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ARTICLE

Hydrogenation Behavior of Ti6Al4V Alloy

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Abstract: The hydrogenation behavior of Ti6Al4V alloy was investigated at different hydrogenation temperatures, holding time and hydrogen pressures. The distribution of hydrogen in titanium alloy was studied by OM. Results show that the hydrogen content of Ti6Al4V alloy is controlled by hydrogenation temperature, hydrogen pressure and holding time. Hydrogen content increases first and then decreases with the increasing of hydrogenation temperature. Hydrogen content increases linearly with the increasing of hydrogen pressure. The process of hydrogenation is diffusion of hydrogen into titanium alloy, and the distribution of hydrogen becomes uniform with the increase of holding time.

Key words: titanium alloy; thermohydrogen processing; hydrogenation behavior; dynamic rule

Light weight metals have received much attention in various engineering applications over recent years [1-6]. Titanium and titanium alloys have the characteristics of non-magnetism, low density, small coefficient of linear expansion, excellent mechanical properties and good corrosion resistance, which are widely used in aerospace, biomedical and chemical industries. But the shortcomings of high yield ratio, low room temperature plasticity and large deformation resistance restrict the cold forming of titanium alloys. Therefore, how to improve the properties of titanium alloys at room temperature is of great application value.

Recently, the research to use hydrogen for improving the mechanical properties of titanium alloy has become a hot topic, which is called thermohydrogen processing (THP)[7-12]. THP of titanium alloys, a technique in which hydrogen is used as a temporary alloying element in titanium, allows to enhance microstructural control and improve mechanical properties [13]. As hydrogenation is actually a diffusion process, the distribution of hydrogen in titanium alloy has an important effect on processabilities and service properties after hydrogenation processing. For the machining technology, it just needs to improve its organization in a certain range of cutting level to achieve the purpose of improving machining ability. So it is of more practical significance to obtain gradient organization which can improve the processing performance by controlling the hydrogenation process. At present, few researches on the laws of the hydrogenation are carried out, in-depth study on hydrogen absorption behavior of titanium alloy and the hydrogen distribution in titanium alloy is of an important academic value and a practical significance.

In the present investigation, hydrogenation treatment was carried out on Ti6Al4V alloy by controlling variables methods to study the hydrogenation behavior of the titanium alloy, the effects of hydrogenation temperature, holding time and hydrogen pressure on the hydrogen absorption law of the titanium alloy were studied. The distribution of hydrogen in titanium alloy was analyzed.

1 Experiment

The material used in the present work was Ti6Al4V alloy, which consisted of α phase and β phase, and its microstructure was shown in Fig.1. Specimens were cylinders with 8 mm in diameter and 12 mm in height, they were hydrogenated in an atmosphere of hydrogen in a tube-type furnace at a set hydrogenation temperature and hydrogen pressure for a set holding time, and then air cooled

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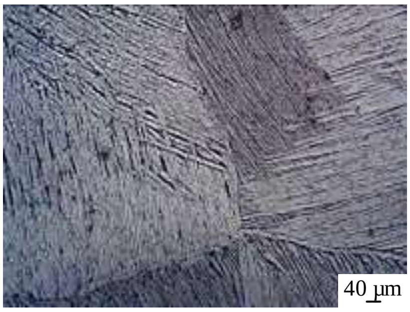

Fig.1 Microstructure of Ti6Al4V alloy

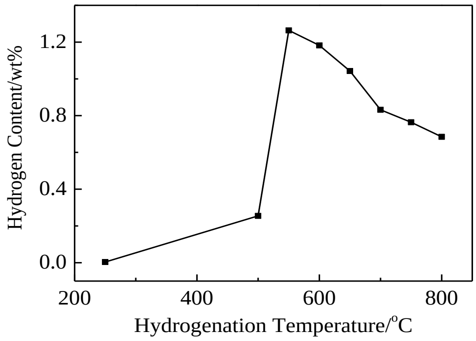

Fig.2 Effect of hydrogenation temperature on hydrogen content of Ti6Al4V alloy

to room temperature. Hydrogenation temperature was in the range of 250~800 ℃. Hydrogen pressure was in the range of 0.026~0.101 MPa. Holding time was in the range of 0~120 min. The hydrogen level was determined by weighing the specimens before and after hydrogenation by an electronic analytical balance with a measurement accuracy of 10^{-5} g.

