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ARTICLE

Kinetics of Hydrogen Absorption in TC4 Alloy

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Abstract: Kinetics of hydrogen absorption in TC4 alloy was studied by hydrogenation experiments at different temperatures and initial hydrogen pressures, and the effects of hydrogenation on the microstructure and phase composition of TC4 alloy at room temperature were studied. The results show that the reaction rate constant of TC4 alloy increases with the rise of hydrogenation temperature, and the time required for the reaction to reach equilibrium is gradually shortened. The apparent activation energy of hydrogen absorption reaction of TC4 alloy is 79.42 kJ/mol by solving the Arrhenius equation. δ hydride and α' martensite appear in the hydrogenated TC4 alloy.

Key words: TC4 alloy; thermohydrogen processing; kinetics; microstructure

As an important light structural material, titanium and titanium alloys are widely used in aerospace, chemical industry and biomedical fields nowadays due to their high specific strength, excellent elevated temperature property, strong corrosion resistance and great biochemical compatibility[1-5]. TC4 (Ti-6Al-4V) alloy is one of the most widely used titanium alloys because of its good comprehensive properties. However, the formability of TC4 alloy at room temperature is poor. The plastic deformation of TC4 alloy needs to be carried out at high temperature. The former West German scholars found that introducing an appropriate amount of hydrogen into titanium alloys can improve their thermoplasticity[6]. Hydrogen is a stable element of β phase in titanium alloys, which can enlarge the β phase region and reduce the β phase transus temperature of titanium alloys. Appropriate hydrogenation treatment can increase the number of β phase in quenched titanium alloys. The addition of hydrogen can change the room temperature microstructure of titanium alloys. When hydrogen content reaches a higher level, hydrogen embrittlement of titanium alloys occurs[7]. A new technology, thermohydrogen processing (THP)[8-10] has been developed through continuous research, which can refine microstructures, reduce β transus temperature, and improve the plasticity, machinability and deforming limits[11-15]. Yuan et al[16] studied the hydrogenation behavior of TC4 alloy and found the relationship between hydrogen content and hydrogenation parameters. However, kinetics of hydrogenation absorption in TC4 alloy and its microstructure evolution has not been fully studied and needs further research.

Therefore, kinetics (including the hydrogen absorption reaction process, the reaction rate constant, the apparent activation energy) and transformation of microstructure in TC4 alloy before and after hydrogenation were studied in the present work, which provides a theoretical basis for the application of thermohydrogen processing in TC4 alloy.

1 Experiment

Material used in the present work was a TC4 alloy bar. Block specimens, 5 mm in length and width and 6 mm in height, were cut from the starting material by an electric discharging machine (EDM), polished with 500#, 800# and 1000# sandpapers, then ultrasonically cleaned in absolute ethanol, and finally dried to ensure the surface cleanliness and to minimize the influence of oxide film on the hydrogen absorption behavior of TC4 alloy. The initial microstructure of TC4 alloy is composed of α phase and β phase according to the X-ray diffraction pattern (Fig.1), and its morphology is

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strip-like, as shown in Fig.2.

The equipment used in the hydrogenation experiment was a self-made thermohydrogen processing device. Four hydrogenation temperatures were selected (823, 923, 1023 and 1123 K) and four initial hydrogen pressures (16, 31, 46 and 61 kPa) were selected at each temperature. During the process of hydrogenation experiment, the specimens were heated to a predetermined temperature, and then a certain amount of hydrogen was charged into the tube of furnace. The change of hydrogen pressure was recorded by a precise piezometer (accuracy class is 0.25, provided by Shanghai Yichuan Instrument Factory) during the hydrogen absorption process of TC4 alloy.

The phase composition changes of TC4 alloy before and after hydrogenation were analyzed by XRD. The equipment used in the experiment was Panaco X' Pert PRO MPD X-ray diffractometer. The experimental conditions were as follows: Cu Kα, 3°/min as scanning speed, 40 kV as accelerating voltage and 40 mA as working current. The optical microstructure was observed by MR2000 metallographic microscope, and the metallographic specimens were corroded by acid solution containing HF, HNO_3 and H_2O (1:1:8, volume ratio). Thin foils for transmission electron microscopy (TEM, JEOL JEM-2100F) analysis were prepared by Gatan 691 precision ion polishing system.

