



In situ study of phase transformations in Ti–6Al–4V–xH alloys

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Received 22 September 2014; accepted 28 December 2014

Abstract: The hydrogen-induced microstructure evolution and phase transformations in Ti–6Al–4V alloy during heating and cooling were studied. The specimens were heated to 1273 K and subsequently cooled to room temperature. The hydrogen content is up to 0.8% (mass fraction). The hydrogen-induced dynamic phase transformations and the corresponding mechanisms were analyzed. When the hydrogen content increases, the β transus temperature significantly decreases and the magnitude decreases, and the volume fraction of β phase increases. During heating, the phase transformations in hydrogenated Ti–6Al–4V alloys can be divided into three stages, and the phase transformation order is $\delta \rightarrow \alpha + H_2 \uparrow \Rightarrow \delta + \alpha' \rightarrow \beta_H \Rightarrow \alpha' \rightarrow \alpha_H + \beta_H \Rightarrow \alpha_H \rightarrow \alpha + H_2 \uparrow \Rightarrow \alpha \rightarrow \beta \Rightarrow \beta_H \rightarrow \beta + H_2 \uparrow$. In addition, the relationship among hydrogenation and M_s and M_f of α' martensite were determined.

Key words: titanium alloy; phase transformation; hydrogen; in situ

1 Introduction

Because hydrogen has a high solubility and diffusion coefficient in titanium, it can be easily added into and removed from titanium alloys by changing the partial pressure and temperature during heating in vacuum, which makes hydrogen a temporary alloying element [1,2]. In addition, as a body-centered cubic (BCC) β phase stabilizer, hydrogen has a low solubility in the hexagonal close-packed (HCP) α phase and a notably high solubility in the β phase, which means that hydrogen considerably affects the phase composition and kinetics of phase transformations in titanium alloys [3–6]. Therefore, thermohydrogen processing (THP) has been extensively studied. This technology, which uses hydrogen as a temporary alloying element, can improve the workability (such as hot workability [7–9], superplastic forming [10], welding [11], machinability, composite and powder metallurgy product processing [12]) and enhance the final mechanical properties by modifying the effect of hydrogen on the microstructures and phase transformations in titanium alloys. The phase transformations in titanium alloys

during heating and cooling are complex and varied, and they mainly consist of allotropic transformation, eutectoid transformation, ordering transformation and martensitic transformation [13,14]. The phase transformations exhibit important effects on the thermostability of alloys. The effects of alloying elements on the phase transformations have been treated as the basic effect. As a strong β stable alloying element, hydrogen critically affects the phase stability and phase transformations in titanium alloys [15–17]. Therefore, the effects of hydrogen-induced phase transformations and the corresponding mechanisms are the theoretical basis and a fundamental problem to understand and design THP technology. Moreover, studying the phase transformations is essential for establishing the relation between the mechanical properties and the microstructure. However, experiments and empirical data remain central to the hydrogen-induced workability. Hydrogen-induced phase transformations in the Ti–6Al–4V alloy have been suggested by KERR [18], IL'IN et al [9] and QAZI et al [3], but the results obtained by the researchers are essentially different. KERR [18] suggested that the hydride decomposition temperature is near 1073 K. IL'IN et al [9] suggested that

the hydride decomposition temperature is below 573 K and gradually increases with increasing the hydrogen content. QAZI et al [3] suggested that hydride can exist above the β transus temperature (T_β). There are considerable differences in the results because the phase transformations were all deduced and estimated by investigating the room-temperature microstructures that were quenched from high temperatures. It is not in situ, and there is a lack of authenticity in studying the phase transformations using the inference method. In addition, the phase transformations of martensite decomposition ($\alpha \rightarrow \beta$) and transformations during cooling are not studied.

Therefore, this study aims to examine the phase transformations in Ti–6Al–4V– x H alloys in situ during heating and cooling by high-temperature X-ray diffraction (HTXRD), differential scanning calorimetric (DSC), thermogravimetric analysis (TGA) and high-temperature metallographic microscopy.

2 Experimental

The Ti–6Al–4V alloy is a commercial alloy with chemical composition of 6.29% Al, 4.11% V, 0.05% Fe, 0.13% O, 0.03% N, and balance Ti (mass fraction). The hydrogenation process was performed in a special heat treatment furnace in hydrogen atmosphere. The specimens were hydrogenated as follows: making vacuum $\rightarrow$ filling with argon $\rightarrow$ heating to the hydrogenation temperature (1023 K) $\rightarrow$ adding hydrogen $\rightarrow$ insulation for 2 h $\rightarrow$ furnace cooling to room temperature. The hydrogen content of the specimens was controlled using the equilibrium partial pressure of hydrogen in the hydrogen gas. The hydrogen contents of the specimens were measured by weighing the specimens before and after hydrogenation using a Sartorius BT125D electronic balance with an accuracy of 0.01 mg. Hydrogen contents of 0, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7% and 0.8% (mass fraction) were obtained. The hydrogenated alloys were named Ti–6Al–4V– x H, where “ x ” represents the hydrogen content.

The metallographic method was used to study the effect of hydrogen on the β transus temperature, T_β , of Ti–6Al–4V alloy. The samples were immediately water-quenched after being held at different temperatures for 30 min in a heating furnace, and the quenching temperature interval was selected as 5 K. The quenched microstructure was observed by optical microscopy, and the temperature as soon as the primary α phase completely disappeared was defined as T_β .

Electron back-scattered diffraction (EBSD) was used to study the room-temperature microstructure of the Ti–6Al–4V– x H alloys with dimensions of $d8\text{ mm} \times 1.5\text{ mm}$, which were prepared by grinding and

subsequently electropolishing in a 10% (volume fraction) perchloric acid/acetic acid solution. The high-temperature microstructures were observed using a Zeiss Axiophoto2 microscope in an argon atmosphere with the temperature heated to 1673 K, followed by a continuous cooling at a rate of 50 K/min. The differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) measurements were performed using a Netzsch STA–449C apparatus, from room temperature to 1273 K in an argon atmosphere using a heating rate of 20 K/min. The high temperature XRD during continuous heating from room temperature to 1193 K was examined using a Rigaku DMAX 2550 X-ray diffractometer, which was operated at 350 mA and 40 kV with Cu K_α radiation. The XRD patterns were recorded in the 2θ range of 30 to 100° with a step size of 0.02° . The sample was heated to a desired temperature at a heating rate of 20 K/min and held for 10 min for equilibration, after which the XRD data were collected.

The in situ high-temperature metallographic investigations were conducted on an Axiophoto2 microscope (Zeiss). The specimens with a diameter of 5 mm and a height of 0.5 mm were prepared using standard metallographic methods. The specimens were mildly etched to reduce distraction during in situ observation. The heating process was as follows: the specimens were heated to 673 K at a heating rate of 100 K/min and held for 2 min; heated to 723 K at a heating rate of 20 K/min and held for 2 min; heated to 1673 K at a heating rate of 50 K/min, and held at 1023, 1273, 1473 and 1673 K for 2 min, respectively; and cooled to room temperature at a cooling rate of 50 K/min.

