

# Hydrogen-induced room-temperature plasticity in TC4 and TC21 alloys

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**Abstract.** In order to reveal the effect of hydrogen on the room-temperature plasticity of the titanium alloys TC4 and TC21, compression tests have been carried out at room temperature. Results show that an appropriate amount of hydrogen can improve the room-temperature plasticity of both the TC4 and TC21 alloys. The ultimate compression strain of the TC4 alloy containing a hydrogen concentration of 0.5 wt.% increases by 39% compared to the untreated material. For the TC21 alloy the ultimate compression strain is increased by 33% at a hydrogen concentration of 0.6 wt.%. The main reason for the improvement of hydrogen-induced room-temperature plasticity of the TC4 and TC21 alloys is discussed.

## 1. Introduction

Titanium and its alloys are widely used in the aerospace, chemical, petroleum, automobile and marine industries because of their low density, high specific strength, superior corrosion and erosion resistance, excellent fatigue properties, non-toxicity, and good biochemical properties [1]. However, the plasticity of most titanium alloys at room temperature is low, which restricts their applications. Therefore, how to improve the room-temperature plasticity of titanium alloys has become an important research topic.

The method of using hydrogen to improve the plasticity of titanium alloys was first proposed by Zwicker and Hans in 1959 [2], who found that the hot workability (such as forging, rolling and extrusion) of titanium alloys can be improved after hydrogenation. In recent years, further research has demonstrated that addition of hydrogen can result in improved mechanical properties of titanium alloys [3-5]. The technology of using hydrogen as a temporary alloying element to improve properties of titanium alloys is called thermohydrogen processing (THP) [6-8]. In this technology, hydrogen is introduced into the titanium alloy, which is then processed, and finally hydrogen is removed by vacuum annealing to avoid hydrogen embrittlement during service. THP can not only improve the hot workability of titanium alloys [9, 10], but can also improve its formability by cold working [11-13] and superplastic forming [14]. Hydrogen-induced plasticity of titanium alloys are mainly studied in Russia and China.



Hydrogen-induced room-temperature plasticity of titanium alloy results in an increase in the limiting degree of deformation prior to appearance of the first crack, first noted for the quenched  $\beta$ -titanium alloys VT15 and VT30 [12]. It has been found that the quenched VT30 alloy charged with more than 0.1 wt.% hydrogen (cylindrical specimens of 10 mm in diameter and 15 mm in height) can be flattened into a “cake” with sharp edges and no cracks are found on its lateral surfaces. Kolachev et al report that hydrogen-induced room-temperature plasticity can also be observed in  $\alpha+\beta$  titanium alloys with a large amount of  $\beta$  phase [12, 15]. The limiting degree of deformation prior to appearance of the first crack during jumping-up tests of VT16 alloy at room temperature increases from less than 40% to about 75% as the hydrogen content is increased from 0.005% to 0.1%. Hydrogen-induced room-temperature plasticity has also been observed in the TC4 alloy [11, 16], but the plasticity of hydrogenated TC4 alloy is still not high enough for the cold working of complicated titanium alloy parts. The technology has, however, been applied to produce anchor nuts and large diameter bolts [15]. For wider application further research and development are still required.

## 2. Hydrogenation method

There are many ways to add hydrogen into a titanium alloy. The first hydrogenation method applied is to melt titanium alloy in a hydrogen atmosphere [2, 17]. The ingots are melted under a gaseous mixture of hydrogen and argon. Hydrogen molecules decompose and diffuse into the melt. The second hydrogenation method is an electrolytic method [18], where a specimen is charged with hydrogen in an electrolyte consisting of phosphoric acid and glycerin for different lengths of charging time. The third hydrogenation method is to diffuse hydrogen into a solid-state titanium alloy at high temperatures, where different hydrogen contents can be obtained by controlling the temperature, hydrogen pressure (or hydrogen flow rate) and the holding time. The actual hydrogen content in a titanium alloy is determined by weighing the specimen before and after hydrogenation using a high precision electronic balance. The third hydrogenation method is preferred for THP studies [19, 20] and is applied to TC4 and TC21 titanium alloys in the present work.

## 3. Results

In the present work, the effect of hydrogen on the room-temperature plasticity of TC4 and TC21 titanium alloys is studied by room temperature compression tests.