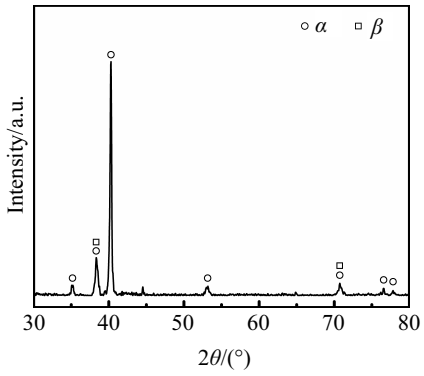

Fig.1 X-ray diffraction pattern of original TC4 alloy

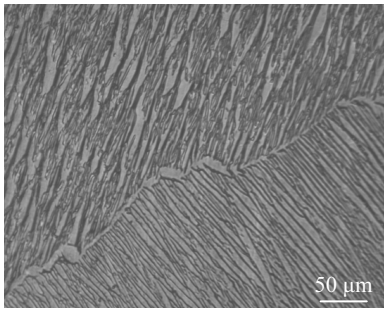

Fig.2 Initial microstructure of TC4 alloy

2 Kinetic Principle of Hydrogen Absorption

According to the change of hydrogen pressure during hydrogen absorption of TC4 alloy, the reaction fraction of hydrogen absorption reaction is as follows[17,18]:

$$\alpha = \frac{P_0 - P_t}{P_0 - P_f} \quad (1)$$

where α is reaction fraction, P_0 is initial hydrogen pressure, P_t is hydrogen pressure during the reaction, and P_f is equilibrium hydrogen pressure.

The change rate of hydrogen pressure during the hydrogen absorption reaction of TC4 alloy is as follows:

$$\frac{dP}{dt} = k_a(P - P_f) \quad (2)$$

where k_a is the reaction rate constant.

By integrating Eq.(2) and combining the initial hydrogen pressure in the furnace tube, it can be concluded that[19]:

$$\ln\frac{P_t - P_f}{P_0 - P_f} = -k_a t \quad (3)$$

The Arrhenius equation for the rate of chemical reaction is as follows:

$$k_a = A e^{-E_a/RT} \quad (4)$$

where A is a constant, E_a is apparent activation energy, R is ideal gas constant, and T is thermodynamic temperature.

According to Arrhenius equation, the reaction rate constant of hydrogen absorption reaction of TC4 alloy is only related to the hydrogenation temperature, not to the concentration of reactant and the pressure related to the concentration. According to the hydrogen pressure-time data recorded during the experiment and Eq.(3), the curve of relationship between $\ln[(P_t–P_f)/(P_0–P_f)]$ and hydrogenation time can be obtained. According to the relationship between the slope of the fitting line and the reaction rate constant, the reaction rate constant of hydrogen absorption reaction of TC4 alloy at a certain reaction temperature can be obtained by linear fitting of the curve.

By taking natural logarithms on both sides of the Arrhenius equation, we can obtain the equation:

$$\ln k_a = \ln A - \frac{E_a}{RT} \quad (5)$$

According to Eq.(5), the curve of relationship between $\ln k_a$ and $1/T$ can be obtained by combining the reaction rate constants at different reaction temperatures. The apparent activation energy of hydrogen absorption reaction of TC4 alloy can be obtained by linear fitting of the curve and manipulating the slope of the fitting line according to Eq.(5).

3 Results and Discussion

3.1 Kinetics of hydrogen absorption of TC4 alloy

3.1.1 Hydrogen absorption reaction process of TC4 alloy

The hydrogenation experiment of TC4 alloy was carried out at a certain reaction temperature and initial hydrogen pressure. The relationship between hydrogen pressure and holding time is shown in Fig.3 when the initial hydrogen pressures are 31

and 61 kPa. It can be seen that the slope of the *P-t* curve in the primary stage increases gradually under both initial hydrogen pressures with the rise of hydrogenation temperature, which indicates that the hydrogen absorption rate of TC4 alloy increases with the rise of hydrogenation temperature. The relationship between reaction fraction and holding time of TC4 alloy under initial hydrogen pressures of 31 and 61 kPa is shown in Fig.4. It can be seen from Fig.4 that when hydrogenation temperature is 823 K, the time required for hydrogen absorption reaction of TC4 alloy to reach equilibrium is the longest, and the time required for reaction to reach equilibrium is gradually shortened with the rise of hydrogenation temperature, which is in accordance with the trend of hydrogen pressure change at different hydrogenation temperatures.