3 Results and discussion

3.1 Room-temperature microstructure

The room-temperature microstructures of Ti–6Al–4V– x H alloys were observed using EBSD, and the images are shown in Fig. 1. The results suggest that the volume fractions of β phase are 40% and 85% in the Ti–6Al–4V–0.3H specimen and Ti–6Al–4V–0.5H specimen, respectively. It is confirmed that more β phase can be stabilized and remained at room temperature using hydrogenation.

3.2 Effect of hydrogen on β transus temperature

T_β is the main basis to determine the hot-working process for titanium alloys because the microstructure and mechanical properties greatly differ in the two-phase region and the single β phase field [19,20]. In addition, the hot-working temperature range for titanium alloys is notably narrow. Therefore, to obtain an ideal microstructure and properties by selecting the appropriate

technological parameters, it is essential to precisely determine the phase transformation temperature.

The degree of the phase transformation was traced using metallographic examination. The microstructures of Ti–6Al–4V– x H specimens quenched at different temperatures are shown in Fig. 2. As observed, the

Ti–6Al–4V– x H alloys quenched at low temperatures exhibit a typical two-phase microstructure, and the existence of prior α phase implies that the quenching temperature is below T_β , as shown in Figs. 2(a), (c) and (e). When the quenching temperature is above T_β , fully martensite structures with coarse β grains are obtained,

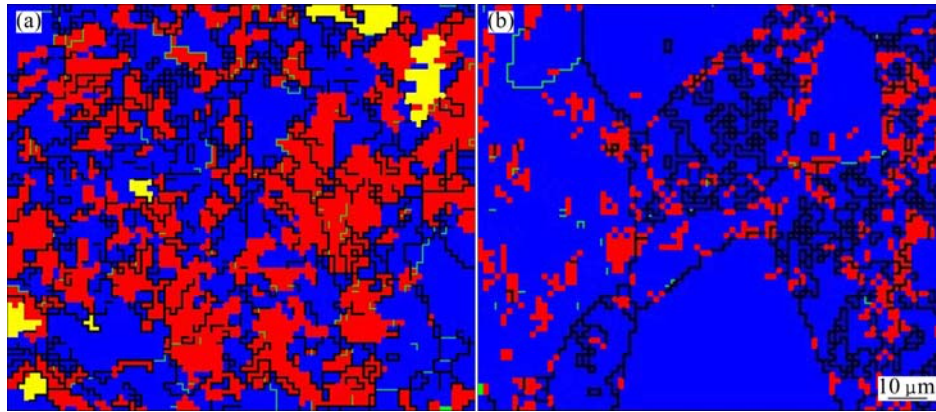


Fig. 1 Effect of hydrogen content on phases volume fraction of Ti–6Al–4V– x H alloys (red region: α phase, blue region: β phase): (a) Ti–6Al–4V–0.3H alloy; (b) Ti–6Al–4V–0.5H alloy

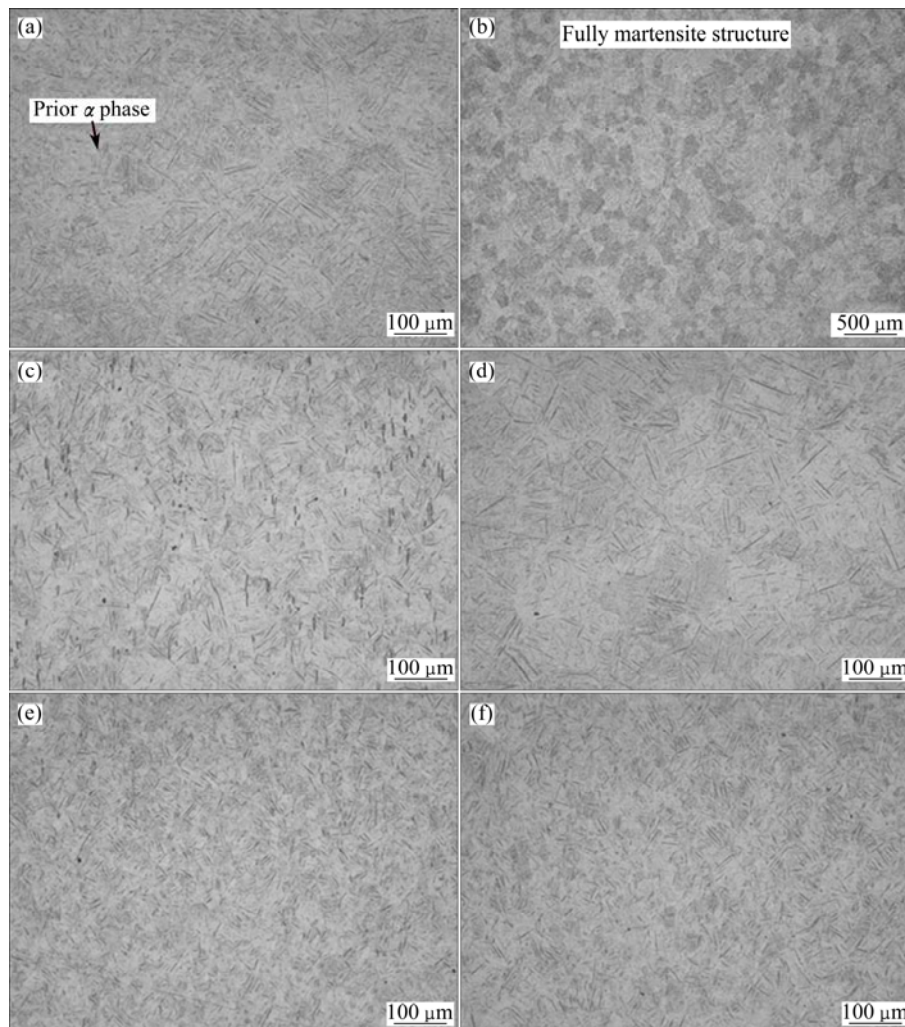


Fig. 2 Photomicrographs of Ti–6Al–4V– x H specimens after heating at different temperatures for 30 min and then water quenching: (a) Ti–6Al–4V, 1243 K; (b) Ti–6Al–4V, 1253 K; (c) Ti–6Al–4V–0.2H, 1153 K; (d) Ti–6Al–4V–0.2H, 1163 K; (e) Ti–6Al–4V–0.3H, 1088 K; (f) Ti–6Al–4V–0.3H, 1093 K

which indicates that the α phase has completely transformed to the β phase before quenching, as shown in Figs. 2(b), (d) and (f). At temperatures below T_β , the amount of prior α phase gradually decreases with increasing the quenching temperatures. Moreover, acicular martensite α' is observed in all specimens because the quenching temperatures are above the martensite start temperature M_s . However, there remains some prior α phases, and the transformed β phase is small and separated, which results in short acicular martensite. As soon as the quenching temperature reaches T_β , the grain boundary rapidly migrates because of no inhibition by the α phase, which results in the rapid growth and coarse grains of β phase and the occurrence of β brittleness. During quenching, long acicular α' martensite with certain orientation precipitates from β grains, as shown in Fig. 2(b). The microstructural evolution below T_β is favorable to improve the microstructure and properties of Ti–6Al–4V alloy.

