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# Hydrogenation reaction of metallic titanium prepared by molten salt electrolysis

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**Abstract:** The hydrogenation reaction of electrolyzed titanium, as the first step during hydrogenation−dehydrogenation for the preparation of titanium powder, was studied. The titanium hydride was prepared through the reaction between electrolyzed titanium and hydrogen at different hydrogenation temperatures and different time. The evolutions of hydrogen and oxygen contents, density, hardness and phase composition before and after hydrogenation were characterized under different hydrogenation conditions. The results show that the main phases of titanium hydride were $TiH_{1.924}$, $TiH_{1.971}$ and $TiH_2$. Increasing the hydrogenation temperature could not enhance the hydrogen content but increase the oxygen content. The effect of the hydrogenation time on the hydrogen content was not obvious. The optimal parameters of the hydrogenation process were obtained: heating at 400 °C and holding for 2 h, by which the hydrogen content of 3.63% and oxygen content of 0.18% (mass fraction) can be obtained. In addition, the microstructure, orientations and tissues of electrolyzed titanium and titanium hydride were detected.

**Key words:** titanium powder; hydrogenation reaction; molten salt electrolysis; hydrogen content

## 1 Introduction

Owing to its excellent physical and chemical properties, titanium powder has found its widespread applications in biomaterials [1,2], powder metallurgy (PM) [3], additive manufacturing [4,5], electronic target [6,7], aerospace [8] and pressure hull [9]. The main preparation methods of titanium powder are rotating electrode atomization and hydrogenation−dehydrogenation (HDH). The rotating electrode atomization could produce spherical powder, but its diameter is coarse and the cost is high. The HDH is another important preparation method for titanium powder [10]. During HDH, the sponge titanium reacts with hydrogen and forms the brittle $TiH_x$, which can be crushed into powder easily, and then the $TiH_x$ powder transforms into Ti powder by decomposition reaction at a more high temperature [11,12]. HDH is easy to produce fine Ti powder with concentrated particle size compared with rotating electrode atomization. The study on preparation of Ti powder by HDH is thus necessary. The other important index for elevating property of Ti powder is the oxygen content. The high oxygen content is detrimental for the final properties of titanium components produced from as-obtained titanium powder in powder sintering and additive manufacturing [13−16]. For example, the oxygen in titanium powder is apt to decrease the mechanical strength. Moreover, when the titanium powder is applied to 3D printing additive manufacturing, the oxygen in powder can lead to balling phenomenon, which worsens the forming quality. Usually, the raw material used for HDH process is sponge titanium. The oxygen content in sponge titanium is high, which is unfavorable for the powder properties. Recently, the preparation of high purity titanium has considered to be very important in electronic target, high-quality PM part, additive manufacturing.

Molten salt electrolysis (MSE), as an important purification method of titanium, has been highly valued. The MSE uses low purity sponge titanium as anode material. In the anode process of MSE, the impurities with anode potential higher than that of titanium ion tend to be reserved in anode while the titanium will be

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dissolved in molten salt. In the cathode process of MSE, the impurity ion with cathode potential lower than that of titanium ion will be reserved in molten salt [17,18]. Thus, the MSE can yield high purity metallic titanium and has been widely applied in industry. Therefore, when MSE-prepared titanium is used for the raw material of HDH, the purity of as-obtained titanium powder could be enhanced compared with that with conventional sponge titanium as raw material. However, the electrolyzed titanium exhibits different microstructures and crystallization characterizations, thus, the hydrogenation reaction behavior may be different from conventional HDH using sponge titanium as raw material. As the first step of HDH, hydrogenation of electrolyzed titanium should be studied carefully.

The hydrogenation of raw titanium material is the primary step of preparation of titanium powder by HDH, which largely determines the hydrogen content, oxygen content and contents of other impurities. Hydrogen in solid solution goes into the titanium material at high temperature, and then reacts with titanium over the critical solubility, which makes the non-stoichiometric compounds-$TiH_x$ precipitate. The brittle $TiH_x$ is the key to determine whether the titanium hydride can be effectively broken down to the appropriate size range during the subsequent ball milling procedure and the effect of oxygen content on the mechanical properties of the final titanium powder products should not be ignored [19]. Existing research showed that oxygen could greatly improve the strength of titanium and titanium alloy, but could also greatly reduce its plasticity, heat resistance, thermal stability and solderability [19,20]. Therefore, controlling the oxygen content of the finally obtained titanium powder is essential. Among other impurity elements, the TiFe phase intermetallic compound formed by Fe and Ti will decrease the pitting corrosion potential and provide the core of the localized corrosion, which is harmful to the corrosion resistance of the titanium [21]. The fatigue properties of titanium products are greatly affected by the common Cl element in sponge titanium [22]. In the traditional process of HDH, $TiCl_4$ is used as raw material for the reduction of sponge titanium. Although the yield of conventional sponge titanium has advantages in terms of cost, the contents of sodium, magnesium and chloride ion in the sponge titanium obtained by the conventional procedure are high. More than half of impurities of the final titanium products are derived from raw materials, which will make the equipment polluted and the welding properties of materials deteriorate during the sintering process.

Therefore, the MSE titanium, as the raw material for hydrogenation reaction, is favorable for decreasing the oxygen content of the final product. Simultaneously, the hydrogenation reaction kinetics may differ from conventional sponger titanium due to the difference of microstructure. Thus, it is necessary to study the hydrogen reaction of electrolyzed titanium. In the present work, the evolution behaviors of element content, phase, microstructure, hardness and density of $TiH_x$ were studied and the optimal techniques were studied.

## 2 Experimental

The high purity titanium prepared by MSE was used as raw material with particle size ranging from 1 to 10 mm. The hydrogenation process was as follows. First, the titanium powder was placed in vacuum furnace and the furnace was pumped below 1 Pa and then 99.999% purity Ar gas was injected into the furnace. The pumping and injecting Ar gas were repeated 3 times to eliminate the oxygen inside. Second, the electrolyzed titanium was heated in the furnace at 350, 400, 450, 500 and 550 °C and then injected $H_2$ with 99.999% purity and incubated for 0.5−8 h. The pressure of $H_2$ in the furnace is 0.13−0.15 MPa. After hydrogenation, the density, H/O contents, and hardness were measured. After being ground into powder and sifted, titanium hydride was taken to analyze its phase. Optical microscope (Leica, MeF3A) and field emission scanning electron microscope (Nova, NanoSEM 230) were used to observe the microstructure of the alloy after mechanical and chemical polishing and chemical etching. The phase compositions of the samples were characterized by X-ray diffraction (XRD) (Rigaku, D/max 2550VB). The hydrogen content and oxygen content of raw material and titanium hydride were analyzed with an oxygen analyzer (LECO, TCH−436). The density of titanium hydride was measured by a micro-hardness detector (MicroMet 5104).

The electrolytic titanium was the product of Guizhou Zunyi Titanium Industry. In this experiment, titanium hydride, which was prepared with high purity hydrogen at different hydrogenation temperatures and hydrogenation time, was used to study the hydrogenation mechanism, microstructure evolution and appropriate hydrogenation process.

## 3 Results and discussion

### 3.1 hydrogen and oxygen contents

Figure 1(a) shows the hydrogen and oxygen contents in raw materials and titanium hydride samples which were hydrogenated and heated at different temperatures for 2 h. In $TiH_x$, the range of $x$ value was 0−2. By calculating the highest hydrogen content in $TiH_2$, the hydrogen content of $TiH_x$ was equal or lesser than 4% (mass fraction). Under all the conditions, with the