]. Titanium alloys are often used in heat exchangers and condensers due to their excellent corrosion resistance and are also used in other equipment such as nuclear power plants and thermal power plants [6–8].

However, when titanium and titanium alloys are used in a hydrogen-rich environment, they will absorb a large amount of hydrogen, which leads to hydrogen embrittlement and even cracking [9,10]. The hydrogen embrittlement behavior in the material is mainly related to the formation of several microscopic defect structures during the diffusion

and penetration of hydrogen in the material [11,12]. Therefore, studying the hydrogen-induced defect behavior of titanium and titanium alloys in a hydrogen environment is significant for understanding the effect of hydrogen on the properties of structural materials and solving practical application problems, including problems related to the hydrogen embrittlement [13–15].

At present, most researchers have mainly used transmission electron microscopy, 3D atom probes, and X-ray analysis techniques to study the hydrogen-induced defect behavior of hydrogen atoms in structural materials [16–18]. In comparison with these methods, positron annihilation technology is a self-seeking detection technology, which is more sensitive to micro-defects collecting the annihilation information of positrons in structural materials to reflect the structure of defects in structural materials and the distribution of elements [19,20]. Therefore, positron annihilation spectroscopy (PAS) has become a characteristic method for studying microscopic defects, electron density distribution, and electron momentum distribution in metal alloys, semiconductor materials, polymers, and some new functional materials [21–23].

In this work, the electrolytic hydrogen charging experiments were carried out on cold-deformed and well-annealed pure titanium samples. The defect structure and defect distribution of the samples were characterized by Doppler broadening energy positron annihilation spectroscopy (DB-PAS) and coincidence Doppler broadening positron annihilation spectroscopy (CDB-PAS). The phase structure of the hydrogen-charged samples were analyzed by X-ray diffraction and provided a data reference and theoretical basis for the service of titanium and titanium alloy under extreme conditions.

2. Experimental Procedure

2.1. Sample Preparation and Process

In this work, an industrial pure titanium TA1 (99.9 wt%) was used. The pure titanium sheet sample was cut into 0.5-mm-thick slices by electric spark wire cutting. To remove the oxide layer and surface stains formed during the smelting and wire cutting processes, the cut samples were mechanically polished and then placed in an ultrasonic cleaner to clean in alcohol for 10 minutes. The cleaned pure titanium plate sample was cold rolled to 0.25 mm (deformation rate of 50%) on a double-roll cold-rolling mill. Afterward, the wire cutting was continuously used to make a $10 \times 10 \times 0.25\text{-mm}^3$ square sheet. After mechanical polishing of the mirror surface, ultrasonic cleaning was performed on all samples to make the surface clean and pollution free. Part of the samples was selected for annealing treatment. The annealing experiment was performed in a tubular vacuum annealing furnace ($\sim 10^{-5}$ Pa) at 700 °C for 2 h to eliminate all defects in the samples; the cooling method was furnace cooling [24]. In order to avoid an experimental error caused by sample storage and surface oxidation caused by long-time contact with air, in addition to contacting air during the experiment, the rest of the time the samples were placed in the vacuum drying oven.

2.2. Electrolytic Hydrogen Charging Experiment

Electrochemical hydrogen charging experiments were carried out on samples with different pretreatment conditions at room temperature. In the electrochemical hydrogen charging experiment, a constant current regulator was used to regulate the current and voltage of hydrogen charging. The anode of the constant current power supply was connected to the platinum plate and the cathode was connected to the sample. The increase in charging time theoretically meant the increase in hydrogen content in the sample. The specific charging parameters are shown in Table 1. The electrolytic hydrogen charging solution was $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ and $2 \text{ g}\cdot\text{L}^{-1} \text{ CH}_4\text{N}_2\text{S}$.

Table 1. Sample treatment conditions and electrolytic hydrogen charging parameters.

Sample Number	Annealing Temperature	CD/mA·cm ^{−2}	Time/h
No. 1	700 °C, 2 h	Uncharged	-
No. 2	700 °C, 2 h	100 mA·cm ^{−2}	4 h
No. 3	700 °C, 2 h	100 mA·cm ^{−2}	8 h
No. 4	Un-annealed	Uncharged	-
No. 5	Un-annealed	100 mA·cm ^{−2}	4 h
No. 6	Un-annealed	100 mA·cm ^{−2}	8 h

Note: sample number, No.; CD, current density.