The β transus temperatures of Ti–6Al–4V–xH alloys are listed in Table 1. The T_β linearly decreases when the hydrogen content increases from 0 to 0.3% (mass fraction) and 0.4% to 0.8% (mass fraction), which is shown in Fig. 3. The results fit the following linear relations:

Table 1 Relationship between hydrogen content and β transus temperature of Ti–6Al–4V–xH alloy

Alloy	T_β /K
Ti–6Al–4V	1248
Ti–6Al–4V–0.1H	1190
Ti–6Al–4V–0.2H	1159
Ti–6Al–4V–0.3H	1088
Ti–6Al–4V–0.4H	1072
Ti–6Al–4V–0.5H	1070
Ti–6Al–4V–0.8H	1062

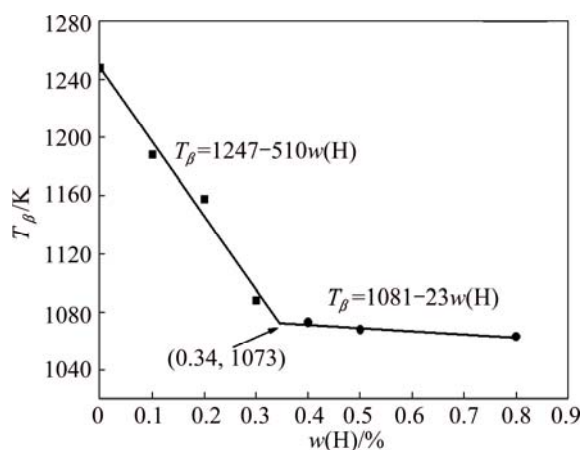


Fig. 3 Relationship between β transus temperature and hydrogen content

$$T_\beta = 1247 - 510w(H), (0 \leq w(H) \leq 0.3\%) \quad (1)$$

$$T_\beta = 1081 - 23w(H), (0.4\% \leq w(H) \leq 0.8\%) \quad (2)$$

where $w(H)$ is the hydrogen content in mass fraction.

The intersection of the two lines is (0.34, 1073). T_β rapidly decreases from 1248 to 1073 K when the hydrogen content increases from 0 to 0.34%. However, the decrease trend slows down when the hydrogen content is above 0.34%. When the hydrogen content is lower than 0.34%, the volume fraction of β phase rises sharply with increasing the hydrogen content, thus, the T_β decreases sharply. When the hydrogen content is above 0.34%, the excess hydrogen mainly exists as hydride in titanium alloy, then, the T_β decreases slowly.

3.3 DSC and TGA studies

The DSC curves of Ti–6Al–4V–xH alloys are shown in Fig. 4.

As shown in Fig. 4(a), there is an endothermic peak at 1248 K for the nonhydrogenated alloy, which corresponds to the allotropic transformation. In addition, the martensite decomposition reaction processes in this area. The peak of the martensite decomposition transformation $\alpha' \rightarrow \alpha + \beta$ overlaps with that of $\alpha \rightarrow \beta$, which results in an obvious peak. In addition, the transformation $\alpha' \rightarrow \alpha + \beta$ occurs earlier than $\alpha \rightarrow \beta$. The allotropic transformation in pure Ti occurs at 1155 K with the transformation of $\alpha \rightarrow \beta$. However, it is noted that the allotropic transformation in the Ti–6Al–4V alloy is processed in a temperature range and expressed as $\alpha \rightarrow \alpha + \beta \rightarrow \beta$. The temperatures that correspond to the peak are clear and easily detectable, which are defined as T_β . The start temperature of the $\alpha \rightarrow \alpha + \beta$ transformation and the finish temperature of that are determined using the intersections of two tangents. The temperature range from the start temperature to the finish temperature is defined as the $\alpha + \beta$ two-phase field. The start and finish temperatures of the transformations are approximately 1073 and 1303 K, respectively, which indicates that the two-phase field is approximately 230 K.

For the hydrogenated alloys, it should be noted that there are two endothermic peaks at approximately 593 and 998 K. Because the degree of transformation is equal to the fraction of the absorbed/released heat, the endothermic peak at 998 K is obvious, which implies that the heat absorption capacity is high and the $\alpha \rightarrow \beta$ transformation occurs in this range. The obvious endothermic peak shifts towards low temperature with increasing the hydrogen content, which confirms the metallographic results that the T_β decreases with increasing the hydrogen content. However, the T_β value measured using DSC is lower than that measured using metallography, because that is defined as the peak temperature, as shown in Figs. 3 and 4. The T_β value

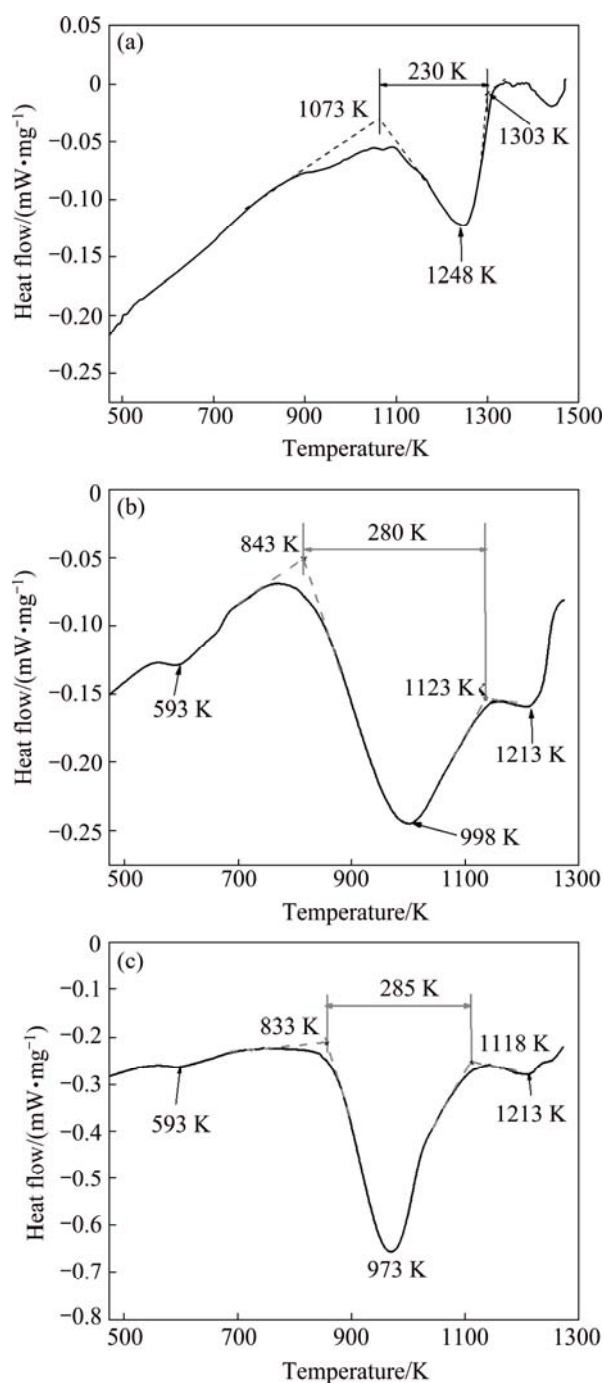


Fig. 4 DSC curves of Ti-6Al-4V-xH alloys: (a) Ti-6Al-4V; (b) Ti-6Al-4V-0.3H; (c) Ti-6Al-4V-0.5H.

