Study of the deuterated titanium Ti^2H_x sample by using nuclear reaction analysis and material analysis methods

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Abstract Titanium is one of the best hydrogen loading material. The predicted maximum loading ratio of hydrogen in titanium may reach to 2.0. In this work, a titanium layer on molybdenum substrate was deuterated with the atomic ratio $X = {}^2H/Ti \geq 1.6$. The change of the surface topography and microstructure of the sample before and after loading was observed by using Scan Electron Microscopy (SEM). The surface segregation of the samples after deuteron bombardment was also observed. A fluctuatingly-increasing trend of the deuterium density in titanium target was detected in the deuteron implantation experiments, which indicated a suddenly explosion (segregation) or fast diffusion of deuterium in the titanium. Significant amount of nitrogen contamination was found in the Ti^2H_x sample by nuclear reaction analysis (NRA), which indicated that the Ti^2H_x structure might have the feature to trap nitrogen from air. The nitrogen contamination in Ti^2H_x significantly affects the increase of the atomic ratio $X = {}^2H/Ti$.

Keywords Deuterated titanium (Ti^2H_x), Nuclear reaction analysis, Scan electron microscopy

CLC numbers O571.33, O483, O614.41

1 INTRODUCTION

The embrittlement phenomena can be induced by the ingression of hydrogen in materials, since the different contents and distributions of hydrogen in solids may significantly affect the mechanical and chemical characteristics of materials[1~6]. Study of hydrogen behaviors, including the accumulation and diffusion of hydrogen in solids and the segregation, changes of nano-and macro-mechanical characteristics of materials etc. are very essential to understand the embrittlement and corrosion. A lot of work was brought out[1~12]. However, studies of hydrogen behaviors under some extreme condition and some new materials are insufficient. Titanium and its alloys are widely applied, due to their good chemical stability and mechanical features. Titanium is also one of the best hydrogen loading metal. The predicted maximum loading ratio of hydrogen in

Supported by a fund of the Chinese Academy of Sciences and the special fund of the Nuclear Power Institute of China

Manuscript received date: 2000-08-07

titanium may reach to 2.0. Therefore, the fundamental study of hydrogen behaviors in titanium and its alloys are very essential for the new material research and engineering applications[1~3,6~12]. In this work, some preliminary studies on pure titanium are brought out.

2 LOADING THE HYDROGEN INTO TITANIUM SAMPLES

Three methods gas loading, ion beam implantation and electrolysis, are usually used for loading hydrogen in to metals. However, the loading ratio (H/Ti) in electrolysis method is very difficult to be controlled. So, the gas loading and implantation methods were used in this work. Since the hydrogen isotopes have the same chemical and mechanical features, instead of hydrogen, deuterium was applied in order to study its diffusion and distribution by using nuclear reaction analysis (NRA) methods.

2.1 Gas loading

The sample for gas loading was a thin titanium layer formed on a molybdenum substrate by sputtering. The sample was put in a vessel with deuterium gas and the titanium layer was deuterated with changing temperature. The loading ratio was determined by the change of the deuterium gas pressure before and after the loading process. The atomic loading ratio (D/Ti) may be reached up to 2.0, while in this work it is larger than 1.6.

2.2 Ion beam implantation

Deuteron implantation experiments were performed in a 600 kV high voltage accelerator. The deuteron beam was analyzed after acceleration and then implanted into a titanium sample. The ion beam energy and density were 300 keV and $125\mu A/cm^2$. D(d,p)T reaction was used to monitor the deuterium density in the sample. The charged particles emitting from D-D fusion during the implantation were detected by a Si(Au) detector and data acquisition system. The diffusion, accumulation and escaping of deuterium in the sample may be indicated by the change of D-D fusion yields. The atomic ratio of deuterium to titanium (D/Ti) is hard to be more than 1.4.

3 RESULTS AND ANALYSES

3.1 Topography of the titanium deuterides

The change of titanium nano-structure was observed with scanning electron microscopy (SEM) (Fig.1).