When the initial hydrogen pressures are 31 and 61 kPa, the hydrogen absorption reaction of TC4 alloy shows a similar regularity. When the hydrogenation temperature is lower, the initial hydrogen absorption rate of TC4 alloy is lower, and the reaction time required to reach equilibrium is longer. It indicates that the hydrogenation temperature is the main factor affecting the hydrogen absorption rate of TC4 alloy, showing the same laws as the formula $k_a = A e^{-E_a/RT}$, which indicates that the reaction rate constant is a temperature-dependent constant.

3.1.2 Reaction rate constant

The hydrogen pressure-time data obtained from hydrogenation experiments at different temperatures were processed by Eq.(3). For obtaining the reaction rate constant of hydrogen absorption of TC4 alloy, the data of $\ln[(P_t-P_f)/(P_0-P_f)]$ and holding time obtained by Eq.(3) was linearly fitted, and the results are shown in Fig.5. The reaction rate constants (k_a) of hydrogen absorption reaction of TC4 alloy at various temperatures and the linear correlation coefficients are shown in Table 1.

It can be seen that the linear correlation coefficients of fitting lines at all temperatures are above 0.98, which suggests that there is a good linear relationship between $\ln[(P_t-P_f)/(P_0-P_f)]$ and holding time, indicating a high reliability of the

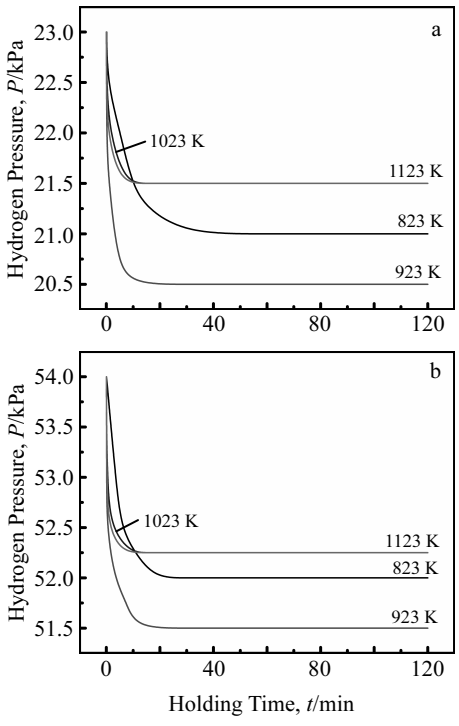

Fig.3 Hydrogen pressure-holding time (*P-t*) curves of hydrogen absorption reaction of TC4 alloy at different temperatures under the initial hydrogen pressure of 31 kPa (a) and 61 kPa (b)

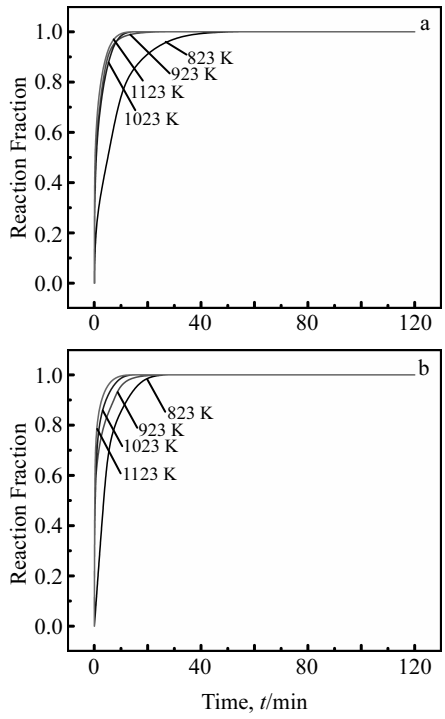

Fig.4 Hydrogen absorption reaction fractions of TC4 alloy at different temperatures under the initial hydrogen pressure of 31 kPa (a) and 61 kPa (b)