measured using metallography is defined as the prior α phase completely disappears, and the $\alpha+\beta \rightarrow \beta$ transformation finishes. As shown in Fig. 4(b), for the alloy hydrogenated with 0.3% H, the $\alpha \rightarrow \alpha+\beta$ transformation temperature decreases to 843 K, the $\alpha+\beta \rightarrow \beta$ transformation temperature decreases to 1123 K, and the two-phase field is approximately 280 K. For the alloy hydrogenated with 0.5% H, the $\alpha \rightarrow \alpha+\beta$ transformation temperature decreases to 833 K, the $\alpha+\beta \rightarrow \beta$ transformation temperature decreases to 1118 K, and the two-phase field increases to 285 K, as shown in

Fig. 4(c). These results indicate that hydrogenation can reduce the T_β and enlarge the $\alpha+\beta$ two-phase field, which is supported by the high-temperature metallographic analysis. This result indicates that hydrogenation can enlarge the hot-workability two-phase temperature range of titanium alloys, which is meaningful to adjust the microstructure by controlling the forming temperature. In other words, hydrogenation can improve the hot workability of titanium alloys.

With increasing the hydrogen content, the peaks at 593 K are nearly unchanged and notably small, which illustrates that there is phase transformation but the reaction norm is notably little. The endothermic peaks at 593 K correspond to the decomposition reaction of hydride, which can be verified using HTXRD.

The TGA curves of nonhydrogenated and hydrogenated (0.5% H) Ti-6Al-4V alloys are shown in Fig. 5(a). The mass of nonhydrogenated alloy remains constant below 773 K during heating, which suggests that the Ti-6Al-4V alloy is relatively stable below 773 K. The mass starts to increase at 773 K and rapidly increases above 973 K because of heavy oxidation. The sample mass increases by approximately 0.03% at the end of heating. The mass of the hydrogenated alloy is nearly unchanged below 893 K and subsequently decreases sharply, which implies that dissolved hydrogen atoms begin to escape. The mass remains constant again above 1273 K. However, the mass change of the hydrogenated alloy can be attributed to the combined effects of oxidation and dehydrogenation. Therefore, the difference of the TGA curves of nonhydrogenated and hydrogenated samples is plotted, which represents the mass loss caused by dehydrogenation, as shown in Fig. 5(b). The final mass loss of Ti-6Al-4V-0.5H is approximately 0.5%, which suggests a complete escape of the dissolved hydrogen. From thermodynamics, this TGA curve verifies the possibility of vacuum dehydrogenation annealing temperature of 948 K, which was proposed by KERR [18].

3.4 High-temperature XRD analysis

The XRD patterns of hydrogenated alloys at different temperatures are shown in Fig. 6. The room-temperature (RT) phases of the two hydrogenated alloys are identified as HCP α , HCP α' , BCC β and FCC δ . All of the diffraction angles of α , α' and β phases shift towards low angles because of the crystal structure distortion caused by the solid solution of hydrogen atoms. α' is a supersaturated solid solution of stable elements such as hydrogen for the β phase in the HCP structure. The diffraction peaks of δ phase disappear, the diffraction peaks of α phase are strengthened, and other diffraction peaks are basically unchanged at 623 K. In addition, the DSC results show that an endothermic

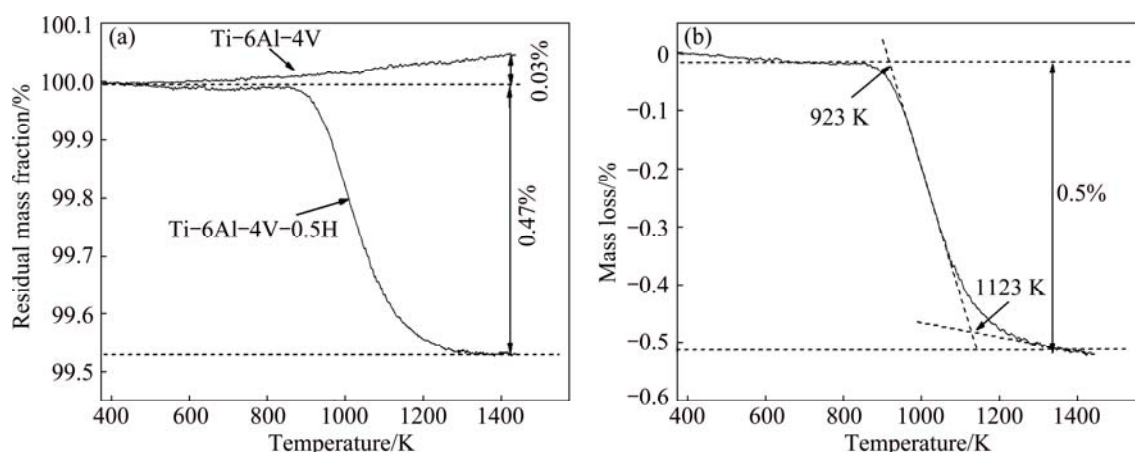


Fig. 5 TGA curves of Ti-6Al-4V- x H ($x=0, 0.5$) alloys (a) and difference between TGA curves of nonhydrogenated and hydrogenated alloys (b)