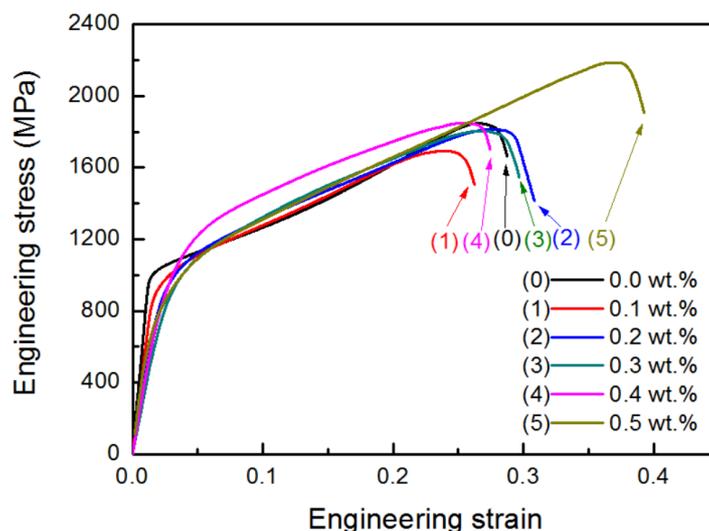
### 3.1. Compression of TC4 alloy

The nominal composition of the TC4 alloy is Ti-6Al-4V. Compression tests of TC4 alloys with different amounts of hydrogen were carried out at room temperature on a Zwick Z100 machine with a compression speed of 0.05 mm/min. The specimens were cylinders of 4 mm in diameter and 6 mm in height. The specimens were hydrogenated in an atmosphere of hydrogen at 750 °C for 1 h, air cooled to room temperature, and then solution treated at 850 °C for 0.5 h followed by furnace cooling to 700 °C, and finally quenched in water at room temperature. MoS<sub>2</sub> lubricant was coated on both end faces of the specimens. Engineering stress-strain curves of TC4 alloys with different amounts of hydrogen, based on load-displacement measurements are shown in figure 1. From figure 1, it can be seen that compression properties of TC4 alloy are changed obviously after hydrogenation. The plasticity index is defined as the compressive strain when the first macroscopically observable crack appears at the cylindrical surface of the specimen. The strain termed the ultimate compression strain is expressed:

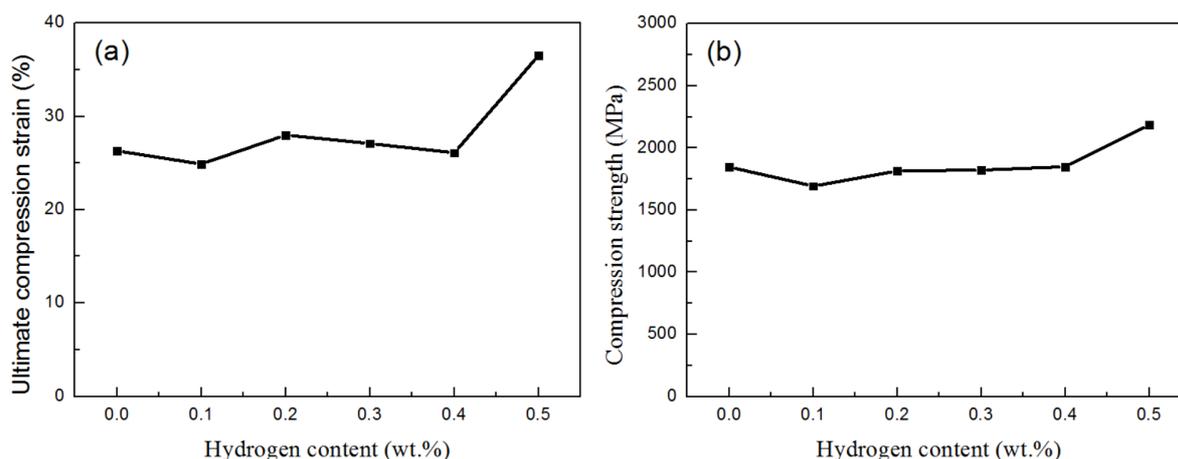
$$\varepsilon_c = \frac{H_k - H_0}{H_0} \times 100\%, \quad (1)$$

where  $H_0$  is the initial height of specimen before compression testing and  $H_k$  is the height of the specimen during the compression when the first macroscopic crack appears at the cylindrical surface of the specimen. The compression strength is taken as the maximum stress on the stress-strain curve. The ultimate compression strain and compression strength of TC4 alloys with different amounts of hydrogen are shown in figure 2. From figure 2a, it can be seen that ultimate compression strain of the

TC4 alloy changes slightly at hydrogen contents of lower than 0.4 wt.%. At a hydrogen content of 0.5 wt.%, the ultimate compression strain of the TC4 alloy increases significantly to a value about 39% higher than that of the un-hydrogenated specimen. From figure 2b, it can be seen that the compression strength changes slightly for hydrogen contents lower than 0.4 wt.%, but increases by 18% for a hydrogen charging concentration of 0.5 wt.%. The ultimate compression strain and compression strength of the TC4 alloys with different amounts of hydrogen compressed at 0.5 mm/min show the same trend as those compressed at 0.05 mm/min [21]. For hydrogen contents exceeding 0.5 wt.%, the ultimate compression strain of the TC4 alloy increases first and then decreases with increasing hydrogen content [16]. Hydrogen has also favorable effects on the compressive properties of TC4 alloy at high strain rate [22].