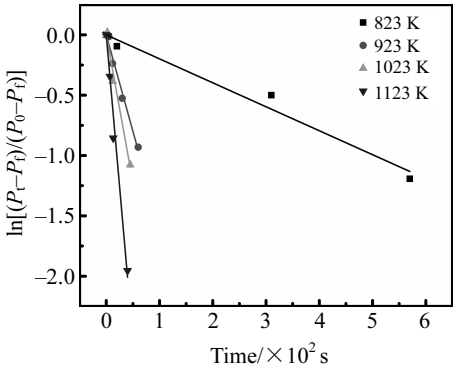

Fig.5 Linear fitting curves of $\ln[(P_t-P_f)/(P_0-P_f)]$ and holding time at different temperatures

Table 1 Reaction rate constants (k_a) and linear correlation coefficients of TC4 alloy at different hydrogenation temperatures

Temperature/K	823	923	1023	1123
k_a/s^{-1}	0.001 99	0.015 96	0.024 41	0.050 21
Linear correlation coefficient	0.988 55	0.992 43	0.991 30	0.987 86

obtained reaction rate constants.

As shown in Table 1, with the rise of hydrogenation temperature, the reaction rate constant of hydrogen absorption of TC4 alloy increases gradually, indicating that the rate of hydrogen absorption of TC4 alloy also increases with the rise of hydrogenation temperature, which is consistent with the Arrhenius equation. In addition, we noticed that the reaction rate constant of hydrogen absorption of TC4 alloy is very small when the hydrogenation temperature is 823 K, which differs greatly from that at 923 K, about 1/8 of that at 923 K, while the difference between the reaction rate constant at 923 and 1023, 1023 and 1123 K is small. This indicates that the hydrogen absorption reaction of TC4 alloy is not fully activated when the hydrogenation temperature is 823 K, at which the hydrogen absorption rate is slower and the reaction time required to reach equilibrium is longer.

3.1.3 Apparent activation energy

The apparent activation energy of hydrogen absorption reaction of TC4 alloy was calculated according to the combination of Eq.(5) and reaction rate constants at different temperatures. The results are shown in Table 2.

The relationship between the natural logarithm value of hydrogen absorption reaction rate constant and reciprocal of hydrogenation temperature of TC4 alloy is shown in Fig.6. The data obtained at four reaction temperatures are linearly fitted. The slope of the fitting line is –0.955 29, and the linear correlation coefficient reaches 0.964 79, which shows that there is a strong linear relationship between $\ln k_a$ and $1/T$.

According to Eq.(5), the slope of the fitting line is $-E_a/R$. The ideal gas constant and the slope of fitting straight line were substituted for the calculation. The apparent activation energy of hydrogen absorption reaction of TC4 alloy is 79.42 kJ/mol.

3.2 Microstructure

The microstructures of TC4 alloy hydrogenated at different temperatures and the initial hydrogen pressure of 16 kPa are shown in Fig.7. As shown in Fig.7a, when the initial hydrogen

Table 2 Data handling of apparent activation energy for hydrogen absorption reaction of TC4 alloy

Temperature/K	823	923	1023	1123
k_a/s^{-1}	0.001 99	0.015 96	0.024 41	0.050 21
$T^{-1}/\times10^{-4}$ K^{-1}	12.150 67	10.834 24	9.775 17	8.904 72
$\ln k_a$	–6.219 62	–4.137 67	–3.712 76	–2.991 54

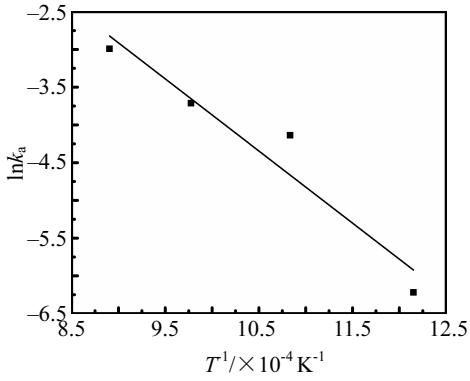

Fig.6 Relationship between $\ln k_a$ and $1/T$ in hydrogen absorption reaction of TC4 alloy

