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ARTICLE

Kinetics and Characteristics of Isothermal Constant Volume Hydrogen Desorption in TC21 Alloy

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Abstract: Hydrogen desorption kinetics and characteristics, residual hydrogen content and activation energy of TC21 alloy were investigated by the constant volume method. Results show that hydrogen desorption temperature and initial hydrogen pressure affect hydrogen desorption characteristics of TC21 alloy. The hydrogen desorption process is mainly dominated by nucleation and growth process ($kt=[-\ln(1-\alpha)]^{2/3}$), chemical reaction process ($kt=(1-\alpha)^{-1/2}$) and three-dimensional diffusion process ($kt=[1-(1-\alpha)^{1/3}]^{1/2}$) when the hydrogenated TC21 alloy is dehydrogenated at temperatures of 700–940 °C. When the hydrogenated TC21 alloy releases hydrogen, the following relationship exists among the rate constants of each process: k (chemical reaction process)>k (nucleation and growth process) >k (three-dimensional diffusion process). The residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption decreases gradually with the increase in hydrogen desorption temperature, and increases gradually with the increase in the initial hydrogen pressure. The activation energy of TC21 alloy in the process of hydrogen desorption is about 26.663 kJ/mol.

Key words: TC21 alloy; hydrogen desorption; kinetics; activation energy

1 Introduction

In recent years, thermo-hydrogen treatment (THT) of titanium alloys[1–3] has attracted much interest due to the extensive applications of titanium alloys in the fields of aerospace and biomedicine[4–6]. In THT, titanium alloy is firstly charged with an appropriate amount of hydrogen to change the microstructure and then improve the workability of titanium alloy[7–9]. After the processing of hydrogenated titanium alloy, hydrogen should be removed from the hydrogenated titanium alloy by vacuum annealing[10–12].

The solid-gas reaction principle in THT includes the kinetics of hydrogen absorption and desorption of titanium alloy. The hydrogen desorption kinetics determines the hydrogen desorption behavior of titanium alloy in the hydrogen desorption process, which is of significance for the determination of the hydrogen desorption process parameters in THT. Wang et al[13] studied the hydrogen desorption kinetics of Ti600, TC21 and Ti40 alloys by differential thermal analysis-thermogravimetry (DTA-TG) apparatus, and concluded that the initial dehydrogenation temperatures of Ti600, TC21 and Ti40 alloys obtained by TG experiments at the heating rate of 5 °C/min were 582, 592 and 544 °C, respectively. The average values of activation energy of hydrogen desorption in Ti600, TC21 and Ti40 alloys were 200±5, 240±5 and 155±5 kJ/mol, respectively. Gao et al[14] investigated the kinetics of hydrogen desorption in Ti and Ti-5Cr alloys by the constant volume method, and obtained that the activation energies for hydrogen desorption of Ti and Ti-5Cr alloys were 67.0 and 61.8 kJ/mol, respectively. Yuan et al[15] investigated the kinetics of hydrogen absorption in TC21 alloy by the constant volume method, and obtained that the activation energy of hydrogen absorption in TC21 alloy was 18.304 kJ/mol. However, fewer studies were conducted on the solid-gas reaction mechanisms for the isothermal constant volume hydrogen desorption process of titanium alloys.

Therefore, the hydrogen desorption behavior of the hydrogenated TC21 alloy during isothermal constant volume hydrogen desorption was investigated in the present work, aiming at exploring the activation energy of hydrogen

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desorption, the law of residual hydrogen content and the mechanism of solid-gas reaction, so as to improve the study of the hydrogen desorption principle of the hydrogenated TC21 alloy.

2 Experiment

The material used in this investigation was TC21 alloy. The specimens of TC21 alloy were cylinders with the size of Φ6 mm×9 mm, which were cut from the as-received TC21 alloy bar by an electric discharging machine. The chemical composition of the as-received TC21 alloy was Ti-6.5Al-3Mo-1.5Cr-2.1Zr-2.2Sn-1.9Nb. The TC21 alloy specimens were polished with sandpapers to remove the oxide layer on the surface and cleaned ultrasonically in anhydrous ethanol in order to keep their finish.

The hydrogen absorption and desorption experiments were conducted in a constant volume system, and the effect of volume on the hydrogen pressure was excluded. Before the hydrogen desorption, the TC21 alloy specimens were hydrogenated. The hydrogen treatment device was a tubular hydrogen treatment furnace. In the process of hydrogenation, the vacuum pressure of the furnace tube system was controlled to lower than 1.0×10^{-3} Pa firstly, and then the resistance furnace was heated at a heating rate of 10 °C/min. When the temperature of the resistance furnace increased to 850 °C, the valve between the furnace tube and the vacuum system was closed, and then a certain amount of hydrogen with the purity greater than 99.999% was charged into the furnace tube. After holding for 120 min, the specimens were finally air-cooled to room temperature. The initial hydrogen pressures were in the range of 56.783–88.350 kPa.