2.3. Sample Characterization and Research Methods

The experiment used Doppler broadened positron annihilation spectroscopy (DB-PAS) to study the distribution of defects in hydrogen-charged samples. The device is a slow positron beam device of the Institute of High Energy Physics, Chinese Academy of Sciences [25,26]. The Doppler broadening of the annihilation peak was measured at 511 keV using a high-purity Germanium detector with an energy resolution of 1.5 keV. The experimental samples were measured with a 0–25-keV energy positron beam at room temperature. Results included *S* and *W* parameters. The *S* parameter was related to vacancy defects, which reflected the annihilation information of positrons and low-momentum electrons. The defined energy region was near the 511-keV (510.24–511.76 keV) annihilation gamma photon count and the full-spectrum range of 501.00–521.00 keV, where the ratio of gamma photon counts was. The *W* parameter is defined as the ratio of the counts in the energy range of 513.6–516.9 keV and 505.10–508.40 keV to the total count of the full spectrum (501.00–521.00 keV), reflecting the positron and high momentum ($13.0 \times 10^{-3} m_0 c \leq P_L \leq 30.0 \times 10^{-3} m_0 c$), where P_L is the component of the total momentum of the annihilation pair along the γ emission direction, m_0 is the resting mass of the electron, and c is the speed [27–29]. Slow positron incidence depth ($Z(E)$) is determined by the incident energy (E) and target material density (ρ) [30]:

$$Z(E) = \frac{4 \times 10^4}{\rho} E^{1.6} \quad (1)$$

The coincidence Doppler broadened positron annihilation spectroscopy (CDB-PAS) is a measurement method based upon the Doppler broadening spectrum, which orients the information in a specific depth range and retains the information of specific elements in the sample [31]. The CDB-PAS spectrum accumulates about 10^7 counts in 8 h by collecting momentum distribution information. Through normalization with the CDB measurement results of the hydrogen-charged samples, the defect structure and element information in the hydrogen-charged samples were obtained [32,33]. In order to further explore the chemical state and phase change of hydrogen in charged samples, the phase structure of all the samples was compared and analyzed with a D8 Advance X-ray diffractometer (XRD). The XRD scan range (2θ) was 30–90°, and the step length was 4° min^{−1}. Under this test condition, the phase change in pure titanium was characterized in detail [34].

3. Results and Discussion

3.1. Analysis of Phase Composition in Hydrogenated Samples

Figure 1 shows the XRD spectra of cold-deformed samples and well-annealed samples after electrolytic hydrogenation. New diffraction peaks ((110) and (200), respectively) were formed after hydrogen charging in the well-annealed samples, indicating that a new phase was formed after hydrogen charging in the well-annealed samples [34]. This is because, in the hydrogenation process of the well-annealed samples, hydrogen atoms mainly diffuse through the lattice and hydrogen is dissolved in the interstitial position of the titanium lattice in an atomic form. When the hydrogen concentration exceeds the solid solubility of H in titanium, the titanium hydrogen compounds (TiH₂) will be formed in the charged

sample [35,36]. However, no new phase was found during the hydrogen treatment of cold-deformed samples. This may have been because pure titanium forms a large number of complex defect structures (high-density dislocations, etc.) during cold-rolling deformation. These complex defect structures hinder the diffusion of hydrogen atoms in the sample, thus reducing the solubility of hydrogen atoms in titanium.

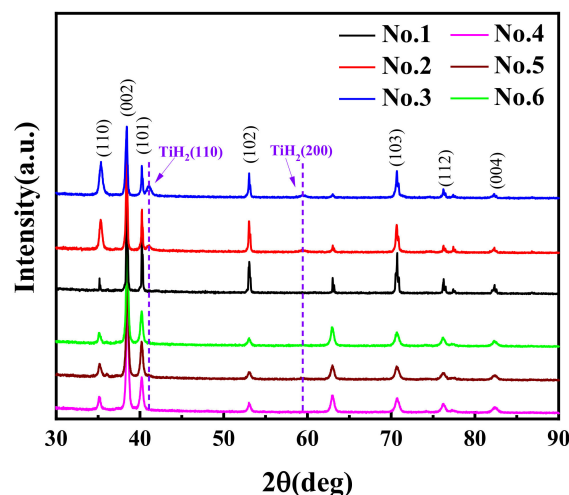


Figure 1. XRD spectra of pure titanium samples before and after electrolytic hydrogen charging under different annealing conditions.