Distribution of hydrogen in Ti6Al4V alloy was investigated by optical microscopy (OM, Olympus BHM-2UM). OM specimens were cut axially on an electric discharging machine, ground with emery papers, then polished on a polishing machine, and finally etched in a mixed solution of HF:HNO_3:H_2O=1:1:8 in volume to reveal the microstructures.

2 Results and Discussion

2.1 Relationship between hydrogenation temperature and hydrogen content

Effect of hydrogenation temperature on hydrogen content of Ti6Al4V alloy is shown in Fig.2. It can be seen that hydrogen content of Ti6Al4V alloy increases first and then decreases with the increasing of hydrogenation temperature. Hydrogen content increases slowly when hydrogenation temperature is below 550 ℃ because the chemical activity of Ti and the nucleation rate are lower when the temperature is low. Another reason is the natural oxide film on the surface of the specimen which can restrict the diffusion of hydrogen when the annealing temperature is below 550 ℃. So the process of hydrogen absorption is limited when the hydrogenation temperature is below 550 ℃. Hydrogen content increases rapidly when hydrogenation temperature exceeds 550 ℃ because of the higher chemical activity of Ti and diffusion coefficient of hydrogen at high temperature and the better surface quality (the natural oxide film on the surface of the specimen disappears when the annealing temperature is higher than 550 ℃). Hydrogen content reaches its maximum value when the hydrogenation temperature is about 550 ℃ and decreases with the increasing of hydrogenation temperature. The reason is that titanium and hydrogen can react to generate Ti-H compound, and absorbing of hydrogen into titanium alloy is an exothermal reaction[14,15]. With the increasing of hydrogenation temperature, the equilibrium of hydrogen absorption reaction moves towards the direction of reactants, Ti-H compound decomposes, and then hydrogen content decreases until the reaction reaches the equilibrium.

2.2 Relationship between hydrogen content and hydrogen pressure

When the holding time is 120 min, hydrogenation temperature is 750 ℃, the effect of hydrogen pressure on hydrogen content of Ti6Al4V alloy is shown in Fig.3. It can be seen that hydrogen content of Ti6Al4V alloy increases linearly with the increasing of hydrogen pressure. Hydrogen content increases by 124.5% when hydrogen pressure increases from 0.026 MPa to 0.101 MPa. As the solid solubility C_H of hydrogen in metal has relationship with ambient pressure, the C_H can be deduced by the thermodynamic equation, as shown in Eq.(1)[15].

$$C_H = AP^{1/2}\exp(-\Delta E/RT) \quad (1)$$

where A is constant, P is pressure, ΔE is the change in energy of phase transition from gas to solid, R is the gas constant and T is the temperature of metal. It can be seen that C_H increases when the hydrogen pressure increases, leading to an increase of the hydrogen content in Ti6Al4V alloy.

2.3 Relationship between hydrogen pressure and holding time

As shown in Fig.4, hydrogen pressure decreases during the process of hydrogenation. Hydrogen pressure decreases severely when the holding time is less than 10 min, and by 32% when the holding time increases from 0 min to 10 min. Hydrogen pressure decreases slowly when the holding time exceeds 10 min, and by 4% when the holding time increases from 10 min to 120 min. Hydrogen content becomes stable finally with the increasing of holding time. Since the gas pressure is proportional to amount of substance in an airtight container, as shown in Eq.(2).

$$P = nRT/V \quad (2)$$

where P is the gas pressure, n is the amount of substance, R is the gas constant, T is the temperature, and V is the volume