The hydrogenated TC21 alloy was dehydrogenated in the tubular hydrogen treatment furnace at hydrogen desorption temperatures in the range of 600–940 °C. In the process of hydrogen desorption, the vacuum pressure of the furnace tube system equipped with the hydrogenated TC21 alloy specimen was controlled to lower than 1.0×10^{-3} Pa firstly, and then the resistance furnace was heated at a heating rate of 10 °C/min. When the temperature of the resistance furnace reached the predetermined hydrogen desorption temperature, the valve between the furnace tube and the vacuum system was closed, and the resistance furnace was rapidly pulled to a specific position. The hydrogenated TC21 alloy specimen was located in the middle of the constant temperature zone of the resistance furnace, and after holding for 120 min, the specimen was finally air-cooled to room temperature. The hydrogen pressure during the hydrogen desorption process was recorded by a Pirani vacuum gauge (INFICON PCG554). The temperature during the hydrogen desorption process was recorded by means of a thermocouple which was settled into the resistance furnace. The hydrogen contents in the hydrogenated and dehydrogenated specimens of TC21 alloy were determined by weighing the specimens before and after the hydrogenated and dehydrogenated treatments using an electronic analytical balance (METTLER TOLEDO ME-55) with an accuracy of 10^{-5} g.

The hydrogen desorption kinetics of TC21 alloy can be investigated using the solid-gas reaction mechanism, and the rate equation of kinetics for the solid-gas reaction is shown in Eq. (1)[16–17].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

where α is the reaction fraction, t is time, k is the rate constant, and $f(\alpha)$ is the function determining the reaction mechanism. $g(\alpha)$ is the integral form of $f(\alpha)$, as shown in Eq. (2). $f(\alpha)$ or $g(\alpha)$ has about 42 mechanism equations[16], as shown in Table 1.

$$g(\alpha) = \int \frac{\mathrm{d}\alpha}{f(\alpha)} = kt \tag{2}$$

Based on the data of hydrogen pressures and time during the isothermal constant volume hydrogen desorption, the reaction fraction α can be expressed by Eq. (3)[16].

$$\alpha = \frac{p_0 - p_t}{p_0 - p_{\mathrm{eq}}} \tag{3}$$

where, P_0 is the initial hydrogen pressure, P_t is the hydrogen pressure at time t of the reaction process, and P_{eq} is the equilibrium hydrogen pressure. Thereby, the data of α can be derived from the data of hydrogen pressures and time according to Eq. (3). The $\mathrm{d}\alpha/\mathrm{d}t$ data can be derived from the derivation of the α-t kinetic curve. The hydrogen desorption reaction mechanism of TC21 alloy is the optimal linearly fitted $f(\alpha)$ or $g(\alpha)$ function, the hydrogen desorption rate equation represented by Eq. (2) can be determined by the linear fitting of the $g(\alpha)$-t data, and the kinetic parameter k (the slope of the hydrogen desorption rate equation) can be obtained after determining the hydrogen desorption rate equation.

3 Results and Discussion

3.1 Effect of hydrogen desorption temperature on hydrogen desorption characteristics of TC21 alloy

Fig. 1 shows the hydrogen pressure, reaction fraction and hydrogen desorption rate of the TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa during hydrogen desorption at different temperatures. From Fig. 1a, it can be seen that the change of hydrogen pressure with the prolongation of holding time is similar when the hydrogenated TC21 alloy is dehydrogenated at temperature in the range of 700–940 °C. With the prolongation of holding time, the hydrogen pressure rises slowly in the first few minutes, then rises rapidly, decreases slowly for a period of time, rises again, and finally stabilizes. The corresponding changes of time and hydrogen pressure at each stage of hydrogen desorption at different temperatures for TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa are shown in Table 2.

It takes some time for the hydrogenated TC21 alloy to rise from room temperature to the hydrogen desorption temperature during the hydrogen desorption treatment. The time required for the TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa to rise from room temperature to the hydrogen desorption temperatures of 600, 700, 800, 840,

Table 1 Mechanism functions of kinetics[16]

Mechanism	$f(\alpha)$	$g(\alpha)$	r
Nucleation and growth	$(1/r)(1-\alpha)[-\ln(1-\alpha)]^{1-r}$	$[-\ln(1-\alpha)]^{r}$	1/4, 1/3, 2/5, 1/2, 2/3, 3/4, 1, 3/2, 2, 3, 4
Power law	$(1/r)\alpha^{1-r}$	α^{r}	1/4, 1/3, 1/2, 1, 3/2, 2
Exponential	$(1/r)\alpha$	$\ln\alpha^{r}$	1, 2
Branching nucleation	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	
Phase boundary reaction	$(1-\alpha)^{r}/(1-r)$	$1-(1-\alpha)^{1-r}$	1/2, 2/3
Chemical reaction	$(1/r)(1-\alpha)^{r}$	$1-(1-\alpha)^{r}$	1/2, 2, 3, 4, 1/4, 1/3
	$(1/2)(1-\alpha)^{3}$	$(1-\alpha)^{-2}$	-
	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$	-
	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$	-
	$(1/2)(1-\alpha)^{-2/3}$	$(1-\alpha)^{-1}$	-
One-dimensional diffusion	$(1/2)\alpha^{-1}$	α^{2}	-
Two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	-
	$(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{-1}$	$[1-(1-\alpha)^{1/2}]^{2}$	-
	$4(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]^{1/2}$	$[1-(1-\alpha)^{1/2}]^{1/2}$	-
Three-dimensional diffusion	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$	-
	$6(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{1/2}$	$[1-(1-\alpha)^{1/3}]^{1/2}$	-
	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$1-2\alpha/3-(1-\alpha)^{2/3}$	-
	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^{2}$	-
	$(3/2)(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$[(1-\alpha)^{-1/3}-1]^{2}$	-
	-	$(1+\alpha)^{2/3}+(1-\alpha)^{2/3}$	-