The titanium deuteride was observed (in Fig.1), and the metal structure cracked into powder, while the loading ratio (D/Ti) was larger than 1.4. A quite symmetrical crystal grain were formed while the loading ratio was larger than 1.6. The sizes of titanium crystal grains are between 100 nm and 500 nm. It was found that the metal

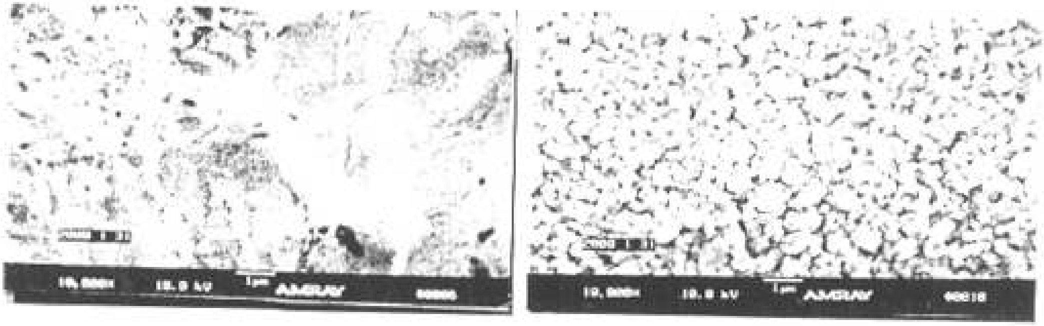

Fig.1 Topographies of Ti sample before (left) and after (right) loading deuterium (×10,000)

crystal cracked into nano crystal grains with very clear-cut boundary while the loading ratio was larger than 1.6, and the metal crystal just partly cracked into nano crystal grains while the ratio was between 1.4 and 1.6.

3.2 Accumulation of deuterium in titanium during deuteron implantation

The accumulation and diffusion of hydrogen in titanium metal were studied qualitatively by using D-D fusion reaction analysis. The average deuterium density in the titanium target was directly corresponding to the D-D reaction yield induced by each implanted deuteron, while the deuterium distribution in the target and the deuteron beam parameters were the same. The experimental curve obtained in the deuteron beam implantation with constant parameters is plotted in Fig.2.

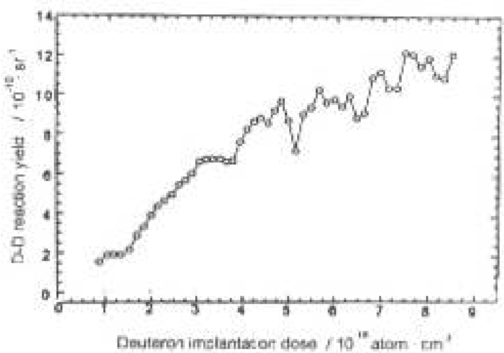

Fig.2 D-D reaction yield vs. deuteron implantation dose on titanium

A fluctuatingly-increasing trend of the deuterium density in titanium target is shown by the curve of Fig.2. At some points, there are significant decreases before next increase. The higher the implantation dose is, the more frequent the fluctuations are. The fluctuation of D-D fusion yield directly corresponds to the density change of deuterons in the target, which is related to the accumulation, diffusion and escapping of deuterium in target. Each fluctuation might indicate an event of deuterium escaping from the reaction zone while the next increase is just a new accumulation process. A saturated trend is also shown in the Fig.2, but the maximum loading ratio (D/Ti) was much less than 1.4.

