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技術報告

# 水素イオン照射装置の構築と Ti 板へのイオン照射試験

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# Construction of hydrogen ion irradiation apparatus and preliminary experiment for hydrogen ion irradiation using Ti sheet

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**Abstract**

A hydrogen ion irradiation apparatus was constructed, and the amount of implanted hydrogen in a Ti sheet was evaluated. A focused hydrogen ion beam having a spot area of approximately 3×3 $mm^2$ was used to irradiate a Ti sheet. After hydrogen irradiation for 12 h, the Ti sheet surface showed an irradiated mark. The thermal desorption spectrum indicated that hydrogen was possibly soluble in the Ti metal without Ti hydride formation. As the irradiation time was extended to 36 h, the amount of implanted hydrogen increased. These results proved that the Ti sheet captured the irradiated hydrogen.

## 1. Introduction

Hydrogen atoms in a steel and aluminum alloys cause the hydrogen embrittlement. To study the mechanism of hydrogen embrittlement, the amount of hydrogen in a metal should be controlled. A simple method to charge hydrogen is to immerse a metal in hydrogen gas under high pressure and temperature, thus controlling the amount of charged hydrogen in a metal. However, this method is rarely applied to aluminum alloys because their surface is, in most cases, covered with a native oxide layer, which prevents dissociation of hydrogen molecules. So, aluminum alloys hardly absorb hydrogen atoms under moderate hydrogen-gas conditions.

Hydrogen ion irradiation with accelerating voltage of several kilovolts allows the introduction of hydrogen to overcome the native oxide layer and to easily control the amount of hydrogen in the materials. Therefore, this technique can contribute to the study of the hydrogen embrittlement mechanism.

In this study, a hydrogen ion irradiation apparatus was constructed and the amount of implanted hydrogen in a titanium sheet was evaluated. Since titanium is a hydrogen absorbing material, it can capture irradiated hydrogen. And there are few reports about the introduction of hydrogen into Ti by the method of low-energy (several kV) hydrogen ion irradiation [6]. A vacuum system for thermal desorption spectrometry (TDS) measurement was also constructed to evaluate the hydrogen retention in the titanium sheet.

## 2. Constructed systems

### *2.1. Hydrogen ion irradiation apparatus*

We constructed an ion irradiation apparatus equipped with a sample heating stage. The apparatus consisted of an ion gun (ACIG-3P-2, AVC Co., Ltd.), a gas supply system, vacuum pumps, and sample heating stage. A schematic of the apparatus is shown in Fig.1. The sample

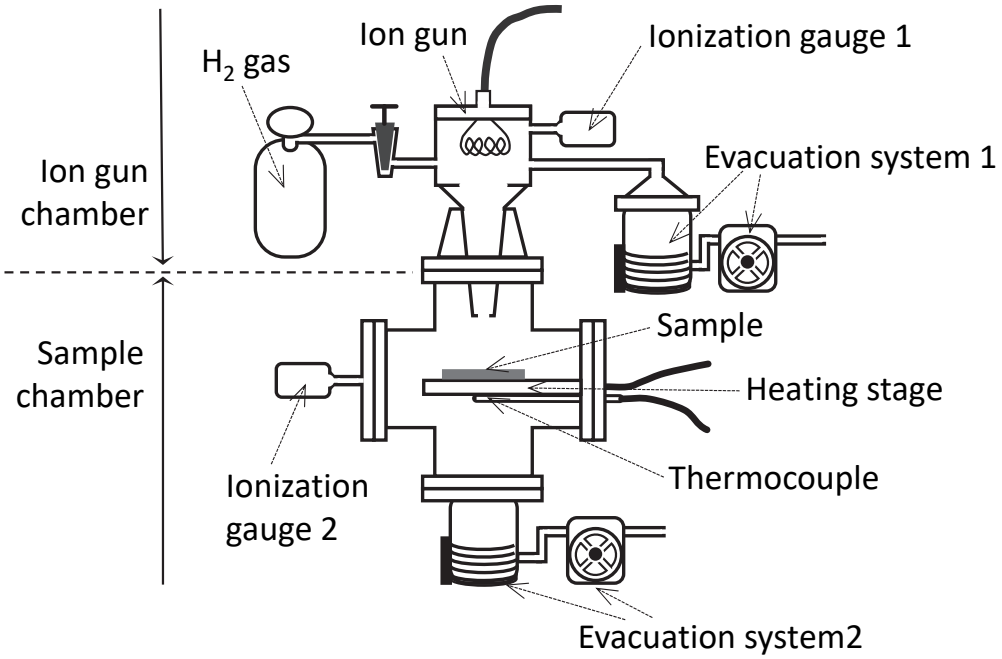


Fig. 1 Schematic of ion implantation apparatus.