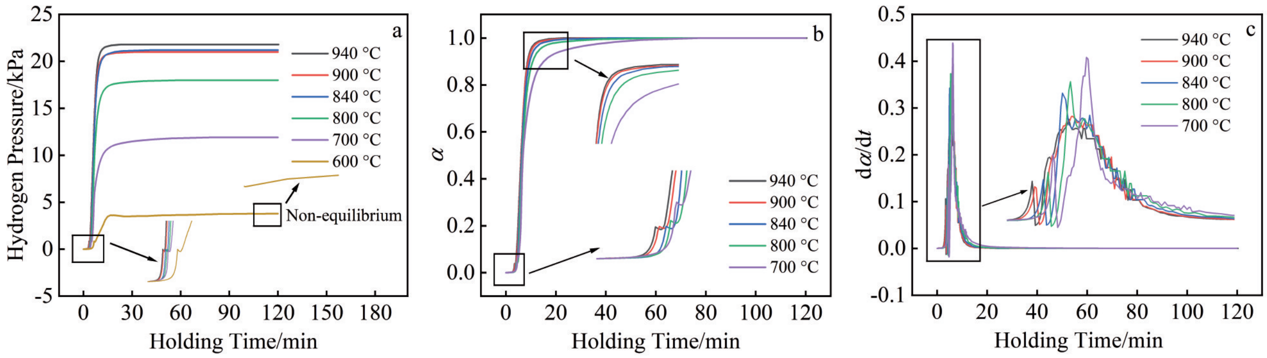

Fig.1 Hydrogen pressure (a), reaction fraction α (b), and hydrogen desorption rate $d\alpha/dt$ (c) of TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa during hydrogen desorption at different temperatures

900 and 940 °C is 3.83, 5.00, 6.00, 6.50, 6.97 and 7.67 min, respectively, which is prolonged gradually with the increase in hydrogen desorption temperature. During the temperature rise of the hydrogenated TC21 alloy from room temperature to hydrogen desorption temperature, the hydrogen desorption process is non-isothermal due to the temperature rise. In the non-isothermal hydrogen desorption stage, the hydrogen pressure rises slowly before the temperature reaches the beginning temperature of hydrogen desorption in TC21 alloy. The changes of hydrogen pressure are relatively small at all hydrogen desorption temperatures.

When the temperature of TC21 alloy reaches the beginning temperature of hydrogen desorption in the hydrogenated TC21 alloy, hydrogen starts to escape from the hydrogenated TC21 alloy driven by the hydrogen concentration gradient between the interior and exterior of the hydrogenated TC21 alloy specimen[18], leading to the rapid rise of the hydrogen pressure. With the increase in hydrogen desorption temperature, the duration in the rapid rise stage of hydrogen pressure is shortened, but the change of hydrogen pressure is not obvious.

When the hydrogen pressure rises to a certain value, the hydrogen pressure begins to decrease slowly, indicating the occurrence of hydrogen absorption in the hydrogenated TC21 alloy. Because the hydrogen absorption and hydrogen desorption of titanium alloy is a dynamic equilibrium process, the process of hydrogen absorption in titanium alloy is an exothermic reaction ($\Delta H<0$) [19–21]. Therefore, the hydrogen absorption reaction is easy to occur for TC21 alloy when the temperature of TC21 alloy is low[22]. The changes of time and hydrogen pressure in the decrease stage of hydrogen pressure are similar at different hydrogen desorption temperatures.

When the temperature of TC21 alloy continues to rise, the rate of hydrogen desorption in TC21 alloy is greater than that of hydrogen absorption, leading to the release of hydrogen in the hydrogenated TC21 alloy, and the hydrogen pressure rises rapidly again. In the constant volume vessel, the hydrogen pressure finally stabilizes when the hydrogen desorption and hydrogen absorption of TC21 alloy reach equilibrium. The equilibrium time (the time required for the hydrogen pressure to reach equilibrium) and the equilibrium hydrogen pressure are different when the hydrogenated TC21 alloy is dehydrogenated at different temperatures, as shown in Table 2. The equilibrium time of the hydrogenated TC21 alloy shortens gradually with the increase in the hydrogen desorption temperature, and the equilibrium time is shortened by 70.17% when the hydrogen desorption temperature increases from 700 °C to 940 °C. The equilibrium hydrogen pressure of the hydrogenated TC21 alloy increases gradually with the increase in hydrogen desorption temperature, and the equilibrium hydrogen pressure is the highest when the hydrogen desorption temperature is 940 °C. The equilibrium hydrogen pressure increases by 83.19% when the hydrogen desorption temperature increases from 700 °C to 940 °C. The diffusion of hydrogen molecules becomes faster with the increase in the hydrogen desorption temperature, and the process of hydrogen desorption from titanium alloy is an endothermic reaction (ΔH>0)[19,23]. Therefore, the increase in the hydrogen desorption temperature promotes the desorption of hydrogen from the hydrogenated TC21 alloy, which results in the presence of more hydrogen in the environment at the final equilibrium stage, and then the equilibrium hydrogen pressure increases with the increase in hydrogen desorption temperature.