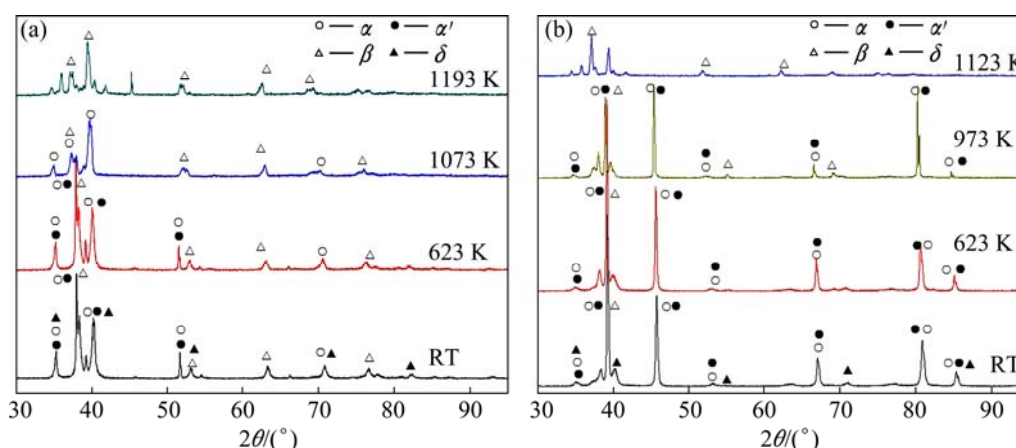


Fig. 6 High temperature XRD patterns of Ti-6Al-4V- x H alloys during heating: (a) Ti-6Al-4V-0.2H; (b) Ti-6Al-4V-0.5H

reaction occurs at 593 K. Thus, the hydride decomposition reaction of $\delta \rightarrow \alpha + \text{H}_2\uparrow$ and the eutectoid transformation of $\delta + \alpha' \rightarrow \beta_{\text{H}}$ (β_{H} represents the β phase that is saturated with hydrogen) occur at 593 K.

The diffraction peaks of α' phase remain at 973 K (Fig. 6(b)), but no α' diffraction peaks are detected at 1073 K (Fig. 6(a)). Hence, α' martensite decomposes at temperatures between 973 and 1073 K. The martensite decomposition temperature of $\alpha' \rightarrow \alpha + \beta$ in a non-hydrogenated alloy is approximately 1073 K [3]. Therefore, hydrogenation can reduce the martensite decomposition temperature in titanium alloys, which proves that hydrogen can stabilize the β phase. The final decomposed products of α' martensite are the α and β phases, which strengthens the β phase diffraction peaks and weakens the diffraction peaks of HCP structure after the decomposition reaction. The diffraction peaks of HCP structure completely disappear for the Ti-6Al-4V-0.2H and Ti-6Al-4V-0.5H alloys at 1193 and 1123 K, respectively, and there are only diffraction peaks of the BCC structure, which indicates that the XRD patterns are conducted in the β phase range. The experimental results

of QAZI et al [8] suggest that when the hydrogen content is 10% (mole fraction) (equal to 0.24%, mass fraction) and 20% (mole fraction) (equal to 0.54%, mass fraction), the decomposition temperatures of α' martensite in the Ti-6Al-4V alloy are 1023 K and 993 K, respectively, and the data are consistent with the experimental results of this study.

Combining the results of DSC, TGA and HTXRD, the phase transformations in Ti-6Al-4V-0.5H alloy during heating can be divided into three stages: 1) below 923 K, the mass slowly decreases, and the endothermic effect is not notable, which indicates that the phase transformations of $\delta \rightarrow \alpha + \text{H}_2\uparrow$ and $\delta + \alpha' \rightarrow \beta_{\text{H}}$ occur; 2) between 923 and 1123 K, the mass sharply decreases, and the endothermic effect is notable, which indicates that the phase transformations of $\alpha' \rightarrow \alpha_{\text{H}} + \beta_{\text{H}} \Rightarrow \alpha_{\text{H}} \rightarrow \alpha + \text{H}_2\uparrow \Rightarrow \alpha \rightarrow \alpha + \beta \Rightarrow \alpha + \beta \rightarrow \beta \Rightarrow \beta_{\text{H}} \rightarrow \beta + \text{H}_2\uparrow$ occur (α_{H} represents the α phase that is saturated with hydrogen); 3) above 1123 K, the mass slowly decreases, and the endothermic effect is not notable, which indicates that the phase transformation of $\beta_{\text{H}} \rightarrow \beta + \text{H}_2\uparrow$ occurs until hydrogen is completely removed.

3.5 In situ high temperature metallographic study

The in situ high-temperature metallographic images of nonhydrogenated alloy during heating are presented in Fig. 7. According to the in situ observation results, the microstructure is nearly unchanged below 773 K. However, the specimen surface turns black at approximately 773 K because of oxidation, which is unfavorable for in situ observation. The alloy is oxidized at 773 K, which is consistent with the TGA results. When the temperature reaches 873 K, the oxidation becomes severe, and almost the entire surface of the sample presents black, as shown in Fig. 7(b). When the specimen is continually heated to 1023 K, the oxide layer that formed on the surface of specimen begins to break because of high temperature and completely flakes off at 1073 K. This result occurs because the oxide layer

formed at low temperatures is notably compact and closely attaches to the metal surface. At high temperature, a thick grey oxide layer forms, which is porous, incompact, and easy to break and flake off. The $\alpha \rightarrow \beta$ transformation occurs at approximately 1123 K and first occurs at the grain boundary, which has high energy, high differences in composition and a fast pathway for the atom diffusion (Fig. 7(c)). Correspondingly, the α phase along the grain boundary first transforms to the β phase through diffusion and nucleation. Above 1173 K, the α phase quickly transforms to the β phase (Fig. 7(d)). When the transformation proceeds, the atoms inside the α phase diffuse towards the β phase until the α phase completely transforms to the β phase. However, the elements of the transformed β phase are uneven. At approximately 1233 K, the $\alpha \rightarrow \beta$ transformation