stage made of Cu can be heated up to 573 K using an inserted sheath heater during ion irradiation. The temperature of the sample stage was measured by a thermocouple attached to it. The sample was placed on the Cu stage and its temperature was represented by the stage temperature. The apparatus was evacuated by two set of vacuum pumps (evacuation system 1 and 2 in Fig. 1). The pressure in a sample and ion gun chambers could be as low as $1\times10^{-5}$ and $1\times10^{-4}$ Pa, respectively. B-A type ionization gauge (MG-2F and MG-2, ANELVA Co., Ltd.) were used for pressure measurements. Hydrogen gas (Taiyo Nippon Sanso Co., Ltd., purity 99.9999%) was introduced to the ion gun chamber through a needle valve. The pressure of the ion gun chamber was adjusted to approximately $5\times10^{-2}$ Pa during hydrogen ion beam irradiation. At that time the sample chamber was maintained at approximately $5\times10^{-4}$ Pa. The acceleration voltage was fixed at 3 kV and the ion current at the sample surface was approximately 3 μA. In this system, the irradiated hydrogen ions were assumed as $H_2^+$ and $H^+$ (the ratio of the ions was not examined). After hydrogen ion irradiation, the sample was kept in vacuum for 12 h for ion gun cooling before introducing air.

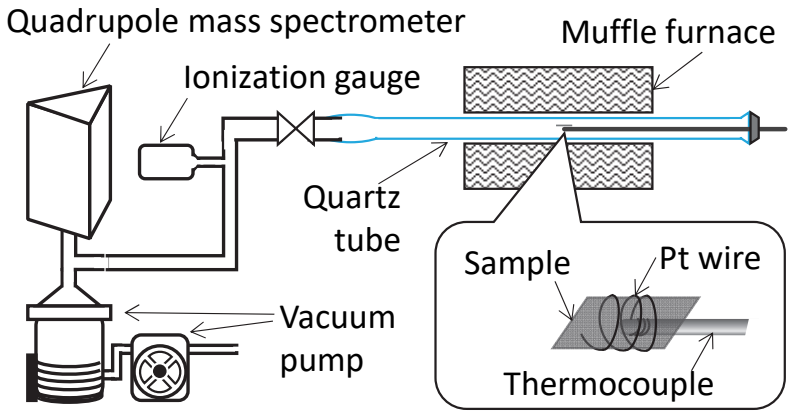


Fig. 2 Schematic of thermal desorption spectrometry system.

*2.2. Thermal desorption spectrometry*

Figure 2 shows the thermal desorption spectrometry (TDS) system used in this study. The sample was bound to the contact point of the sheathed thermocouple using a φ0.45 mm Pt wire. The thermocouple was introduced into a quartz tube evacuated to $2\times10^{-5}$ Pa. The sample was heated at a constant rate of 3 K/min up to 873 K using a tubular furnace. The amount of desorbed gas species was analyzed using a quadrupole mass analyzer (QMA-200, Balzers). The peak intensities of mass numbers 2, 17, 18, and 28 corresponding to $H_2^+$, $OH^+$, $H_2O^+$, and $CO^+/N_2^+$, respectively, were monitored during sample heating.

## 3. Experimental

A Ti sheet sized 12×25 $mm^2$ with 0.3 mm thickness (JIS H 4600 1$^{st}$ grade, TP-270) was used as the sample. Only one Ti sheet was repeatably used for hydrogen irradiation and desorption in this study. Exceptionally, a Ti sheet sized 25×25 $mm^2$ was used for adjusting the position of the focused ion beam. Experimental scheme of hydrogen implantation and TDS measurements is as follows.

(1) The as-received Ti sheet (Ti sheet cut to a certain size was cleaned with acetone) was

set to the TDS system. The first TDS measurement was performed to examine the content of impurity hydrogen.

(2) The Ti sheet was annealed at 873 K in vacuum for completely release of impurity hydrogen.

(3) The sample was then set to the hydrogen ion irradiation system and was irradiated with hydrogen ions for 12 h at room temperature (about 290 K). The second TDS measurement was carried out to evaluate the amount of implanted hydrogen.

(4) The hydrogen ion irradiation for 36 h was performed at room temperature (hydrogen irradiation for 12 h and then keeping in vacuum for 12 h were repeated 3 times). It was followed by the third TDS measurement.

## 4. Results

Figure 3 shows the Ti sheet surface after hydrogen ion irradiation. A triangle mark (3 mm in height, 3 mm in base) of the irradiation center indicated by the red circle can be observed in this figure, suggesting that the ion beam was focused on the area indicated by the mark. The mark disappeared after annealing in vacuum at 873 K.