When the hydrogenated TC21 alloy is dehydrogenated at the temperature of 600 °C, the hydrogen pressure rises constantly and does not reach equilibrium within the holding time of 120 min because of the slower reaction rate of hydrogen desorption. Therefore, the reaction fraction α of TC21 alloy dehydrogenated at the temperature of 600 °C cannot be derived according to Eq. (3).

Fig. 1b indicates that the reaction fraction increases firstly, then decreases slightly, and finally increases to 1 with the prolongation of holding time when the hydrogenated TC21 alloy is dehydrogenated at different temperatures. The holding time required for the reaction fraction to reach 1 shortens with the increase in hydrogen desorption temperature, which is the same as the holding time required for the hydrogen pressure to reach equilibrium at different hydrogen desorption temperatures. Derivation of the α-t curve yields the

Table 2 Corresponding changes of time and hydrogen pressure at each stage of hydrogen desorption at different temperatures for TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa

Hydrogen desorption temperature/°C	Change stage of hydrogen pressure	Change of holding time/min	Change of hydrogen pressure/kPa
700	Slow rise	0–2.25	0–0.023
	Rapid rise	2.25–4.67	0.023–0.818
	Decrease	4.67–4.92	0.818–0.775
	Rise	4.92–77.67	0.775–11.900
	Stabilization	77.67–120.00	11.900
800	Slow rise	0–2.50	0–0.031
	Rapid rise	2.50–4.33	0.031–0.835
	Decrease	4.33–4.58	0.835–0.777
	Rise	4.58–60.55	0.777–18.000
	Stabilization	60.55–120.00	18.000
840	Slow rise	0–2.50	0–0.0291
	Rapid rise	2.50–4.08	0.0291–0.832
	Decrease	4.08–4.33	0.832–0.777
	Rise	4.33–41.87	0.777–21.200
	Stabilization	41.87–120.00	21.200
900	Slow rise	0–2.13	0–0.029
	Rapid rise	2.13–3.72	0.029–0.820
	Decrease	3.72–3.97	0.820–0.775
	Rise	3.97–32.38	0.775–21.000
	Stabilization	32.38–120.00	21.000
940	Slow rise	0–2.08	0–0.034
	Rapid rise	2.08–3.50	0.034–0.839
	Decrease	3.50–3.83	0.839–0.776
	Rise	3.83–23.17	0.776–21.800
	Stabilization	23.17–120.00	21.800

hydrogen desorption rate, which is important for understanding the hydrogen desorption process of the hydrogenated TC21 alloy.

Fig. 1c shows that when the hydrogenated TC21 alloy is dehydrogenated at different temperatures, the hydrogen desorption rate rises firstly, then decreases, rises to the maximum value, and finally decreases to 0 with the prolongation of the holding time. With the increase in the hydrogen desorption temperature, the maximum value of the hydrogen desorption rate decreases gradually, and it decreases by 14.72% when the hydrogen desorption temperature increases from 700 °C to 940 °C.

From the above analysis, the hydrogen desorption process of the hydrogenated TC21 alloy is extremely complex, and the reaction mechanism of hydrogen desorption in TC21 alloy changes with the change of hydrogen desorption temperature. The hydrogen desorption reaction mechanisms of TC21 alloy after reaching the hydrogen desorption temperatures in the range of 700−940 °C are obtained by fitting different rate equations for different holding time periods, as shown in Table 3.

The fitted equations for the reaction mechanism of TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa during hydrogen desorption at different temperatures and holding time are shown in Fig.2. The reaction mechanism of the hydrogen desorption process of the hydrogenated TC21 alloy can be regarded as the one corresponding to the fitted equations when the absolute value of the correlation coefficient is the closest to 1. The final results of the fitted equations are shown in Table 3, which shows that all of the linear correlation coefficients of the fitted straight lines are all above 0.99, indicating that the rate constants derived from the calculations are highly reliable. As can be seen from Fig. 2, the kinetic plots are composed of several different linear segments, each of which corresponds to a unique dominating mechanism, as listed in Table 3. From the fitting results of the mechanism equations, the hydrogen desorption process is mainly dominated by nucleation and growth process ($kt=[-\ln(1-\alpha)]^{2/3}$), chemical reaction process ($kt=(1-\alpha)^{-1/2}$) and three-dimensional diffusion process ($kt=[1-(1-\alpha)^{1/3}]^{1/2}$) when the hydrogenated TC21 alloy is dehydrogenated at temperature in the range of 700−940 °C. The values of the rate constant of each process increase with the increase in the hydrogen desorption temperature, indicating that the increase in the hydrogen desorption temperature can accelerate the hydrogen desorption reaction of the hydrogenated TC21 alloy. When the hydrogenated TC21 alloy releases hydrogen, the following relationship exists among the rate constants of each process: *k* (chemical reaction process) >*k* (nucleation and growth process) >*k* (three-dimensional diffusion process). The rate constant of three-dimensional diffusion process is the lowest at different hydrogen desorption temperatures, so the three-dimensional diffusion process is the main step for restricting the hydrogen desorption rate of hydrogen desorption process.