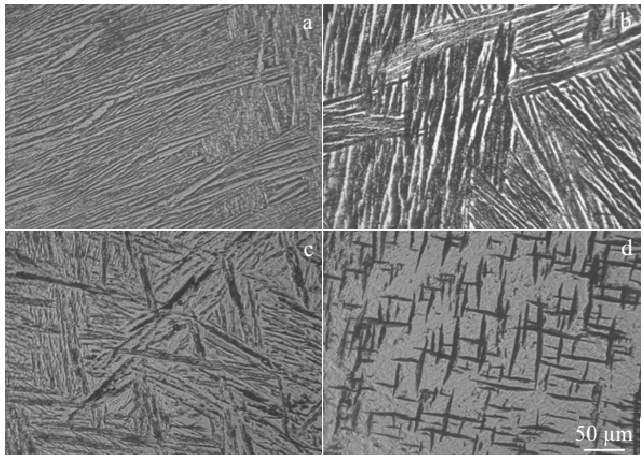

Fig.7 Microstructures of TC4 alloy hydrogenated under the initial hydrogen pressure of 16 kPa at different temperatures: (a) 823 K, (b) 923 K, (c) 1023 K, and (d) 1123 K

pressure is 16 kPa, the room temperature microstructure of TC4 alloy hydrogenated at 823 K is similar to that of the original TC4 alloy, still showing the strip-like structure, which indicates that the hydrogenation temperature is lower than the β transus temperature of the alloy under this condition, and no β transformation occurs during hydrogenation processing, resulting in no significant change in the room temperature microstructure compared with the original microstructure of TC4 alloy. As shown in Fig.7b~7d, needle-like structures appear in the microstructure of TC4 alloy after hydrogenation due to the rise of hydrogenation temperature, and acicular martensite appears in the alloy, and with the rise of hydrogenation temperature, the needle-like structure becomes smaller gradually.

The X-ray diffraction patterns of the original TC4 alloy and the TC4 alloy hydrogenated at different temperatures under the initial hydrogen pressure of 16 kPa are shown in Fig.8. As shown in Fig.8, the original TC4 alloy is composed of α and β

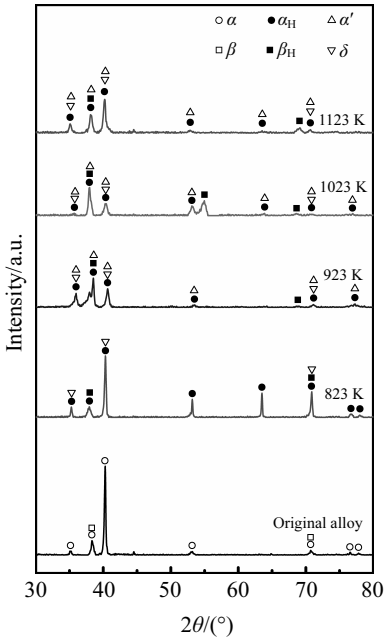

Fig.8 X-ray diffraction patterns of original TC4 alloy and TC4 alloy hydrogenated under the initial hydrogen pressure of 16 kPa at different temperatures

phases. The X-ray diffraction patterns of TC4 alloy change greatly after hydrogenation: (1) the diffraction peaks of δ hydride are found in the diffraction patterns of TC4 alloy after hydrogenation, and its chemical composition is $TiH_{1.5\sim2}$ [20], which is confirmed by TEM; (2) diffraction peaks of α' martensite with hexagonal structure is found when the hydrogenation temperature reaches 923 K, due to the martensitic transformation of the β phase formed during hydrogenation processing when cooled rapidly in the air condition; (3) the peak broadening occurs in the diffraction patterns of hydrogenated TC4 alloy, which is the result of the overlapping of the diffraction peaks of the δ hydride and the α phase, and crystallographic textures of α' martensite and α phase are identical, so the interaction of the two factors leads to the broadening of the diffraction peaks of TC4 alloy after hydrogenation[20]; (4) diffraction peak of TC4 alloy shifts to low angle after hydrogenation, which is due to the lattice expansion of the α and β phases caused by the solid solution of hydrogen atoms, and as a result, the lattice constant increases and the diffraction angle decreases, so the diffraction peak shifts to a low angle[21].

TEM images of TC4 alloy hydrogenated at 1023 K are shown in Fig.9. Fig.9a shows α' martensite formed during the hydrogenation process of TC4 alloy, which is an hcp structure with a zone axis of $[2\bar{1}\bar{1}0]$ according to its SAED patterns (Fig.9b). Fig.9c shows the δ hydride in the hydrogenated TC4 alloy and its SAED pattern is shown in Fig.9d, showing that the δ hydride is an fcc structure with a zone axis of [001].