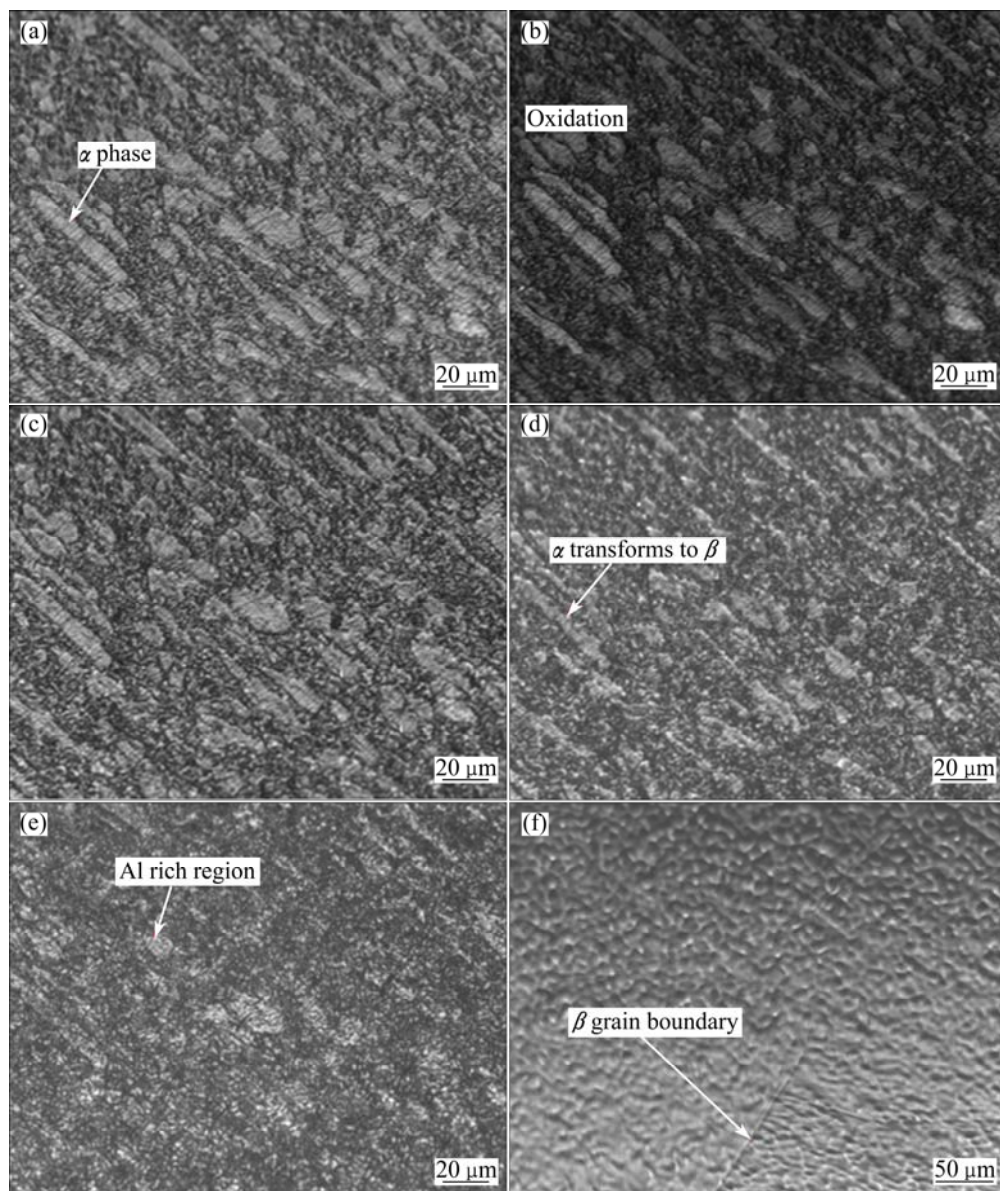


Fig. 7 Microstructures of Ti-6Al-4V alloy at different temperatures during heating: (a) Room temperature; (b) 873 K; (c) 1123 K; (d) 1173 K; (e) 1233 K; (f) 1253 K

completely proceeds and the element homogenization of β phase begins, as shown in Fig. 7(e). The $\alpha \rightarrow \beta$ transformation determines by diffusion, and when the transformation finishes, the Al content is high where there is prior α . When the heating process proceeds, the atoms diffuse until they become homogeneous. When the temperature reaches 1253 K, the homogeneous process finishes, and coarse β grain boundaries are observed (Fig. 7(f)).

The Ti-6Al-4V-0.2H alloy during heating has a similar phase transformation as the nonhydrogenated alloy. However, the start temperature of the $\alpha \rightarrow \beta$ transformation decreases to 1033 K, and the final temperature is 1163 K, which indicates that hydrogenation can decrease the $\alpha \rightarrow \beta$ transformation temperature and enlarge the two-phase field. The microstructures of the nonhydrogenated Ti-6Al-4V

alloy during cooling from 1273 K are shown in Fig. 8. The β grain boundary at 1273 K is clearer, deeper and wider than that at 1253 K. This is because that the formed thermal-etching ditch gradually begins to be deeper and wider with increasing the temperature and prolonging the heating time, and the changing speed increases, which results in a clearer grain boundary. The martensite transformation occurs during cooling. Martensite needle colonies, which consist of many parallel α' lamellas that share similar crystal orientation, begin to nucleate from the β grain boundary at 1173 K, which indicates that 1173 K is M_s , as shown in Fig. 8(b). With decreasing the temperature, the martensite needles grow into the β grain interior until they impinge with other colonies, as observed in Fig. 8(c). When the temperature continually decreases, martensite precipitates in the grain interior and gradually grows, as