3.2. Formation of Vacancy-Type Defects before and after Electrolytic Hydrogen Charging

In order to characterize the vacancy defects formed in pure titanium during electrochemical hydrogen charging, all samples were characterized by Doppler broadened positron annihilation spectroscopy. Figure 2a,b shows the S - E curve and ΔS - E curve of the cold-deformed sample and the well-annealed sample before and after electrolytic hydrogen charging, respectively, where $\Delta S = S_{\text{hydrogen charging}} - S_{\text{hydrogen free}}$. The S parameters of all samples gradually decreased in the range of positron energy of 0–2 keV, which was due to the change of S parameters in the near-surface region of the samples (~50 nm) due to the surface effect and the production of ortho-positronium. The results showed that the S parameter of the No. 1 sample increased after electrolytic hydrogen charging (the S parameter of No. 2 and No. 3 was higher than of No. 1), which was due to the formation of vacancy defects caused by the diffusion behavior of hydrogen atoms in the lattice during charging. When the incident positron was captured and annihilated by the vacancy defects formed by this hydrogen damage, the S parameter increased and obviously depended on the hydrogen charging time [37,38]. On the other hand, in addition to forming a large number of vacancies during hydrogen charging, excess hydrogen (H_m) atoms were captured by vacancies and vacancy clusters (V_n) to form a hydrogen vacancy complex ($H_m V_n$) [39], which reduced the positron annihilation rate in vacancies. When the hydrogen charging time increased to 8 h, the concentration of hydrogen atoms in the sample was high. In addition to the combination of some hydrogen atoms with vacancies to form hydrogen vacancy complexes, the excess hydrogen atoms continued to expand, resulting in hydrogen damage. Therefore, with the increase in charging time, the S parameter always kept an upward trend [40]. A large number of deformation defects were formed in pure titanium during cold-rolling deformation. These deformation defects promoted the annihilation of the positron in the sample, increased the annihilation rate of the positron, and finally led to the S parameter being higher than that of the sample without cold deformation. This work carried out electrolytic hydrogen charging experiments on cold-deformed pure titanium samples in studying the damage behavior of hydrogen in cold-deformed pure titanium samples. The results showed that the S parameter of No. 5 did not change significantly because the hydrogen atoms diffused into the deformed samples were mainly captured by the open volume defects formed by cold rolling, which inhibited the formation of vacancies [41].

When the electrolytic hydrogen charging time increased to 8 h, the concentration of hydrogen atoms captured by deformation defects reached the limit, the excess hydrogen atoms diffused in the lattice, the formation rate of vacancy defects increased, and the S parameter began to rise, as shown by No. 6 in Figure 2a.

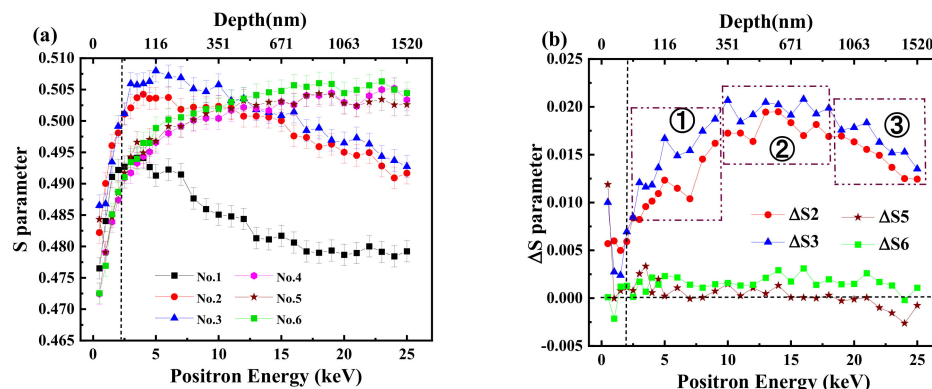


Figure 2. S - E curve (a) and ΔS - E curve (b) of pure titanium samples after electrolytic hydrogen charging under different annealing conditions.