**Figure 1.** Engineering stress-strain curves of TC4 alloys containing different amounts of hydrogen.

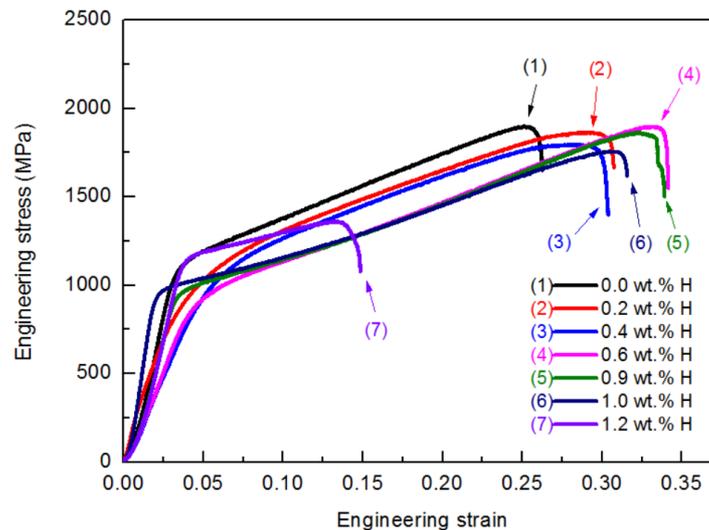


**Figure 2.** Ultimate compression strain (a) and compression strength (b) of TC4 alloys containing different amounts of hydrogen.

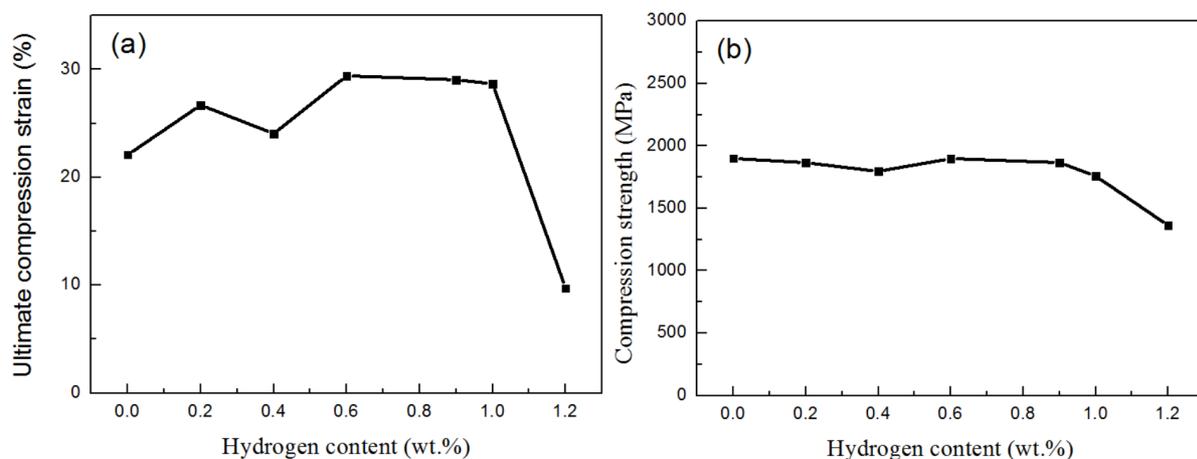
### 3.2. Compression of TC21 alloy

The alloy TC21 is a kind of  $\alpha+\beta$  damage tolerant titanium alloy, with high strength, high fracture toughness and low crack propagation rate. Its nominal composition is Ti-6Al-2Mo-1.5Cr-2Zr-2Sn-2Nb. Compression tests of TC21 alloys containing different amounts of hydrogen were carried out on a MTS 809 materials testing machine at room temperature. The compression specimens were cylinders