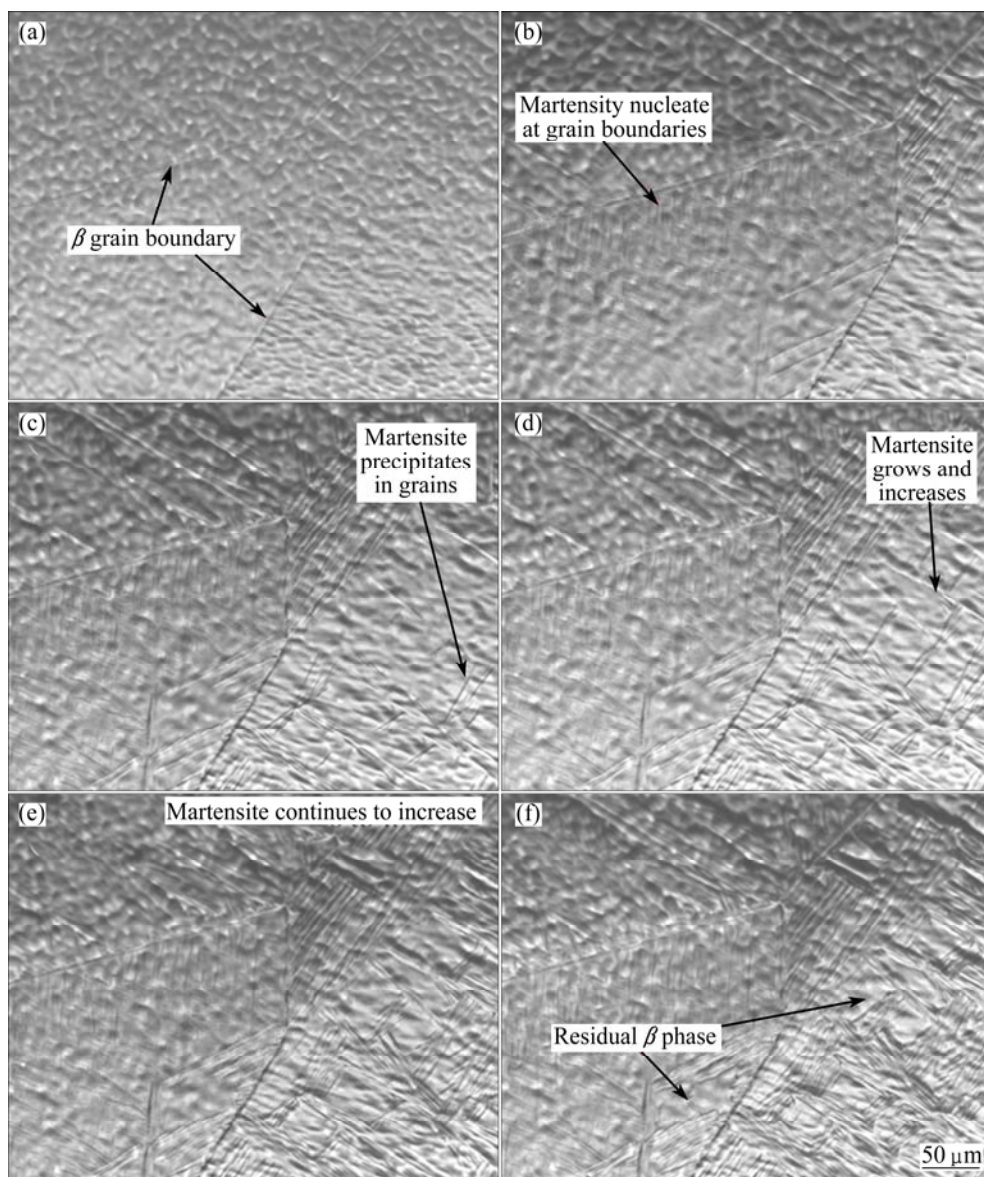


Fig. 8 Microstructures of Ti-6Al-4V alloy at different temperatures during cooling: (a) 1273 K; (b) 1173 K; (c) 1153 K; (d) 1133 K; (e) 1113 K; (f) 1023 K

shown in Figs. 8(d) and (e). The martensite inclines by 0, 30, 60, 90° to each other, which is governed by the symmetry of the hexagonal lattice and the Burgers orientation relationships between the parent BCC and the precipitated HCP phases [3]. The martensite transformation stops at 1023 K, which indicates that 1023 K is the martensite finish temperature (M_f). At this time, a large quantity of β phase transforms to α' and only a small quantity of β phase, β_{residual} remains as an interlayer between α' , as shown in Fig. 8(f).

The microstructures of the Ti-6Al-4V-0.2H specimen during cooling are shown in Fig. 9. It can be observed that the martensite transformation also occurs in the hydrogenated alloy. The M_s and M_f decrease to 1123 K and 973 K, as shown in Figs. 9(b) and (f), respectively, which suggests that hydrogenation decreases the start and finish temperatures of the

$\beta \rightarrow \alpha' + \beta_{\text{residual}}$ transformation in titanium alloys. After the transformation, the volume fraction of β_{residual} in the hydrogenated specimen is higher than that in the nonhydrogenated specimen, which confirms that hydrogen is an effective β -stabilizing element. It can be concluded that hydrogenation can prove the thermodynamics stability of β phase and impede the $\beta \rightarrow \alpha' + \beta_{\text{residual}}$ transformation, which leads to more residual β phase at room temperature. According to the non-equilibrium phase diagram of the Ti- β isomorphous elements, a higher content of stabilizing β -phase elements corresponds to a larger resistance to reconstruct crystal lattice during the martensite transformation. In addition, the β phase can be more stable at low temperature, and the condensate depression for transformation also increases, which results in low M_s and M_f . With increasing the hydrogen content, the M_s and

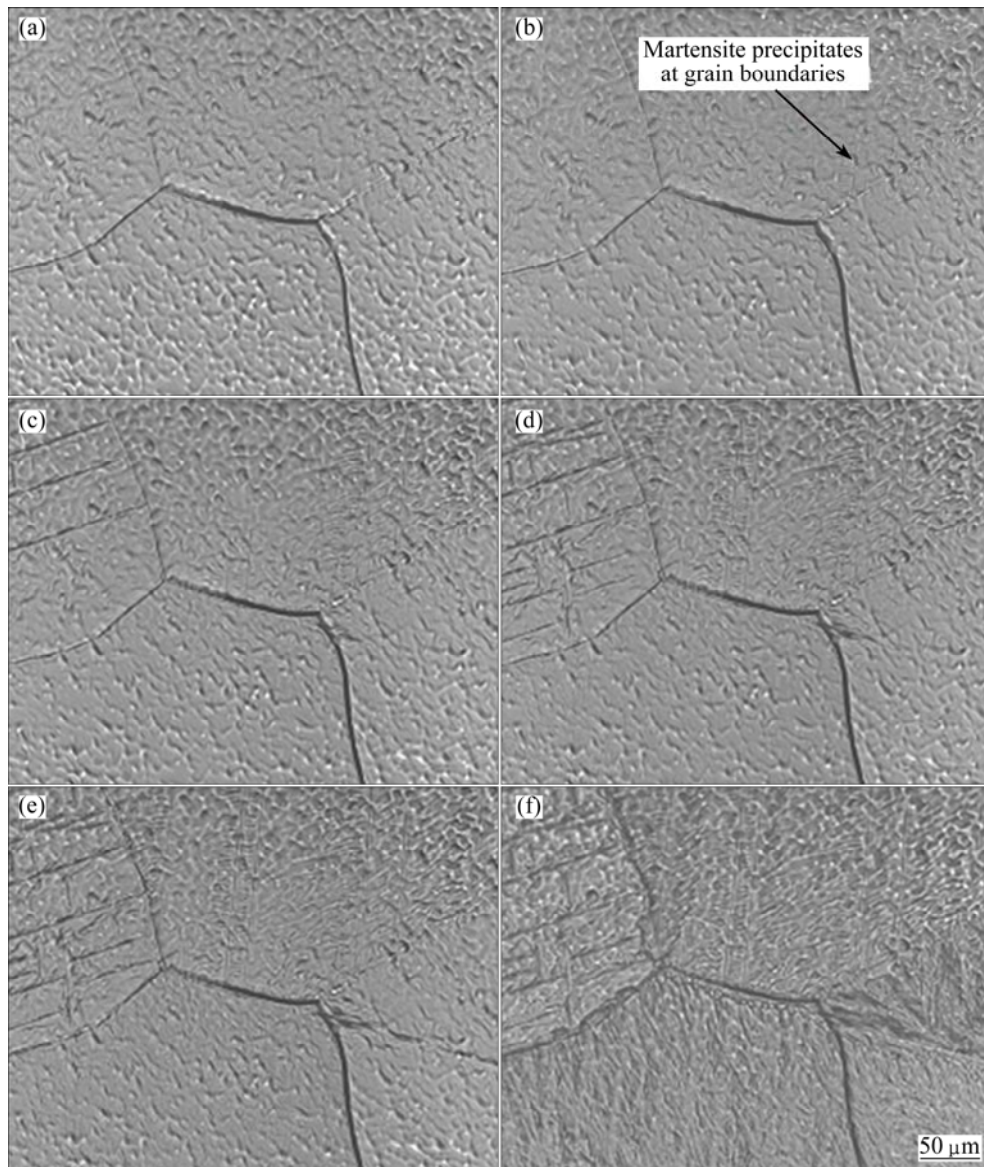


Fig. 9 Microstructures of Ti-6Al-4V-0.2H alloy at different temperatures during cooling: (a) 1273 K; (b) 1123 K; (c) 1103 K; (d) 1093 K; (e) 1073 K; (f) 973 K

M_f gradually decrease. In addition, during cooling, at the same temperature, the hydrogenated specimen has a smaller volume fraction of martensite than the nonhydrogenated specimen, which can be explained using the Magee equation:

$$f = 1 - \exp[-\alpha(M_s - T_q)] \quad (3)$$

where f is the volume fraction of martensite, α is the material constant, and T_q is the quenching temperature. According to Eq. (3), a higher M_s corresponds to a larger f . Hydrogenation decreases M_s , which results in a smaller volume fraction of martensite. The hydrogenated alloy has an obviously higher volume fraction of residual β phase in the final cooling microstructure than the nonhydrogenated alloy, which is consistent with the room temperature EBSD microstructure. Furthermore, the hydrogen stabilization of more hot-workable β phase is directly proven.

