

Hydrogen absorption behavior of TA15 alloy

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(Received: 14 March 2010; revised: 30 April 2010; accepted: 13 May 2010)

Abstract: The hydrogen absorption kinetics of TA15 titanium alloy at 973–1123 K was studied using a tube-type hydrogen treatment furnace. The hydrogen absorption kinetic curves obtained were analyzed according to a series of mechanism equations to reveal the kinetic parameters and mechanism of the hydrogen absorption process. The results show that both the hydrogen absorption rate and the equilibrium hydrogen pressure increase and the time to reach equilibrium is shortened with increasing temperature. It is found that only the second hydrogen absorption period exists in the hydrogen absorption process of TA15 alloy between 973 and 1123 K, and the activation energy is 54.889 kJ/mol for hydrogen absorption. X-ray diffraction (XRD) and scanning electron microscopy (SEM) results demonstrate that δ hydride forms between 973 and 1123 K, and β phase decreases with the increase of temperature. Orthorhombic α'' martensite is generated at 1073–1123 K, and their amount increases with increasing temperature.

Keywords: titanium alloy; kinetics; activation energy; microstructure

[This work was financially supported by the Major State Basic Research and Development Program of China (No.11AZ6305).]

1. Introduction

In recent years, the use of hydrogen as a temporary alloying element in titanium alloys has become an attractive approach for controlling the microstructures, enhancing the processability, and improving the mechanical properties [1–4]. This so-called thermal hydrogen processing (THP), which is based on the modifying effect of hydrogen as an alloying element on phase compositions and kinetics of phase transformations, is widely applied in titanium alloys [5].

TA15 alloy is a near- α titanium alloy with high aluminum equivalence, which was successfully developed as BT20 titanium alloy in Russia in 1964 [6–7]. It is an important alloy extensively used in the fields of spaceflight and aviation, especially for manufacturing aircraft components due to its unique properties, such as high specific strength, thermal stability, and weldability [8]. Currently, studies of

TA15 alloy are mainly focused on microstructures and mechanical properties under different treatment conditions [8–11]. However, there is very limited work reported on hydrogenation of TA15 alloy. Since hydrogen is extensively used to optimize the properties of titanium alloys, it is necessary to comprehend the kinetics of hydrogen absorption in TA15 alloy.

In this paper, TA15 alloy was hydrogenated to investigate the effect of temperature on its hydrogen absorption reactions, activation energy, and the microstructures and phase transformations before and after hydrogenation, which will provide the basis for further research on the modification mechanism of TA15 alloy by hydrogenation, as well as the control and optimization of the THP process.

2. Experimental procedures

The material used in this study was $\phi 23$ mm \times 55 mm

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TA15 alloy. The microstructure of TA15 alloy originally is an α (dark)+ β (light) structure, which is shown in Fig. 1. A constant-volume and variable-pressure method was adopted to study the hydrogen absorption kinetics in TA15 alloy. The tests were carried out in a tube-type hydrogen treatment furnace at 973-1123 K. The specimens were cleaned in acetone for 5 min before thermal hydrogen processing. After the specimen was put into the furnace, the chamber was vacuumized down to 2×10^{-3} Pa and then heated at 10 K/min. After reaching the setting temperature, high-purity hydrogen was filled into the chamber. The specimen was held for 180 min to allow hydrogen to diffuse completely. Then the specimen was cooled down to room temperature in the furnace, and the chamber was vacuumized to 2×10^{-3} Pa again. Finally, nitrogen was filled into the chamber until the atmospheric pressure was reached before the specimen was taken out. Hydrogen pressure was measured by a highly sensitive pressure gauge monitor at regular time intervals during all the hydrogen absorption process. The hydrogen absorption rate was determined by calculating the change of measured hydrogen pressure.

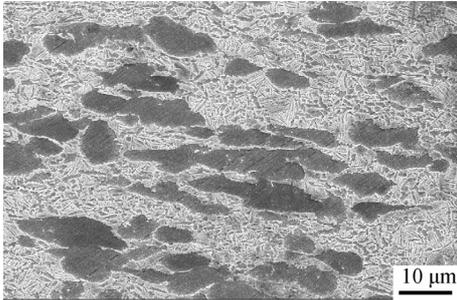


Fig. 1. Microstructures of the original TA15 alloy.