The ΔS - E curve in Figure 2b intuitively reflects the increase in vacancy defects in pure titanium during the electrolytic hydrogen charging process. Results showed that the hydrogen damage was mainly concentrated in the range of 50–1500 nm (deep region). During electrochemical hydrogen charging, hydrogen atoms preferentially formed vacancies in the surface region, accompanied by the formation of hydrogen vacancy complexes. The final ΔS parameter was also positively correlated with the concentration of vacancy defects. For well-annealed samples, there were mainly two processes in the hydrogen charging process: the formation of vacancy defects and the combination of hydrogen and vacancy defects, as shown in area ① in Figure 2b, in which the binding rate of the hydrogen vacancy complex was higher than that of vacancy. At this time, the effective concentration of vacancy defects was low and its ΔS parameter was low. With the progress of hydrogen charging, the excess hydrogen atoms gradually diffused to the deep region (depth > 50 nm) to form vacancy defects. In region ②, the binding rate of the hydrogen vacancy complex decreased, which was mainly caused by the formation of vacancy defects, and ΔS_2 and ΔS_3 increased to 650 nm and reached the damage peak. At this time, the concentration of vacancy defects was high and its ΔS parameter also increased. Finally, a small number of hydrogen atoms continued to diffuse towards the deep region to form vacancy defects and the ΔS parameter decreased gradually. Therefore, in this well-annealed hydrogen-filled sample, the distribution concentration of hydrogen on the surface was higher than that in the deep region. For deformed hydrogenated samples, there was mainly the capture process of hydrogen atoms by deformation defects during hydrogen charging. With the increase in the hydrogen charging time to 8 h, the ability of deformation defects to capture hydrogen atoms decreased, vacancy defects began to form, and ΔS_6 increased as a whole.

Figure 3 shows the W - E curves of different pretreated samples after electrolytic hydrogen charging. Results showed that the W - E curve result was negatively correlated with the S parameter. The concentration of vacancy defects in the electrolytic charging samples strongly depended on the electrolytic hydrogen charging conditions. With the increase in the electrolytic hydrogen charging time, excess hydrogen atoms were easily combined with vacancy defects to form hydrogen vacancy complexes, which reduced the effective open volume of vacancy defects. Finally, the formation of the hydrogen vacancy complex led to the reduction in positron annihilation probability in vacancy defects. At this time, the W parameter of positrons trapped and annihilated by hydrogen vacancy complexes was smaller than that of positrons annihilated in the sample without electrolytic hydrogen charging. Therefore, with the increase in the electrochemical hydrogen charging time, the W parameter in Figure 3 gradually decreased.

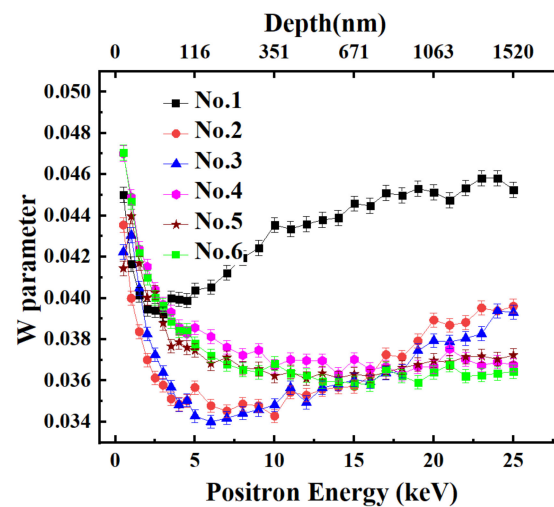


Figure 3. W-E curve of pure titanium samples after electrolytic hydrogen charging under different annealing conditions.

3.3. Analysis of Defect Structure in Hydrogen-Charged Samples

Figure 4a shows the S-W curve of the well-annealed sample after electrolytic hydrogen charging. Compared with un-hydrogenated samples, the S-W curve of hydrogenated samples moved in the direction of the increasing S parameter. The reason was that increasing the electrolytic hydrogen charging time to 8 h in the electrolytic hydrogen charging process led to a gradual increase in the vacancy-type defect concentration, an increase in the annihilation rate of incident positron in the sample, and an increase in the S parameter. On the other hand, the excess hydrogen atoms were easily combined with the vacancy defects to form hydrogen vacancy complexes during the electrolytic hydrogen charging process, which eventually led to the existence of defect structures with different proportions of vacancy defects and hydrogen vacancy complexes [42]. Therefore, the slope of the S-W defect in Figure 4a was obviously different. After electrolytic hydrogen charging, the No. 4 and No. 5 curves in Figure 4b hardly changed. As the hydrogen charging time increased to 8 h, the No. 6 curve began to move in the direction of the increasing S parameter. This is because, with the increase in the electrolytic hydrogen charging time, the retention capacity of the deformation defects to the hydrogen atoms reached the limit and the excess hydrogen atoms gradually diffused inside the sample to form vacancy defects [37], which changed the defect structure inside the sample and finally led to the aggregation of its (S, W) points along the direction of the increase in the S parameters.