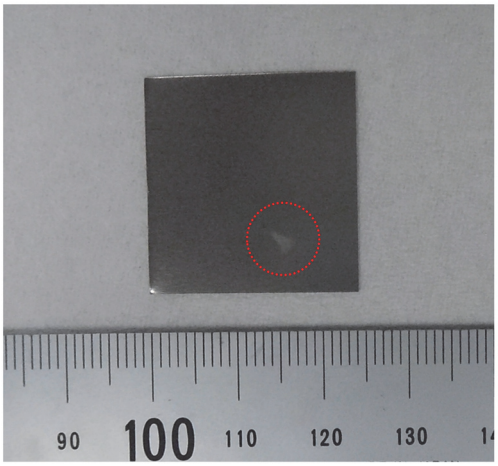


Fig. 3 Ti sheet after hydrogen ion irradiation.

Figure 4 shows the spectrum of TDS measurements for the as-received Ti sheet. Since the change in peak intensity of mass numbers 17, 18, and 28 was negligibly small during the heating process, the ion current of only mass number 2 corresponding to $H_2^+$ was plotted in this figure. The mass current showed a small shoulder at approximately 670 K (~160 min in Fig. 4)

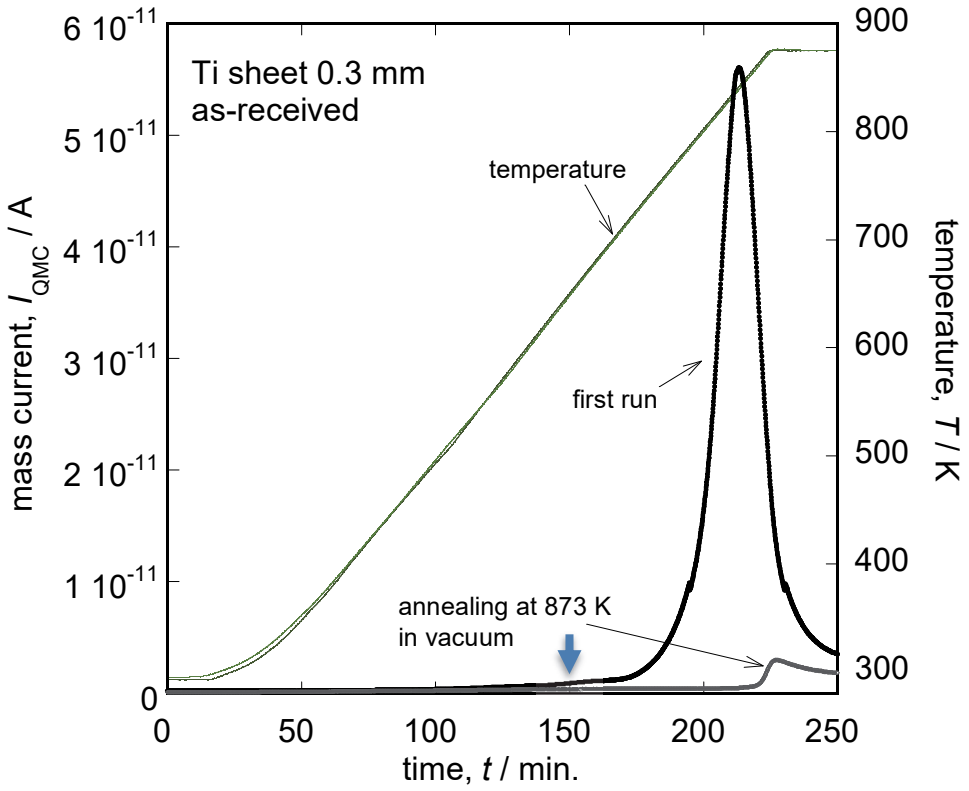


Fig. 4　Thermal desorption spectrums of as-received Ti sheet.

and a large peak at 840 K (210 min in Fig. 4). A x-ray diffraction analysis of the as-received Ti sheet indicated that the Ti sheet consisted of almost all α phase and trace of impurity phase (it was possible to titanium carbide). The large peak was caused by the hydrogen desorption from α-titanium phase. The small shoulder indicated by the blue arrow was possible to desorb hydrogen from impurity, or to decompose a little amount of δ phase because the hydrogen concentration in α and (α+δ) phase boundary at 300 K was considerably low [3-5]. Above 840 K, the rate of hydrogen release decreased smoothly and the mass current decreased to 1/10 at 250 min. After TDS measurement, the Ti sheet was annealed at 873 K in vacuum. The TDS spectrum of the annealed Ti sheet is also shown in Fig. 4. There was no noticeable hydrogen release up to 850 K, suggesting that almost all hydrogen was desorbed from the Ti sheet. The slightly released hydrogen above 850 K can be attributed to the residual hydrogen in the Ti

sheet.