3.2 Effect of initial hydrogen pressure on hydrogen desorption characteristics of TC21 alloy

Fig. 3 shows the hydrogen pressure, reaction fraction and hydrogen desorption rate of the TC21 alloy hydrogenated at different initial hydrogen pressures during hydrogen desorption at the temperature of 800 °C. Fig.3a shows that the changes of hydrogen pressure are similar with the prolongation of holding time. With the prolongation of holding time, the hydrogen pressure rises slowly in the first few minutes, then rises rapidly, decreases slowly for a period of time, rises again, and finally stabilizes. At the hydrogen desorption temperature of 800 °C, the equilibrium time of hydrogen desorption and the equilibrium hydrogen pressure of the TC21 alloy hydrogenated at different initial hydrogen

Table 3 Reaction mechanism and rate constant for TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa during hydrogen desorption at different temperatures

Hydrogen desorption temperature/°C	Holding time/min	Reaction mechanism, $g(\alpha)$	Rate constant/min^{-1}	Correlation coefficient
700	5.00–5.75	$[-\ln(1-\alpha)]^{2/3}$	0.188 73	0.991 71
	5.75–17.98	$(1-\alpha)^{-1/2}$	0.215 58	0.998 13
	17.98–77.67	$[1-(1-\alpha)^{1/3}]^{1/2}$	0.003 81	0.996 39
800	6.00–8.50	$[-\ln(1-\alpha)]^{2/3}$	0.304 74	0.997 78
	8.50–14.68	$(1-\alpha)^{-1/2}$	0.478 08	0.999 86
	14.68–60.55	$[1-(1-\alpha)^{1/3}]^{1/2}$	0.003 84	0.993 52
840	6.50–8.58	$[-\ln(1-\alpha)]^{2/3}$	0.321 38	0.997 78
	8.58–13.22	$(1-\alpha)^{-1/2}$	0.725 87	0.999 52
	13.22–41.87	$[1-(1-\alpha)^{1/3}]^{1/2}$	0.005 58	0.990 91
900	6.97–8.30	$[-\ln(1-\alpha)]^{2/3}$	0.351 85	0.998 69
	8.30–11.73	$(1-\alpha)^{-1/2}$	0.935 26	0.999 19
	11.73–32.38	$[1-(1-\alpha)^{1/3}]^{1/2}$	0.007 69	0.991 76
940	7.67–8.17	$[-\ln(1-\alpha)]^{2/3}$	0.362 10	0.996 77
	8.17–10.30	$(1-\alpha)^{-1/2}$	1.053 65	0.999 25
	10.30–23.17	$[1-(1-\alpha)^{1/3}]^{1/2}$	0.014 19	0.991 41