After the specimens were polished and etched in a solution of HF:HNO₃:H₂O=2:3:95 (vol%) for 15-25 s, metallographic observations were carried out using scanning electron microscopy (SEM, LEO 1450). Phase identification of specimens before and after thermal hydrogenation processing was conducted by DMAX-RB12KW rotating anode X-ray diffraction (Cu K_a radiation, 40.0 kV/150.0 mA).

3. Kinetic equation

Usually, the hydrogen absorption reaction is composed of 5 steps as follows [12-14]: (1) physisorption of hydrogen molecules; (2) dissociation of hydrogen molecules and chemisorption; (3) surface penetration of hydrogen atoms; (4) diffusion of hydrogen atoms through the hydride layer, either by an interstitial or a vacancy mechanism; (5) hydride formation at the metal/hydride interface. The usual method

for studying kinetics is to fit the time-dependent reacted fraction $\alpha(t)$ with various analytical rate expressions, so as to determine the reaction mechanism or intrinsic rate-controlling step.

The rate equation of kinetics for solid-gas reaction is expressed as follows [15].

$$d\alpha/dt = k \cdot f(\alpha) \quad (1)$$

where t is the time, k the rate constant, $f(\alpha)$ a function determining the reaction mechanism. The integral form of $f(\alpha)$ is expressed by $g(\alpha)$.

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

$f(\alpha)$ or $g(\alpha)$ refers to the 41 mechanism functions including chemical reaction, diffusion, nucleating, and nuclei growth, respectively [15].

Based on the experimental data of hydrogen absorption curves, the reacted fraction α can be calculated by the following equation.

$$\alpha = \frac{P_0 - P_t}{P_0 - P_e} \quad (3)$$

where P_0 is the initial pressure; P_t and P_e the pressures at time t and the final equilibrium, respectively.

The data t , α , and $d\alpha/dt$ obtained from α - t kinetic curves of hydrogen absorption were regressed linearly based on Eqs. (1) and (2). The function $f(\alpha)$ or $g(\alpha)$ given the best linearity is considered as the mechanism of hydrogen absorption reaction in TA15 alloy. The rate function of hydrogen absorption and the kinetic parameter k can be obtained from the linear regression fitting. Then the apparent activation energy E of hydrogen absorption in TA15 alloy can be calculated based on the Arrhenius relationship.

4. Results and discussion

4.1. Reaction mechanism

The hydrogen absorption kinetic curves of TA15 alloy at different temperatures are shown in Fig. 2. In the range of 973-1123 K, the hydrogen pressure decreases fast at the beginning, then slows down, and finally reaches equilibrium. The equilibrium pressure increases with the increase of setting temperature. For example, the equilibrium pressure is about 5.37, 8.49, and 13.19 kPa at 973, 1023, and 1123 K, respectively. The reason is that the hydrogen absorption

process is an exothermic reaction [16], and high temperature will inhibit the hydrogen absorption reaction. As the temperature increases, the time required to reach the equilibrium is shortened.

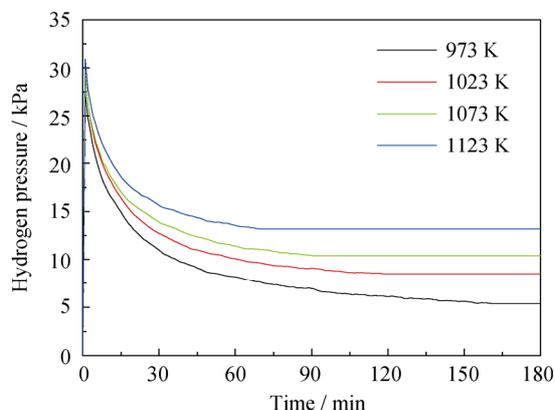


Fig. 2. Hydrogen absorption kinetic curves of TA15 alloy at different temperatures.

Fig. 3 shows a group of curves of the calculated reacted fraction α with time at different temperatures, from which it illustrates that, the higher the temperature is, the less the time needs to reach equilibrium. It took 40 min for the reacted fraction α to reach 0.81, 0.86, 0.88 and 0.92 at 973, 1023, 1073, and 1123 K, respectively. It is also obvious that the shapes of reacted fraction curves do not change at different temperatures. This is most likely associated with no change in the rate-controlling step for the hydrogen absorption process in TA15 alloy [17].