Figure 5 shows the TDS results after the hydrogen ion irradiation of the Ti sheet. For the first run, the TDS spectra sharply increased above 850 K. The mass current at 873 K was larger than that after annealing (before irradiation, gray color in Fig. 4). The mass current after irradiation at 36 h was larger than that after irradiated 12 h. The value of integrated spectrum after irradiated 36 h at 873 K was also two times larger than that after irradiated 12 h. These results indicated that hydrogen was implanted by ion gun apparatus, and the amount of implanted hydrogen increased with the irradiation time. A sharp increase of ion current around 873 K was probably related to the desorption from α phase. The desorption temperature for irradiated Ti sheets slightly higher than that for as-received one. It could be due to the difference of hydrogen distribution in Ti sheet; Since irradiated hydrogen was accumulated near the surface at a small area, hydrogen in Ti sheet easily diffuse into bulk at low temperature. For the

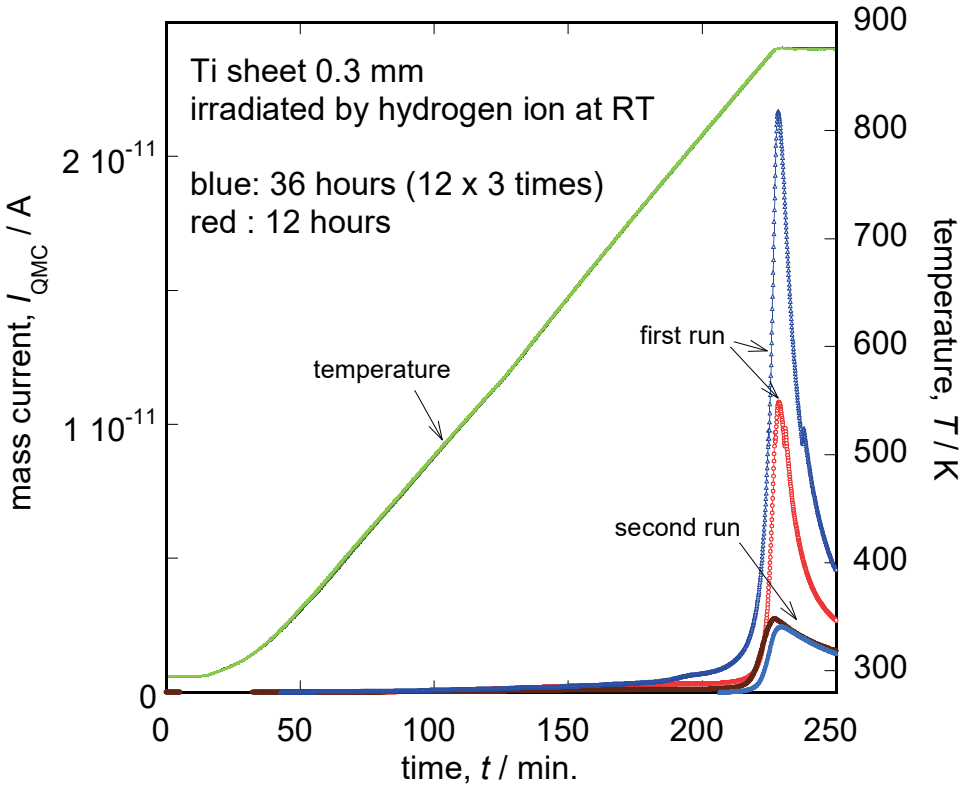


Fig. 5　Thermal desorption spectrum of Ti sheet after hydrogen ion irradiation.

TDS results after the hydrogen ion irradiation for 36 h (blue color in Fig. 5), a small shoulder was observed at approximately 800 K (200 min). Ma et al. reported that peaks in the TDS measurement of titanium hydride corresponded to the phase boundary [1,2]. It seemed that the small shoulder is caused by the formation of a β phase [1,2]. More experimental will be required to determine the relationship between TDS peaks and the phase boundary in consideration of hydrogen distribution in Ti sheet.

## 5. Conclusions

A hydrogen ion irradiation system was constructed to implant hydrogen atoms in metal sheets. The proposed system confirmed that hydrogen atoms could be implanted into Ti sheet using an ion irradiation apparatus. Moreover, from TDS measurements, we note that the amount of implanted hydrogen increased with the irradiation time. The ion irradiation system could be useful for charging hydrogen to aluminum alloys and for further research on hydrogen embrittlement of aluminum alloys.

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