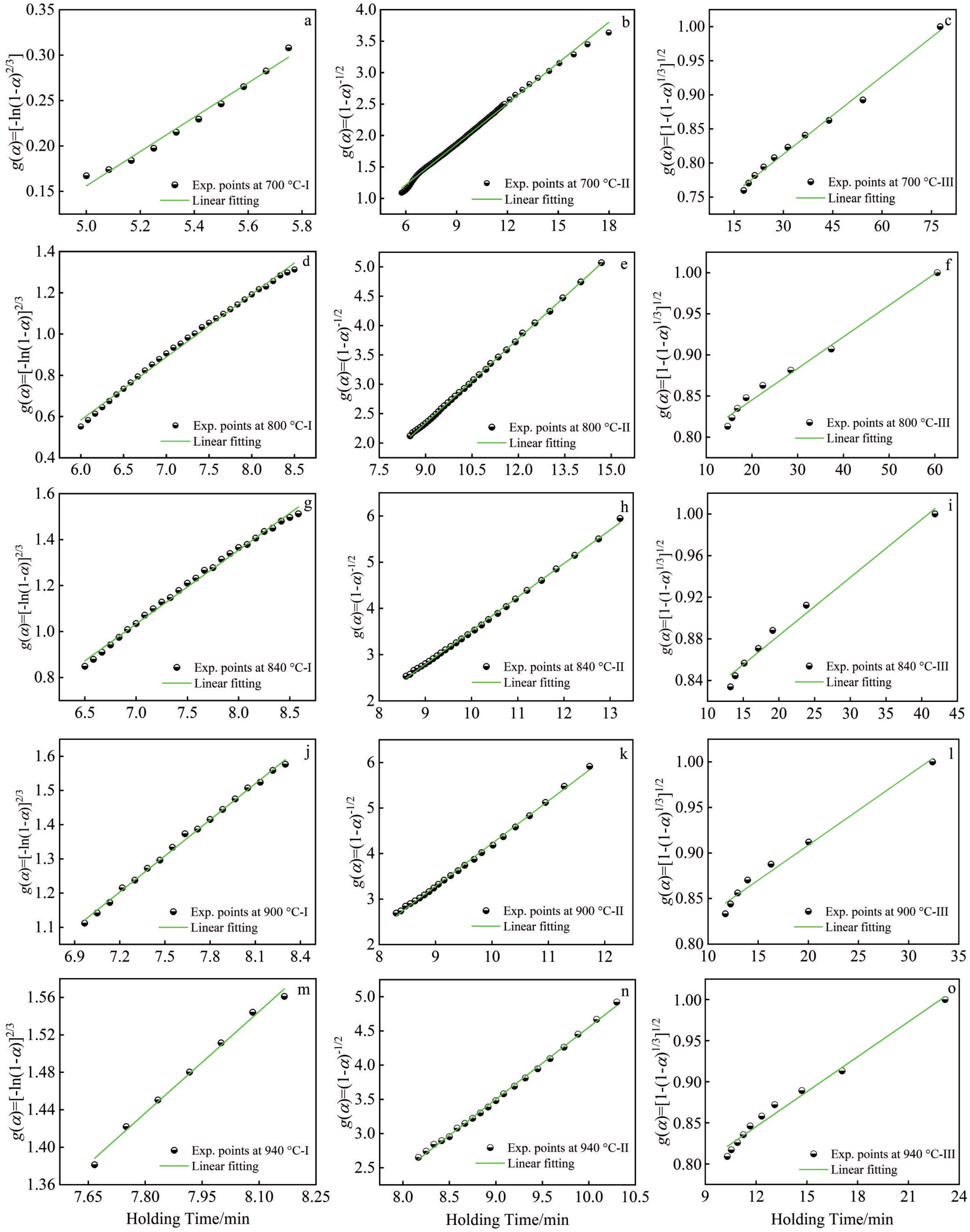

Fig.2 Reaction mechanism of TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa during hydrogen desorption at 700 °C (a–c), 800 °C (d–f), 840 °C (g–i), 900 °C (j–l), and 940 °C (m–o) with different holding time: (a) 5.00–5.75 min, (b) 5.75–17.98 min, (c) 17.98–77.67 min, (d) 6.00–8.50 min, (e) 8.50–14.68 min, (f) 14.68–60.55 min, (g) 6.50–8.58 min, (h) 8.58–13.22 min, (i) 13.22–41.87 min, (j) 6.97–8.30 min, (k) 8.30–11.73 min, (l) 11.73–32.38 min, (m) 7.67–8.17 min, (n) 8.17–10.30 min, and (o) 10.30–23.17 min

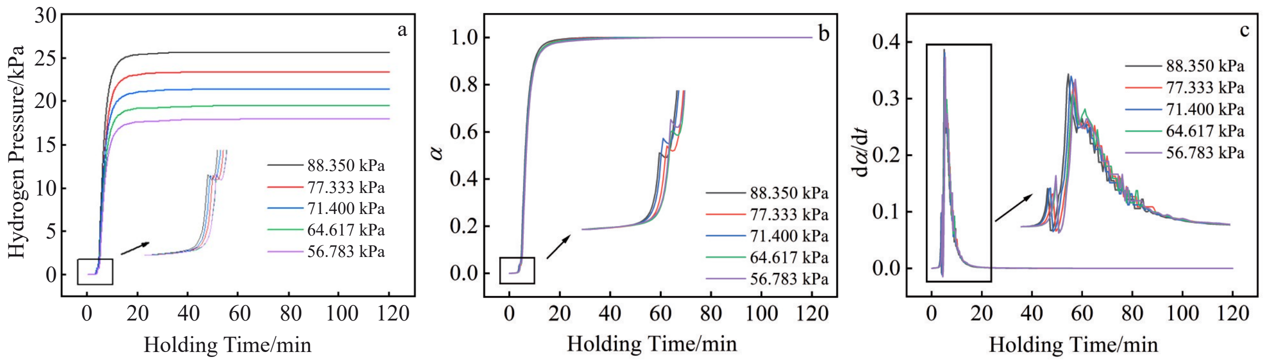

Fig.3 Hydrogen pressure (a), reaction fraction α (b), and hydrogen desorption rate dα/dt (c) of TC21 alloy hydrogenated at different initial hydrogen pressures during hydrogen desorption at the temperature of 800 °C

pressures are also different, as shown in Table 4.

The equilibrium time for hydrogen desorption of the hydrogenated TC21 alloy decreases gradually with the increase in initial hydrogen pressure, and the equilibrium time decreases by 46.77% when the initial hydrogen pressure increases from 56.783 kPa to 88.350 kPa. The equilibrium hydrogen pressure for hydrogen desorption of the hydrogenated TC21 alloy increases gradually with the increase in initial hydrogen pressure, and the equilibrium hydrogen pressure increases by 42.22% when the initial hydrogen pressure increases from 56.783 kPa to 88.350 kPa. The hydrogen content of the hydrogenated TC21 alloy also increases with the increase in initial hydrogen pressure. When the hydrogenated TC21 alloy with higher hydrogen content releases hydrogen, more hydrogen atoms are decomposed from the interior of the hydrogenated TC21 alloy under the action of the high hydrogen concentration gradient. So more hydrogen molecules attach to the surface of the hydrogenated TC21 alloy and then escape to the environment. Hydrogen desorption of titanium alloys is generally divided into several steps, consisting of decomposition of hydrides, hydrogen diffusion from α or β phase, interstitial sites and flaws to the surface, transition of hydrogen atoms from their soluted state into their chemisorbed state and hydrogen atoms bonding into hydrogen molecules at the surface[22,24–26].