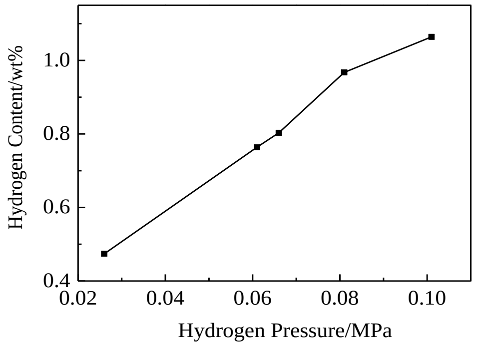

Fig.3 Effect of hydrogen pressure on hydrogen content of Ti6Al4V alloy

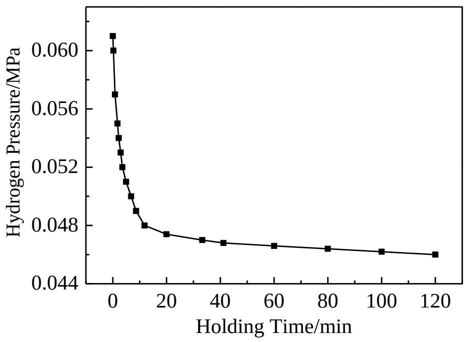

Fig.4 Relationship between hydrogen pressure and holding time during hydrogenation process at 750 ℃

of container. The time is too short for hydrogen to spread into the interior of the specimen at the initial stage because the process of hydrogenation is a diffusion of hydrogen into titanium alloy, resulting in the much higher hydrogen concentration on the surface of the specimen than that in the interior. Hydrogen diffuses from the surface to the interior with the increasing of holding time. At the same time, the amount of hydrogen molecules rapidly declines, leading to a decrease of hydrogen pressure severely. The hydrogen concentration difference between the center and the edge of the sample decreases with the increasing of holding time, hydrogen absorption tends to be an equilibrium state and hydrogen pressure remains stable finally.

From the view of hydrogen absorption kinetics, hydrogen reaction fraction α can be described as Eq. (3) [16].

$$\alpha = \frac{p_i - p}{p_i - p_e} \quad (3)$$

where p_i is the initial hydrogen pressure, p_e is the equalized hydrogen pressure, and p is the hydrogen pressure at t. Hydrogen absorption kinetics curve is shown in Fig.5. Hydrogen absorption process generally includes three stages: the induction period, the first hydrogen absorption stage and the second hydrogen absorption stage [17]. The existence of the induction period is due to the effect of passivation of the oxide layer in surface of alloy; then hydrogen absorption begins, and the reaction rate can be described by the function of hydrogen pressure changing with time; finally the reaction reaches an equilibrium, and the pressure remains a constant at a given temperature. From Fig.5, it can be seen that the hydrogen absorption of Ti6Al4V alloy has no obvious induction period. Once the alloy contacts with hydrogen, the reaction begins immediately and the reaction rate reaches the maximum. With an increase of holding time, hydrogen content in alloy is close to the saturated solid solubility, the reaction rate declines monotonously until to the end of the reaction and hydrogen pressure gradually tends to be equalized.

2.4 Relationship between hydrogen content and holding time

As shown in Fig.6, hydrogen content of Ti6Al4V alloy increases with the increasing of holding time. Hydrogen content in Ti6Al4V alloy increases rapidly at the beginning and slowly with the increasing of holding time. The amplitude of hydrogen content in Ti6Al4V alloy is higher when the holding time is less than 30 min. When the holding time exceeds 30 min, hydrogen content in Ti6Al4V alloy becomes stable. Results indicate that the speed rate of absorbing hydrogen into titanium alloy is fast at the initial stage during the process of hydrogenation, and decreases with the increasing of holding time. This phenomenon is corresponding to the relationship between hydrogen pressure and holding time, as shown in Fig.4 and Fig.5. When H_2 molecules reach the surface of the alloy, physical adsorption occurs on the surface, and then H_2 absorbed on the surface resolve into H atoms (ions state). Under the effect of concentration gradient, hydrogen atoms diffuse into the interior until hydrogen concentration becomes uniform [18]. At the beginning of hydrogenation process, the difference of hydrogen concentration between the center and the edge is larger, leading to a fast diffusion speed of H atom. Therefore hydrogen content of Ti6Al4V alloy increases quickly. The concentration difference becomes smaller with