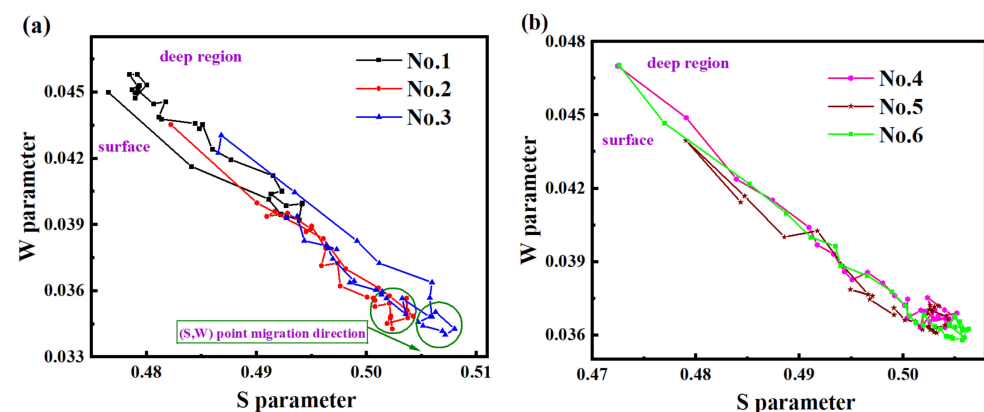


Figure 4. S-W curves of pure titanium samples before and after electrochemical hydrogenation: (a) S-W curves of well-annealed samples after electrochemical hydrogenation; (b) S-W curves of cold-deformed samples after electrochemical hydrogenation (where “surface” represents the position of the surface area and “deep region” represents the interior of the sample.).

3.4. Analysis of Elemental Information of Electrolytic Hydrogen Charging Samples

Based on XRD and DB-PAS results, the TiH_2 and vacancy defects were formed after the hydrogen charging. However, a small number of vacancy defects was formed in the cold-deformed samples and TiH_2 was not observed. On the other hand, through the analysis of the *S-E* and *W-E* curves in the range of about 100–300 nm, it was found that the electrochemical hydrogen charging time promoted the formation of a hydrogen vacancy complex. The existence of a hydrogen atom in the sample will affect the annihilation between the positron and free electron, resulting in the change of the electron momentum distribution near the positron annihilation point [35,43]. At the same time, the chemical environment around the positron annihilation point can be determined by the distribution of core electrons [44]. In this work, CDB-PAS was used to measure all samples. By analyzing the momentum distribution of different hydrogen-filled samples, the distribution law of hydrogen in the samples was further explored. According to the distribution of *S-W* parameters in DBS, when the positron energy was 7 keV, the *S-W* curve changed significantly. At the same time, for well-annealed samples, the damage peak (highest point of vacancy concentration) was reached at the depth of about 200 nm. Therefore, we used the positron incident energy of 7 keV to measure the CDB-PAS of hydrogen-charged samples. The results of the electrolytic hydrogen charging samples and corresponding non-hydrogen charging samples were normalized to determine the influence of electrolytic hydrogen charging conditions on the results of CDB-PAS. Furthermore, the results of the CDB-PAS in the low-momentum region were related to the valence electrons/free electrons distributed near the open-volume defects, while the CDB-PAS in the high-momentum region was related to the distribution information of the core electrons. Figure 5 shows the ratio curve of the hydrogen-charged sample when the positron energy was 7 keV (characterizing the position of the damage peak). In the low-momentum region ($0 < P_L < 5 \times 10^{-3} \text{ m}_0c$), the CDB-PAS ratio curve was greater than 1, which was related to the annihilation of positrons in the open-volume defects, whereas the well-annealed sample in the momentum region of $1.5 < P_L < 4.5 \times 10^{-3} \text{ m}_0c$ showed an obvious peak position after electrolytic hydrogen charging, while the CDB-PAS ratio curve of the deformed electrolytic hydrogen charging sample gradually decreased with the increase in momentum. The hydrogen element in the deformed sample existed in the form of free hydrogen atoms. After annealing, the hydrogen element in the sample mainly existed in the form of hydride and a hydrogen vacancy complex. When free hydrogen reacts with titanium to form TiH_2 during hydrogen charging, the chemical environment around the titanium lattice changes [34]. When the annihilation mode of the positron in these environments changes, the CDB-PAS ratio curve also changes. Therefore, the peaks of the samples in the low-momentum regions, No. 2 and No. 3 in region ①, were mainly related to the TiH_2 formed during electrochemical hydrogen charging. In the high-momentum area ($P_L > 5 \times 10^{-3} \text{ m}_0c$), broad peaks appeared in the CDB-PAS of all hydrogen-charged samples (regions ② and ③). The hydrogen atoms in the cold-deformed, hydrogen-charged samples were mainly retained in the deformation defects. When the characteristic electrons were annihilated in the deformation defects, obtaining hydrogen-related information became easier. Therefore, obvious broad peaks in the range of $10 < P_L < 17 \times 10^{-3} \text{ m}_0c$ were observed. After the well-annealed sample was charged with hydrogen, the hydrogen vacancy complexes with different proportions were mainly used in the sample in addition to the formation of hydrides. When the characteristic electrons were annihilated in the sample, they were affected by the hydrogen vacancy complexes [38], while obvious broad peaks in the higher momentum region ($13 < P_L < 21 \times 10^{-3} \text{ m}_0c$) were observed.