Fig. 3b shows that when the TC21 alloy hydrogenated at different initial hydrogen pressures is dehydrogenated at the temperature of 800 °C, the reaction fraction increases firstly, then decreases slightly, and finally increases to 1 with the prolongation of holding time. The holding time required for the reaction fraction to reach 1 shortens with the prolongation of the initial hydrogen pressure, which presents the same variation trend as that of the holding time required for the hydrogen pressure to reach equilibrium.

Table 4 Equilibrium time and equilibrium hydrogen pressure of TC21 alloy hydrogenated at different initial hydrogen pressures during hydrogen desorption at 800 °C

Initial hydrogen pressure/kPa	Equilibrium time/min	Equilibrium hydrogen pressure/kPa
56.783	60.55	18.000
64.617	49.90	19.500
71.400	41.65	21.400
77.333	37.17	23.400
88.350	32.23	25.600

Fig. 3c shows that when the TC21 alloy hydrogenated at different initial hydrogen pressures is dehydrogenated at the temperature of 800 °C, the rate of hydrogen desorption increases firstly, then decreases, increases to the maximum value, and finally decreases to 0 with the prolongation of the holding time. With the change of the initial hydrogen pressure, the maximum value of the hydrogen desorption rate varies in the range of 0.363–0.382. The curves of hydrogen desorption rate with the prolongation of the holding time are similar, which means that the change of the initial hydrogen pressure does not affect the pattern of the hydrogen desorption rate when the hydrogen desorption temperature is constant.

3.3 Relation of residual hydrogen content with hydrogen desorption temperature and initial hydrogen pressure

Fig. 4 shows the residual hydrogen content of the TC21 alloy hydrogenated at an initial hydrogen pressure of 56.783 kPa after hydrogen desorption at different temperatures. It can be seen that the residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption decreases gradually with the increase in hydrogen desorption temperature. When the hydrogen desorption temperature increases from 600 °C to 940 °C, the residual hydrogen content decreases by 43.64%. Because the hydrogen desorption of titanium alloy is an endothermic reaction[19,23], the solubility of hydrogen in titanium alloy decreases with the increase in hydrogen desorption temperature. Therefore, more titanium hydrides decompose with the increase in hydrogen desorption temperature, which is consistent with the result that the equilibrium hydrogen pressure increases gradually with the increase in hydrogen desorption temperature (as shown in Fig. 1a). Therefore, the residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption decreases gradually with the increase in hydrogen desorption temperature.

Fig. 5 shows the residual hydrogen content of the TC21

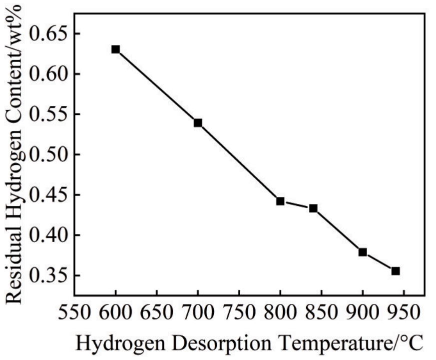

Fig.4 Residual hydrogen content of TC21 alloy hydrogenated at initial hydrogen pressure of 56.783 kPa after hydrogen desorption at different temperatures

alloy hydrogenated at different initial hydrogen pressures after hydrogen desorption at 800 °C. The residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption increases gradually with the increase in initial hydrogen pressure, and it increases by 23.98% when the initial hydrogen pressure increases from 56.783 kPa to 88.350 kPa. With the increase in initial hydrogen pressure, the concentration gradient of hydrogen between the interior and exterior of TC21 alloy specimen becomes larger before the absorption of hydrogen during the hydrogenation stage, and then more hydrogen diffuses into the interior of the hydrogenated TC21 alloy. Therefore, the hydrogen content of the hydrogenated TC21 alloy increases with the increase in initial hydrogen pressure, leading to the increase in residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption at the same hydrogen desorption temperature.

3.4 Hydrogen desorption activation energy

If the hydrogen desorption reaction mechanism of TC21 alloy is the same at different hydrogen desorption temperatures, the rate constant (k) of hydrogen desorption of the hydrogenated TC21 alloy can be expressed by the Arrhenius equation, as shown in Eq. (4)[27–30].

$$k = A\mathrm{e}^{-\frac{E}{RT}} \tag{4}$$

where A is the pre-exponential factor, E is the reaction activation energy, R is the molar gas constant, and T is the hydrogen desorption temperature. Eq. (4) can be transformed into Eq. (5).