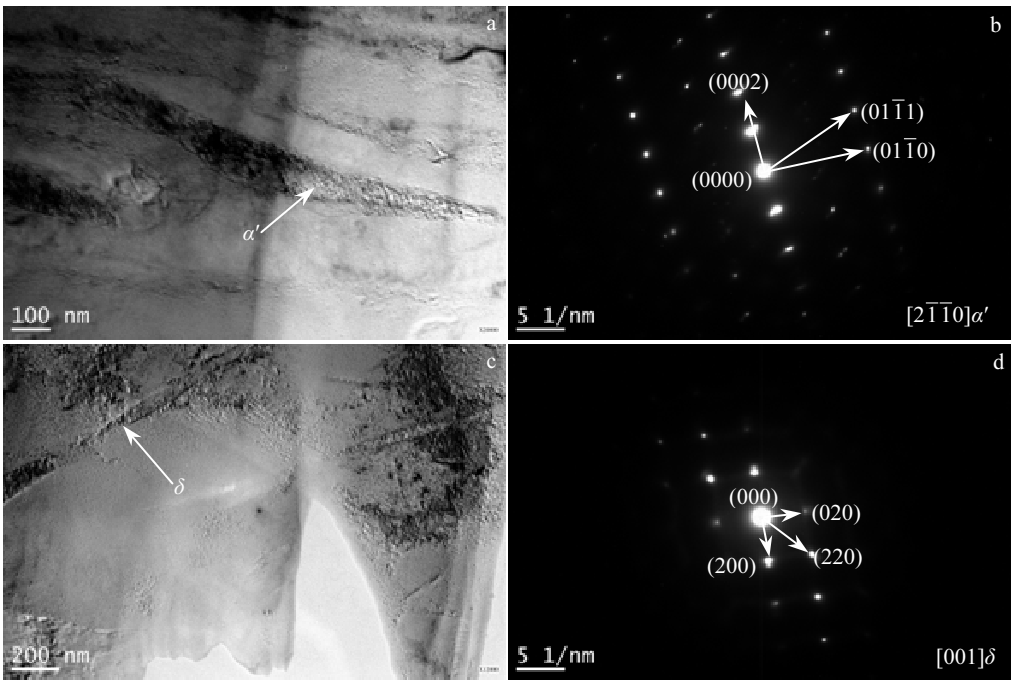

Fig.9 TEM images of TC4 alloy hydrogenated at 1023 K under initial hydrogen pressure of 16 kPa: (a) α' martensite, (b) SAED pattern of α' martensite with $[2\bar{1}\bar{1}0]$ zone axis, (c) δ hydride, and (d) SAED pattern of δ hydride with [001] zone axis

4 Conclusions

1) The reaction rate constant of hydrogen absorption reaction of TC4 alloy increases with the rise of hydrogenation temperature, and the reaction time required to reach equilibrium decreases with the rise of hydrogenation temperature.

2) By solving the Arrhenius equation, it can be obtained that the apparent activation energy of hydrogen absorption reaction of TC4 alloy is 79.42 kJ/mol.

3) The original TC4 alloy is composed of α and β phases, and its morphology is strip-like at room temperature. Needle-like structure can be found in the room temperature microstructure of TC4 alloy after hydrogenation. With the increase of hydrogenation temperature, the needle-like structure becomes smaller gradually. δ hydride and α' martensite can be found in the hydrogenated TC4 alloy.

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TC4 合金吸氢动力学研究

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摘　要：通过不同温度和初始氢压下的氢处理实验，研究了 TC4 合金的吸氢动力学，并研究了氢处理对 TC4 合金室温微观组织和相组成的影响。结果表明，随着氢处理温度的升高，TC4 合金的反应速率常数升高，且反应达到平衡所需的时间逐渐缩短。通过求解阿伦尼乌斯方程，得出 TC4 合金吸氢反应的表观活化能为 79.42 kJ/mol。在置氢 TC4 合金中发现了 δ 氢化物和 α'马氏体。

关键词：TC4 合金；热氢处理；动力学；微观组织

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