3.3 Damages of the sample after implantation

Serious damages of the sample surface were observed by using SEM. The surface

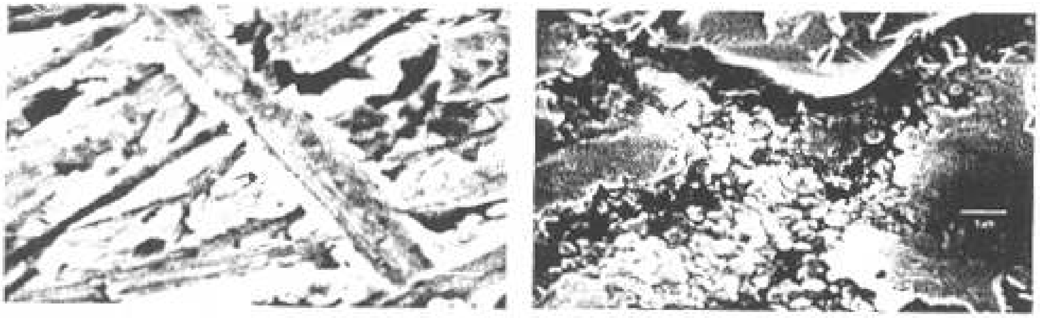

Fig.3 Comparison of topographies before (left) and after (right) bombarding (×10,000)

topographies of the sample before and after implantation are displayed in Fig.3. Many segregation layers are shown in the Fig.3. Many crystal grains with the size of few hundreds nano-meters were formed under the surface. However, the crystal grains are round like beans.

3.4 Anomalous nitrogen contamination

Significant contamination of nitrogen in the sample was found in the experiments. The contents of nitrogen-15 in different metal samples were determined by resorting to the $^{15}N(p,\alpha)^{12}C$ nuclear reaction analysis (NRA). The results are listed in Table 1.

Comparing with other metal samples, the nitrogen contamination in Ti^2H_x samples is about two orders of magnitude higher and the amount of ^{15}N in used Ti^2H_x sample is four times of the amount in fresh Ti^2H_x. This indicats that the Ti^2H_x sample has strong ability to trap nitrogen from air, the longer of the sample stored in air, the more nitrogen contamination accumulated in Ti^2H_x sample. The nitrogen contamination might relate to the titanium hydride structure, but the ingression of nitrogen might affect the deuterium loading ratio in titanium.

Table 1 Content of ^{15}N in different samples (NRA results)

Samples	^{15}N density/atom·cm^{-2}
Used Ti^2H_x	4×10^{16}
Fresh Ti^2H_x	1×10^{16}
Ti	2×10^{14}
Mo	3×10^{14}
TiMo	6×10^{14}

4 CONCLUSIONS

The crystal nano-structure is changed evidently while deuterium ingresses into titanium; cracks were observed while the deuterium loading ratio was larger than 1.4; and the titanium metal was completely cracked into crystal grains with the size of a few hundred nano-meters while the deuterium loading ratio was larger than 1.6. However, the shape of crystal grains formed by using the deuteron beam implantation method is different from the grains formed by gas loading method. The loading ratio is larger in the case of gas loading, comparing with the implantation method. The larger the loading ratio is, the finer the crystal grains are. This phenomenon may be applied to prepare nano-size titanium hydride powder.

The deuterium density in the titanium target changed abruptly during the implantation process, which implies a suddenly explosion (segregation) or fast diffusion of deuterium in titanium. There is usually a very serious surface effect of hydrogen in titanium alloy. The most of hydrogen atoms diffused to the near surface region after implantation. When the surface is destroyed by the new bombardment, an amount of hydrogen could escape due to the surface segregation. An out-diffusion could also happen suddenly, while the loading ratio is much higher than the saturated value. The surface segregation may depend on the implantation dose. The higher is the implantation dose, the more frequent is it. However, the kinetics is very complicated process. In order to understand the kinetics of this phenomenon, some fine *in situ* analyses by elastic recoil detection analysis (ERDA) or resonance nuclear reaction analysis (NRA) should be brought out in future. Ti^2H_x has strong ability to trap nitrogen from air, comparing to the metals such as titanium, stainless steel and molybdenum etc. The amount of nitrogen contamination might reach to a level comparable to the deuterium in titanium. It may affect significantly the charge of deuterium in titanium.

Acknowledgement

We are grateful to Pingzhi WANG and Jiyuan HAO who operated the accelerator for the experiments.

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