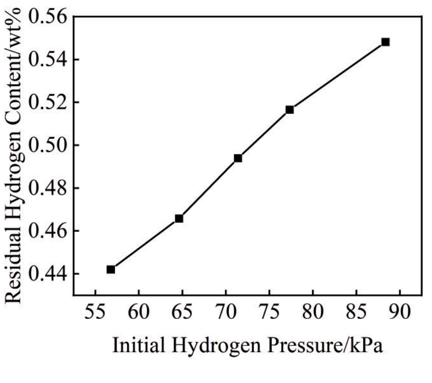

Fig.5 Residual hydrogen content of TC21 alloy hydrogenated at different initial hydrogen pressures after hydrogen desorption at 800 °C

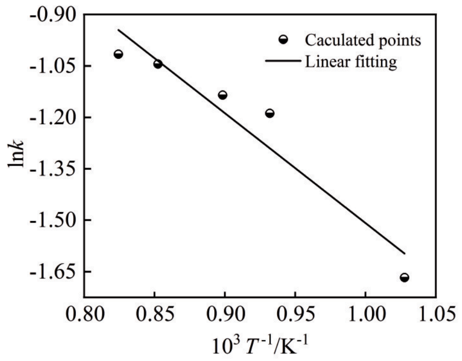

Fig.6 Arrhenius plot of hydrogen desorption reaction rate in TC21 alloy

$$\ln k = \ln A - \frac{E}{RT} \tag{5}$$

From Eq. (5), the hydrogen desorption activation energy E of TC21 alloy can be derived by the Arrhenius plot, as shown in Fig.6. The slope of the linear fitting Arrhenius curve for the hydrogen desorption of TC21 alloy is −3.207, which deduces that the activation energy of the hydrogen desorption of TC21 alloy is about 26.663 kJ/mol.

4 Conclusions

1) During the hydrogen desorption of the hydrogenated TC21 alloy, the hydrogen pressure rises slowly in the first few minutes, rises rapidly, then decreases slowly for a period of time, rises again, and finally stabilizes with the prolongation of holding time. The equilibrium time shortens gradually and the equilibrium hydrogen pressure increases gradually with the increase in hydrogen desorption temperature. The equilibrium time shortens gradually and the equilibrium hydrogen pressure increases gradually with the increase in initial hydrogen pressure.

2) The reaction fraction increases firstly, then decreases slightly, and finally increases to 1 with the prolongation of holding time when the hydrogenated TC21 alloy is dehydrogenated. The holding time required for the reaction fraction to reach 1 shortens with the increase in hydrogen desorption temperature. The hydrogen desorption rate rises firstly, then decreases, rises to the maximum value, and finally decreases to 0 with the prolongation of holding time. With the increase in hydrogen desorption temperature, the maximum value of the hydrogen desorption rate decreases gradually. The change of the initial hydrogen pressure does not affect the pattern of the hydrogen desorption rate when the hydrogen desorption temperature is constant.

3) The hydrogen desorption process is mainly dominated by nucleation and growth process ($kt=[-\ln(1-\alpha)]^{2/3}$), chemical reaction process ($kt=(1-\alpha)^{-1/2}$) and three-dimensional diffusion process ($kt=[1-(1-\alpha)^{1/3}]^{1/2}$) when the hydrogenated TC21 alloy is dehydrogenated at temperatures in the range of 700–940 °C.

The values of the rate constant of each process increase with the increase in hydrogen desorption temperature. The increase in the hydrogen desorption temperature can accelerate the hydrogen desorption reaction of the hydrogenated TC21 alloy. When the hydrogenated TC21 alloy releases hydrogen, the following relationship exists among the rate constants of each process: k (chemical reaction process) >k (nucleation and growth process)>k (three-dimensional diffusion process). The three-dimensional diffusion process is the main step for restricting the hydrogen desorption rate of hydrogen desorption process.

4) The residual hydrogen content of the hydrogenated TC21 alloy after hydrogen desorption decreases gradually with the increase in hydrogen desorption temperature and it increases gradually with the increase in initial hydrogen pressure.

5) The activation energy of TC21 alloy in the process of hydrogen desorption is about 26.663 kJ/mol.

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TC21合金等温定容放氢动力学及特性

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摘　要：使用定容法研究了TC21合金放氢的动力学及特性、剩余氢含量和激活能。结果表明，放氢温度和初始氢压影响TC21合金的放氢特性。当氢化TC21合金在700~940 ℃温度范围内放氢时，放氢过程主要由形核长大过程（$kt=[-\ln(1-\alpha)]^{2/3}$）、化学反应过程（$kt=(1-\alpha)^{-1/2}$）和三维扩散过程（$kt=[1-(1-\alpha)^{1/3}]^{1/2}$）控制。当氢化TC21合金放氢时，各过程的速率常数之间存在以下关系：k（化学反应过程）> k（形核长大过程）> k（三维扩散过程）。氢化TC21合金放氢后的剩余氢含量随着放氢温度的升高而逐渐减少，随着初始氢压的升高而逐渐增加。TC21合金在放氢过程中的激活能约为26.663 kJ/mol。

关键词：TC21合金；放氢；动力学；激活能

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