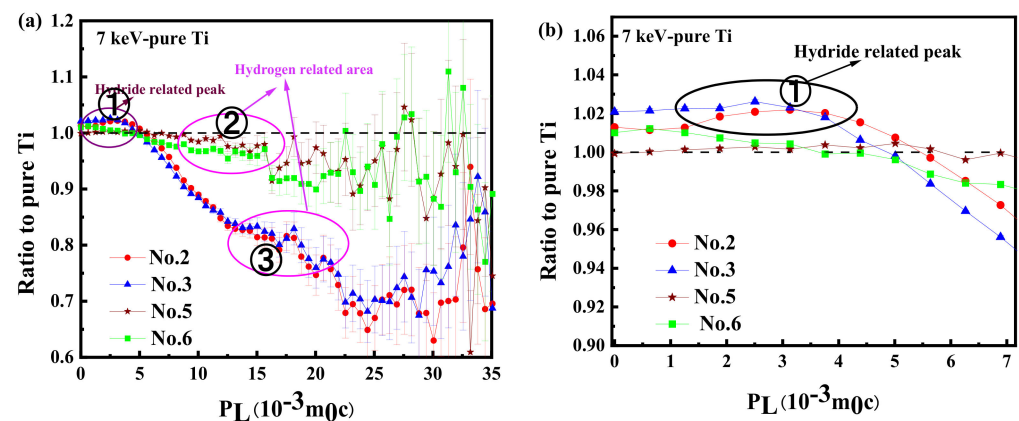


Figure 5. (a) CDB-PAS ratio curves of pure titanium samples before and after electrolytic hydrogen charging. (b) CDB-PAS ratio curves of the momentum region $0\sim6 \times 10^{-3} \text{ m}_0\text{c}$.

4. Conclusions

In this work, X-ray diffraction and PAS were used to study the changes of a micro-defect structure in cold-deformed and well-annealed samples after electrolytic hydrogen charging. A certain number of hydrides formed during the electrolytic hydrogen charging process of the well-annealed samples. However, hydrogen atoms were trapped by high-density dislocations and vacancies in the process of electrolytic hydrogen charging of the cold-deformed samples, which hindered the formation of hydrides. Many vacancy defects formed in the samples during the electrolytic hydrogen charging process. In comparison with the change of the S parameter of the well-annealed samples after electrolytic hydrogen charging, the S parameter of the cold-deformed samples after electrolytic hydrogen charging did not change significantly. This indicated that defects of the interior of the cold-deformed samples hindered the diffusion of the hydrogen atoms; thus, the vacancy defects due to hydrogen atoms' diffusion were reduced. With the increase in the hydrogen charging time, the excess hydrogen atoms gradually diffused to the deep region, resulting in hydrogen damage, and the proportion of the hydrogen vacancy complex gradually decreased.

We analyzed the hydrogen in the annealed samples and the cold-deformed samples, as was shown in the CDB-PAS spectrum. The results showed that the hydrogen atoms in the cold-deformed samples mainly existed in the hydrogen vacancy complex. Accordingly, we found that the defect structure in the sample would affect the state distribution of hydrogen atoms in the titanium.

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