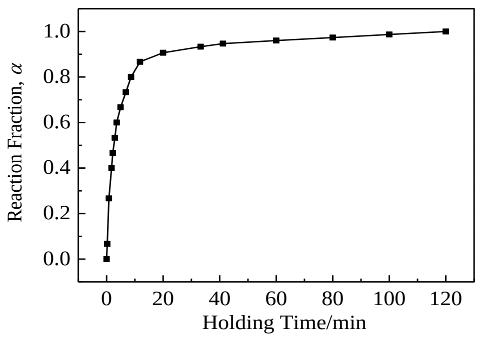

Fig.5 Hydrogen absorption kinetics curve

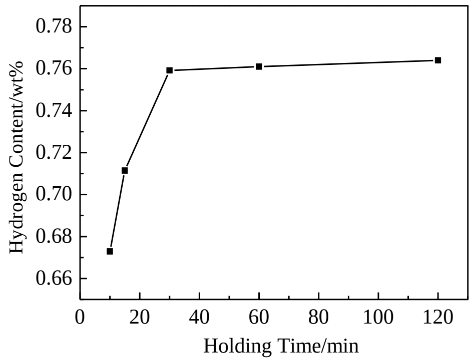

Fig.6 Effect of holding time on hydrogen content of Ti6Al4V alloy

an increase of holding time, causing a decrease of the diffusion speed of H atom. Hydrogenation process will be ended when the hydrogen concentration becomes uniform. Because of high temperature, the diffusion speed of hydrogen and hydrogen absorption rate are very fast. 30 min is enough for H_2 diffusion from the edge to the center of the specimen. When the holding time exceeds 30 min, the hydrogen absorption rate becomes very slow and hydrogen content basically reaches an equilibrium.

2.5 Hydrogen distribution

As shown in Fig. 7, when the holding time is 1 min, microstructure is obviously different between the center and the edge of the specimen, indicating that the distribution of hydrogen in the specimen is not uniform. The microstructure in the central area is similar to the original microstructure. At the edge of the specimen, a complete martensites structure consisting of α' and α'' is observed. In addition, grain boundaries become blurred as the addition of hydrogen reduces the potential difference between α and β when the hydrogen content reaches a certain value. And during the process of metallographic erosion, α and β phases have the same degree of erosion[19]. When holding time is 10 min, the non-uniform area becomes smaller, hydrogen content