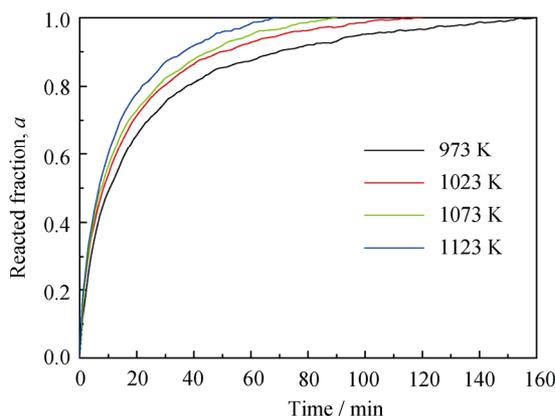


Fig. 3. Reacted fraction curves of hydrogen absorption in TA15 alloy at different temperatures.

The hydrogen absorption rate da/dt is extremely important to understand the reaction mechanism of hydrogen absorption. The hydrogen absorption process is generally divided into three periods: the incubation period, the first hydrogen absorption period, and the second hydrogen absorp-

tion period on the basis of hydrogen absorption rate [18]. The incubation period is defined as the time between the beginning of hydrogen exertion into the chamber and the start of hydrogen absorption, which depends on hydrogen absorption activity and surface conditions of the materials [19]. The first hydrogen absorption period is the activation stage, during which the hydrogen absorption rate increases with increasing activation temperature and time [15]. The reaction rate decreases during the second hydrogen absorption period due to the decrement of driving force [15]. The hydrogen absorption rates in TA15 alloy at different isothermal temperatures are shown in Fig. 4. In the range of 973-1123 K, the reaction rate reaches its maximum at the beginning and then decreases to its minimum level when the hydrogen pressure approaches to its equilibrium pressure. This indicates that only the second hydrogen absorption period exists in the hydrogen absorption process of TA15 alloy between 973 and 1123 K. Comparing the profiles at the beginning of the process, it is shown that the reaction rate increases with increasing temperature.

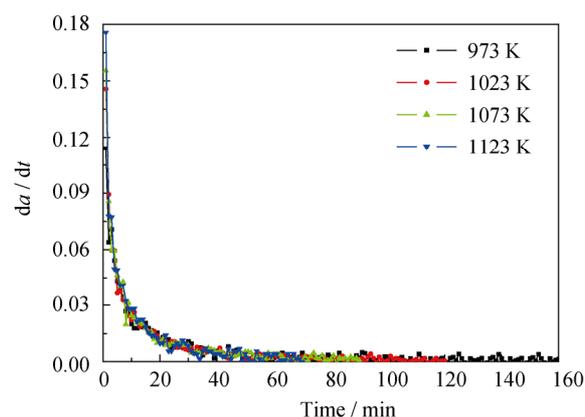


Fig. 4. Hydrogen absorption rate curves of TA15 alloy at different temperatures.

To better understand the mechanism of hydrogen absorption of TA15 alloy, the individual reacted fraction curve was fitted by the equations listed in Ref. [15]. The fitting equations with the largest correlation coefficient r and the smallest standard deviation are considered as the best kinetic reaction mechanisms to describe the hydrogen absorption process. The best fitting function of the hydrogen absorption process from 973 to 1123 K is $[1-(1-\alpha)^{1/2}]^2$, as shown in Fig. 5. It suggests that the rate-controlling step of the hydrogen absorption process is a two-dimensional diffusion mechanism. The slope of the regressed lines indicates that the rate constant k increases with increasing temperature. Table 1 shows the rate constants for hydrogen absorption reaction in TA15 alloy at different temperatures.

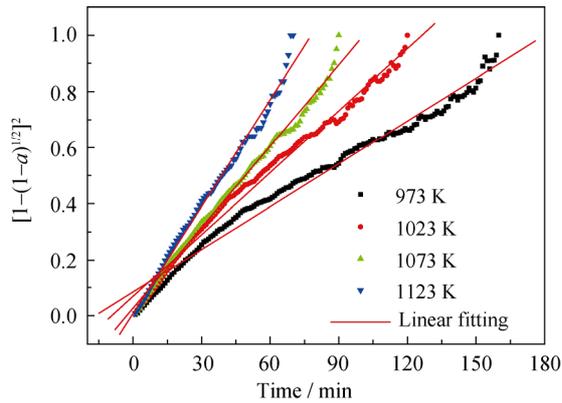


Fig. 5. Relations of reaction function with time in hydrogen absorption reaction of TA15 alloy at different temperatures.