Combining the results of DSC, TGA, HTXRD and high-temperature metallography, it can be concluded that the phase transformations in hydrogenated titanium alloys during heating are as follows: $\delta \rightarrow \alpha + H_2 \uparrow \Rightarrow \delta + \alpha' \rightarrow \beta_H \Rightarrow \alpha' \rightarrow \alpha_H + \beta_H \Rightarrow \alpha_H \rightarrow \alpha + H_2 \uparrow \Rightarrow \alpha \rightarrow \beta \Rightarrow \beta_H \rightarrow \beta + H_2 \uparrow$. The decomposition reaction of hydride $\delta \rightarrow \alpha + H_2 \uparrow$ occurs at 598 K. With increasing the hydrogen content, the transformations of $\alpha' \rightarrow \alpha + \beta$, $\alpha \rightarrow \alpha + \beta$ and $\alpha + \beta \rightarrow \beta$ gradually decrease.

3.6 Thermodynamics and kinetics of hydrogen-induced phase transformations

Phase transformations are influenced by thermodynamic and kinetic driving forces. The thermodynamic calculations can determine the reasons for transformation, and the kinetic calculations can determine the transformation velocity. The $\alpha \rightarrow \beta$ transformation belongs to the solid-state phase transformation, which is controlled by diffusion. The crystal structure and composition of the parent and new phases simultaneously change. Hydrogen is a β phase stabilizer, and the addition of hydrogen improves the crystal structure changes from the α phase to the β phase, which decreases T_β .

The phase transformation velocity is determined from the moving velocity of the phase interface and the long-range diffusion velocity of solute atoms in the parent phase. The moving velocity of the phase interface depends on the thermo active migration of the interface, which indicates that the phase-interfacial atoms of the parent phase reach the new phase side through thermal vibration because of the chemical potential difference, and the interface moves towards the parent phase. Therefore, the migration velocity of the interface depends on the vibration frequency of the atoms that are the nearest to the interface. The vibration frequency

depends on the diffusion characteristic of the atoms, which is the function of diffusion activation energy and temperature. The phase interface is the main site to trap hydrogen atoms. Hydrogen improves the hot vibration of atoms near the phase interface, which promotes the migration of the phase interface.

The phase interface migration depends on the interface migration mechanism and must satisfy the redistribution requirements of solute atoms because the new and parent phases have different chemical compositions. The interface migration accompanies the long-range diffusion of solute atoms in the parent phase. According to this diffusion mechanism, the migration velocity of the phase interface is

$$u = J/C^{\alpha \rightarrow \beta} \quad (4)$$

where J is the diffusion flux of solute atoms in the parent phase, which is related to the diffusion coefficient $D = D_0 \exp[-Q/(kT)]$ of this element in the parent phase and the normal concentration gradient near the interface, $C^{\alpha \rightarrow \beta}$ is the concentration difference of the parent and new phases. The diffusion rate of hydrogen atoms is notably high. Hydrogen decreases the bonding force of α -Ti and increases the bonding force of β -Ti. Therefore, hydrogen can improve the diffusion velocity of both titanium atoms and other solute atoms in the α phase and impede the diffusion velocity of the β phase, which improves the $\alpha \rightarrow \beta$ phase transformation and decreases its phase transformation temperature.

4 Conclusions

1) The β transus temperature decreases with increasing the hydrogen content because hydrogen stabilizes the β phase. The $\alpha + \beta$ two-phase field is enlarged after hydrogenation, which proves that hydrogen addition can enlarge the hot-workability temperature range of titanium alloys. The relationship between the β transus temperature and the hydrogen content can be represented using two linear functions with a dividing point of 0.34% (mass fraction).

2) The phase transformations in hydrogenated titanium alloys during continuous heating are: $\delta \rightarrow \alpha + H_2 \uparrow \Rightarrow \delta + \alpha' \rightarrow \beta_H \Rightarrow \alpha' \rightarrow \alpha_H + \beta_H \Rightarrow \alpha_H \rightarrow \alpha + H_2 \uparrow \Rightarrow \alpha \rightarrow \beta \Rightarrow \beta_H \rightarrow \beta + H_2 \uparrow$.

3) The martensitic transformation temperatures M_s and M_f decrease with the addition hydrogen. The M_s of unhydrogenated and Ti-6Al-4V-0.2H alloys are 1173 K and 1123 K, respectively. The M_f of unhydrogenated and Ti-6Al-4V-0.2H alloys are 1023 K and 973 K, respectively. In addition, the critical cooling rate of the martensitic transformation decreases with the addition of hydrogen, and the transformation time is correspondingly delayed, which leads to more β phase remaining at room

temperature.

4) The mechanisms of the hydrogen-induced phase transformations are: hydrogen is a β -phase stabilizer, and the addition of hydrogen improves the crystal structure changes from the α phase to the β phase; hydrogen improves the hot vibration of atoms and promotes the migration of the phase interface; hydrogen improves the diffusion velocity of atoms in the α phase and impedes the diffusion velocity of the β phase.

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Ti–6Al–4V–xH 合金相转变的原位研究

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摘 要: 研究在加热和冷却过程中的氢致 Ti–6Al–4V 合金组织转变和相转变。试样从室温加热到 1273 K, 随后又冷却至室温。氢含量范围为 0~0.8% (质量分数)。系统研究氢致 Ti–6Al–4V 合金动态相变过程及相应的机制。当氢含量增大时, β 相转变温度显著降低, 但幅度趋缓, 并且 β 相体积分数逐渐增加。在加热过程中, 置氢 Ti–6Al–4V 合金的相转变可以分为三个阶段, 具体的过程是: $\delta \rightarrow \alpha + \text{H}_2 \uparrow \Rightarrow \delta + \alpha' \rightarrow \beta_{\text{H}} \Rightarrow \alpha' \rightarrow \alpha_{\text{H}} + \beta_{\text{H}} \Rightarrow \alpha_{\text{H}} \rightarrow \alpha + \text{H}_2 \uparrow \Rightarrow \alpha \rightarrow \beta \Rightarrow \beta_{\text{H}} \rightarrow \beta + \text{H}_2 \uparrow$ 。另外, 也对氢含量与 α' 马氏体的 M_s 和 M_f 的关系进行研究。

关键词: 钛合金; 相转变; 氢; 原位

(Edited by Mu-lan QIN)