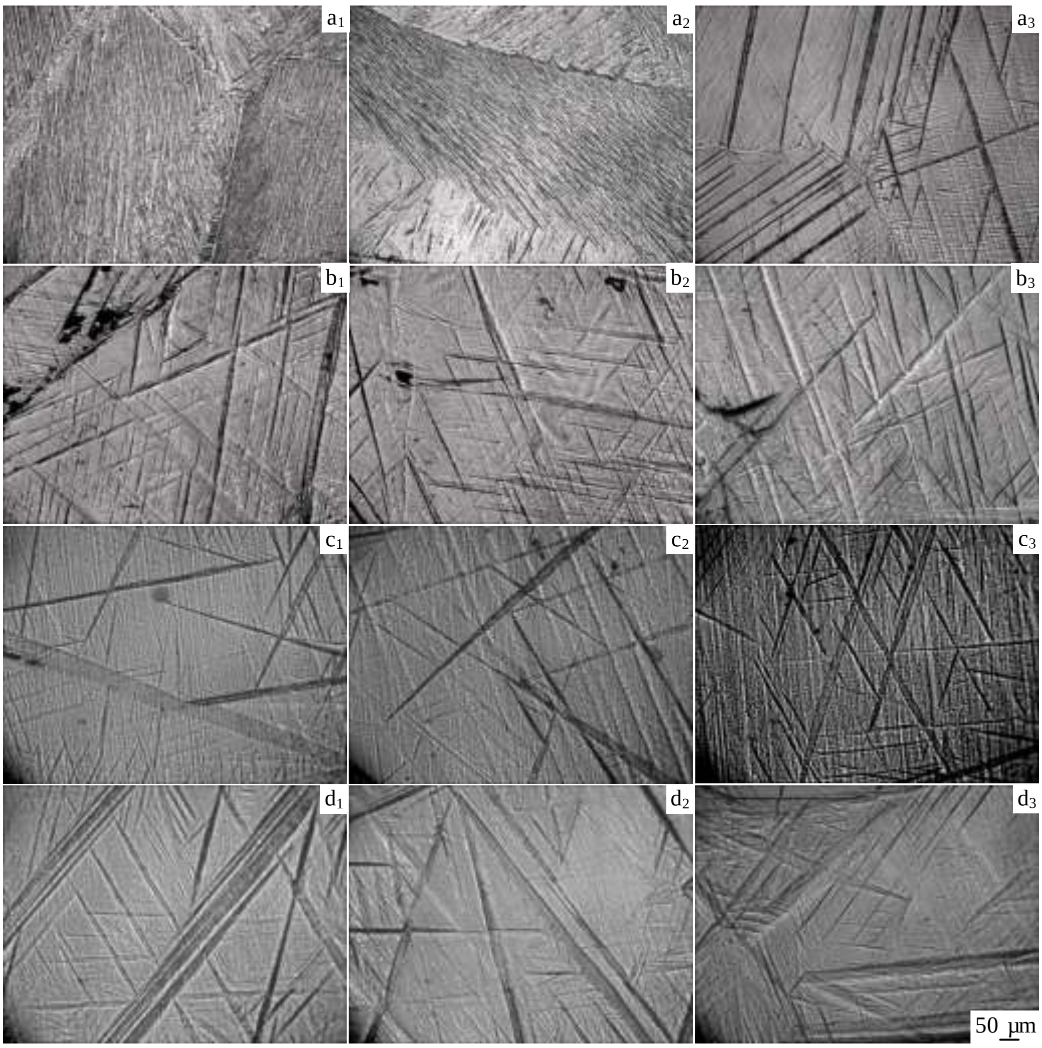

Fig.7 Cross-sectional microstructures of Ti6Al4V alloy hydrogenated for different holding time from the center → the edge (1→2→3): (a) 1 min, (b) 10 min, (c) 30 min, and (d) 120 min

in the central area increases and the microstructure difference between the center and the edge of the specimen gradually decreases. Microstructure becomes uniform when the holding time exceeds 30 min, indicating that hydrogen is distributed uniformly in the specimen. From Fig.7, it can be seen that the microstructures at the edge of the specimens hydrogenated at different holding time are similar. Results show that the process of hydrogenation is a diffusion of hydrogen into titanium alloy. In a short time, the hydrogen concentration on the surface of the alloy will reach the solid solubility which is corresponding to the environmental pressure, and then hydrogen diffuses into the interior of the alloy.

3 Conclusions

1) When hydrogenation temperature is below 550 ℃, hydrogen content of Ti6Al4V alloy is lower and increases slowly. Hydrogen content reaches its maximum value when the hydrogenation temperature is about 550 ℃. When the hydrogenation temperature is over 550 ℃, hydrogen content decreases with the increasing of the hydrogenation temperature.

2) Hydrogen content of Ti6Al4V alloy increases linearly with the increasing of hydrogen pressure.

3) Hydrogen pressure during the hydrogenation process of Ti6Al4V alloy decreases severely when the holding time is less than 10 min, and then decreases slowly when the holding time exceeds 10 min.

4) Hydrogenation is a diffusion process of hydrogen into titanium alloy. When the holding time is short, the amplitude of hydrogen content in Ti6Al4V alloy is higher, and the microstructure is different obviously between the center and the edge of the specimen. When the holding time exceeds 30 min, hydrogen content in Ti6Al4V alloy becomes stable, and the microstructure becomes uniform.

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Ti6Al4V 合金吸氢行为研究

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摘　要：研究了 Ti6Al4V 合金在不同置氢温度、保温时间和氢压下的吸氢行为，利用光学显微镜研究了氢在钛合金中的分布规律。结果表明，Ti6Al4V 合金的氢含量是由置氢温度、保温时间和氢压来控制的。随着置氢温度的升高，氢含量先增加后降低。随着氢压的增加，氢含量直线增加。钛合金的吸氢过程实质上是氢的扩散过程，随着保温时间的增加，合金中的氢分布逐渐趋于一致。

关键词：钛合金；热氢处理；置氢行为；动态规律

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