Table 1. Rate constants for hydrogen absorption reaction in TA15 alloy at different temperatures

Temperature / K	Rate constant / min ⁻¹	Correlation coefficient
973	0.00509	0.99132
1023	0.00737	0.99420
1073	0.0964	0.99678
1123	0.01272	0.99490

4.2. Activation energy

Assuming that the reaction mechanisms are the same at different experimental temperatures, the rate constant can be obtained according to the Arrhenius equation [18]:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where A is the pre-exponential factor; E the activation energy of reaction, $\text{kJ}\cdot\text{mol}^{-1}$; R the molar gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T the hydrogenation temperature, K.

The natural logarithm of the Arrhenius equation is

$$\ln k = \ln A - \frac{E}{RT} \quad (5)$$

When the rate constants at different temperatures are extracted from hydrogen absorption curves, the activation energy E of the hydrogen absorption can be obtained from the slope of the $\ln k$ vs. $1/T$ curve.

As discussed above, the hydrogen absorption process in TA15 alloy is controlled by the same reaction mechanism between 973 and 1123 K. So the Arrhenius plot is possible to be constructed in Fig. 6. The fitting correlation coefficient up to 99.904% indicates that the method is practicable. The calculated activation energy E of hydrogen absorption reaction in TA15 alloy is 54.889 kJ/mol , which is close to that in α -Ti [20-21].

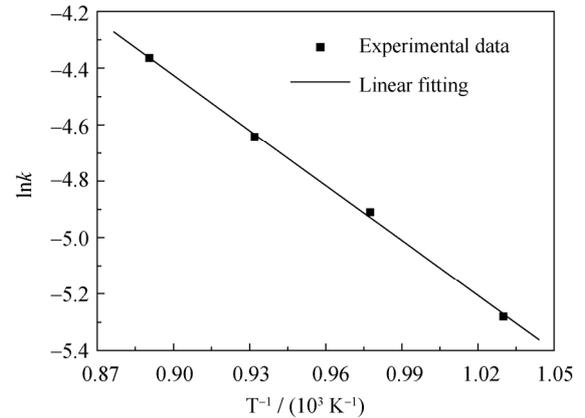


Fig. 6. Arrhenius plot of hydrogen absorption reaction rate in TA15 alloy.

4.3. Microstructures and phase transformations

Phase transformations of TA15 alloy before and after hydrogenation are demonstrated by XRD patterns in Fig. 7. δ hydride is formed between 973 and 1123 K, corresponding to the phase transformations of $\beta \rightarrow \beta + \delta$ in the hydrogen absorption process, $\beta \rightarrow \alpha + \delta$ and $\alpha \rightarrow \alpha + \delta$ in the cooling process [22]. Martensite transformation occurs at 1073 and 1123 K. It is because the cooling rate is larger at a higher temperature during cooling in the furnace, and hydrogen in TA15 alloy decreases the starting temperature and the critical cooling rate of martensite transformation [23]. Furthermore, part of the peaks broaden, as part of the peaks of orthorhombic α'' martensite and δ hydride with a face-centered cubic structure are lapped over those of α and β phase [24].

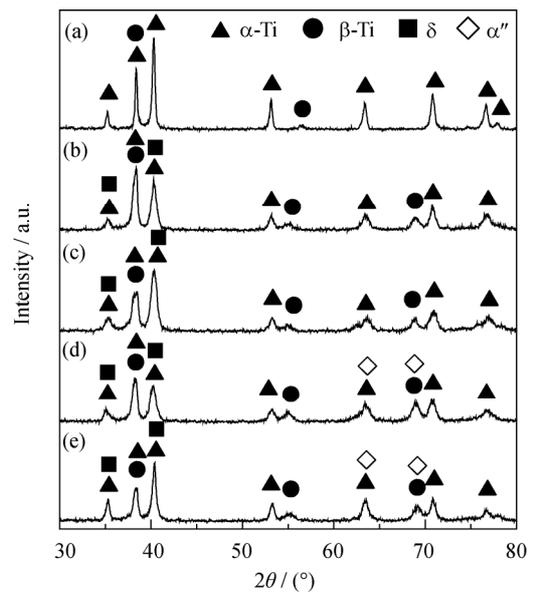


Fig. 7. XRD patterns of TA15 alloy before and after hydrogenation at different temperatures: (a) original sample; (b) 973 K; (c) 1023 K; (d) 1073 K; (e) 1123 K.