of 4 mm in diameter and 6 mm in height. The specimens were first hydrogenated at 750 °C for 2 h, and then air cooled to room temperature. The compression speed was 0.05 mm/min. White Vaseline was used as a lubricant. Engineering stress-strain curves of TC21 alloys with different amounts of hydrogen are shown in figure 3, indicating a marked effect of hydrogenation. The ultimate compression strain and compression strength of TC21 alloys containing different amounts of hydrogen are shown in figure 4. Figure 4a shows that the ultimate compression strain increases with increasing hydrogen content and then decreases. The ultimate compression strain is highest for hydrogen contents in the range of 0.6 wt.% - 1.0 wt.%, with an maximum increase of 33% at 0.6 wt.% hydrogen. The ultimate compression strain decreases by about 56% after introduction of 1.2 wt.% hydrogen into the TC21 alloy. Figure 4b shows that the compression strength decreases slightly with increasing hydrogen concentration, with a decrease of 7% at a hydrogen content of 1.0 wt.%. For hydrogen contents exceeding 1.0 wt.%, the compression strength decreases sharply, showing a decrease of 28% for a hydrogen content of 1.2 wt.%. The present observations are in good agreement with the results for TC21 alloys with different amounts of hydrogen compressed at 0.5 mm/min [13].



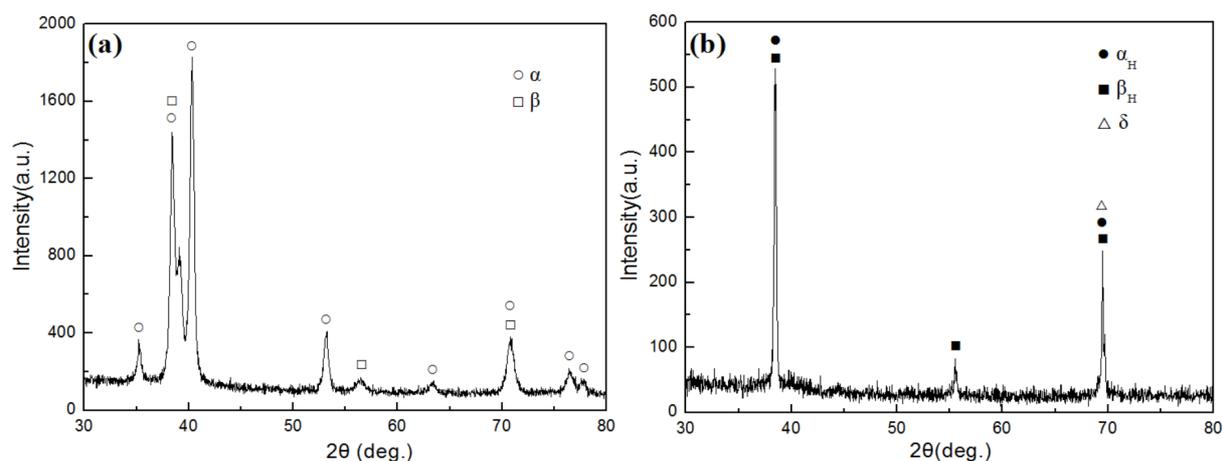
**Figure 3.** Engineering stress-strain curves of TC21 alloys containing different amounts of hydrogen.



**Figure 4.** Ultimate compression strain (a) and compression strength (b) of TC21 alloys containing different amounts of hydrogen.

#### 4. Discussion

The above results show that introduction of hydrogen can improve the room-temperature plasticity of both the TC4 and TC21 alloys. Hydrogen has a similar effect on the room-temperature plasticity on both alloys. The main reason for the improvement is that the amount of the ductile  $\beta$  phase increases with hydrogenation, as shown in figure 5. The  $\beta$  phase, being body-centered cubic with 12 slip systems, is more ductile than the  $\alpha$  phase, which is hexagonal close packed with only 3 slip systems. Hydrogen is a  $\beta$ -stabilizing element and can lower the  $\beta$  transus temperature in titanium alloys. Therefore, more  $\beta$  phase will be present after hydrogenation. However, hydrides will precipitate widely in the structure if the amount of hydrogen in titanium alloys is high enough, and will cause embrittlement. Therefore, the amount of hydrogen in the TC4 and TC21 alloys should be controlled in order to improve its room-temperature plasticity.



**Figure 5.** XRD patterns of TC21 alloys: (a) 0.0 wt.% H and (b) 0.9 wt.% H.

#### 5. Conclusion

Two titanium alloys, TC4 and TC21, have been hydrogenated at high temperature and have been tested in compression at room temperature. By taking the compression strain as a measure of formability, the following conclusions have been reached:

- 1) Hydrogenation up to 0.5 wt.% increases the formability of the TC4 alloy, measured as the strain for the first appearance of macroscopic cracks during compression.
- 2) Hydrogenation up to 1 wt.% increases the formability of the TC21 alloy, which is related to an increased percentage of the more ductile  $\beta$  phase (bcc) compared to the  $\alpha$  phase (hcp).
- 3) Hydrogenation to 1.2 wt.% of the TC21 alloy reduces the formability due to hydride precipitation.

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