The microstructures of TA15 alloy after being hydrogenated at different temperatures are shown in Fig. 8. The hydrogen concentrations are 0.519%, 0.505%, 0.489%, and 0.321% after being hydrogenated at 973, 1023, 1073, and 1123 K, respectively. From the comparison of Figs. 8(a) and 1, it is clear that β phase increases because the $\alpha \rightarrow \beta$ transformation occurs during the hydrogen absorption process. It is because hydrogen is a β stabilizer, and it reduces the β transformation temperature. When the temperature increases to 1023

K, the hydrogen concentration decreases, and thus β phase decreases, as shown in Fig. 8(b). Fig. 8(c) shows that some orthorhombic α'' martensite is generated at 1073 K. With the temperature increasing to 1123 K, mass orthorhombic α'' martensite can be found in Fig. 8(d), despite the lower hydrogen concentration compared with that of 1073 K. It is because of the higher cooling rate at a higher temperature, which is more helpful to the occurrence of martensite transformation. δ hydride is very fine, so it cannot be observed by SEM.

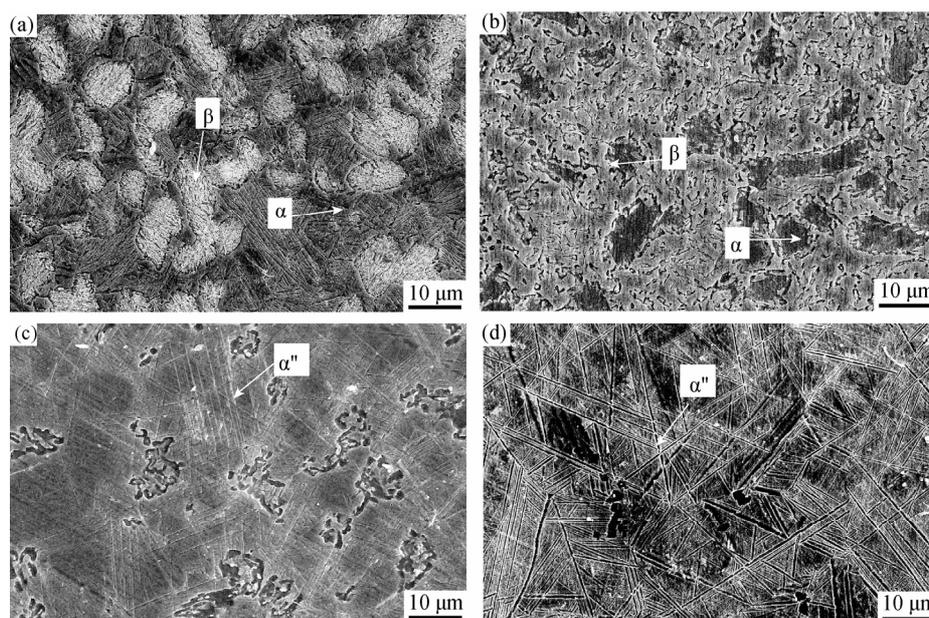


Fig. 8. SEM micrographs of TA15 alloy with hydrogenation: (a) 973 K; (b) 1023 K; (c) 1073 K; (d) 1123 K.

5. Conclusions

(1) When the hydrogen absorption temperature increases from 973 to 1123 K, both the hydrogen absorption rate and the equilibrium hydrogen pressure are increased, and the time required to reach equilibrium is shortened.

(2) Only the second hydrogen absorption period exists in the hydrogen absorption process of TA15 alloy between 973 and 1123 K, with the reaction mechanism function $[1-(1-a)^{1/2}]^2$. The calculated activation energy E of hydrogen absorption reaction in TA15 alloy is 54.889 kJ/mol.

(3) XRD and SEM results show that δ hydride forms between 973 and 1123 K, and β phase reduced with the increase of temperature from 973 to 1023 K. Orthorhombic α'' martensite is generated at 1073 and 1123 K, and increases with increasing temperature.

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