

SIMS analysis of low content hydrogen in commercially pure titanium

Shigeru Hamada · Katsu Ohnishi ·
Hide-aki Nishikawa · Yasuji Oda ·
Hiroshi Noguchi

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Due to their excellent specific strength and environmental resistance, titanium and its alloys have been widely used as structural components. However, titanium is very active, so that not only oxygen and nitrogen, but also hydrogen may be readily introduced into the material during manufacturing. Titanium usually contains a specific amount of hydrogen, and it exists in the titanium as a hydride or solid solution dependent on the hydrogen content. The hydrogen solid solubility limit of pure titanium (α -phase titanium) seems to be higher than 10 ppm [1], although some values are reported. That is to say, if the hydrogen content of pure titanium is less than 10 ppm, all the hydrogen is thought to be a solid solution in the titanium. On the other hand, when the hydrogen content is more than the solid solubility limit, hydrides would appear. As the hydride is brittle, it weakens the strength of the titanium. Therefore, the hydrogen content in commercially pure titanium (CP-Ti) is within 150 ppm [2].

The present authors carried out a fatigue strength evaluation of titanium samples using the hydrogen removed sample (hydrogen content is 2.7 ppm) and normal sample

(34 ppm) [3, 4]. On the surface of the 2.7 ppm one, the hydride did not exist, while on the 34 ppm one, the hydride was present. It was found that the fatigue crack nucleation life of the 34 ppm one is greater than that of the 2.7 ppm one, and the fatigue crack propagation life of the 34 ppm one is the same as the 2.7 ppm one. This specific observation of the crack propagation indicated that the material behavior near the grain boundary is important for the crack propagation [3, 4]. It is then important to understand the actual state of hydrogen near the grain boundary for the CP-Ti applications.

There are some methods to detect hydrogen in materials, and each method has some merits and demerits. The hydrogen thermal desorption analysis method (TDS and TDA) can be used for the average hydrogen content and energy state analysis [5]. As already mentioned, hydrogen in the CP-Ti exists as a solid solution or hydride, and the hydrogen localized around the grain boundary should be evaluated. The localized hydrogen can then be visualized by the following method.

- (1) Secondary ion mass spectrometry (SIMS) [6–12]
- (2) Hydrogen micro-print technique (HMPT) [13–15]
- (3) Tritium autoradiography [16–18]
- (4) Atom field ion microscopy (AP-FIM) [19, 20]

In addition, although the hydrogen content cannot be directly detected, the hydride can be observed using a transmission electron microscope (TEM), scanning electron microscope (SEM), and optical microscope [21–26]. Especially, TEM is suitable for observing the hydride structure and hydride nucleation mechanism at high magnification. However, this technique has demerits; such as the hydride cannot be observed all over the specimen and it takes a long time to prepare a thin specimen for the TEM observation.

S. Hamada (✉) · Y. Oda · H. Noguchi
Department of Mechanical Engineering, Faculty of Engineering,
Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka-shi,
Fukuoka 819-0395, Japan
e-mail: hamada@mech.kyushu-u.ac.jp

S. Hamada · K. Ohnishi · Y. Oda · H. Noguchi
The Research Center for Hydrogen Industrial Use and Storage
(HYDROGENIUS), National Institute of Advanced Industrial
Science and Technology (AIST), Kyushu University,
744 Moto-oka, Nishi-ku, Fukuoka-shi, Fukuoka 819-0395, Japan

H. Nishikawa
Department of Mechanical Engineering Science, Graduate
School of Engineering, Kyushu University, 744 Moto-oka,
Nishi-ku, Fukuoka-shi, Fukuoka 819-0395, Japan

SIMS is one of the best techniques to analyze the local hydrogen content that exists as a hydride or solid solution. On the other hand, there are some reports in which a SIMS analysis was carried out on hydrogen-charged titanium containing a high content of hydrogen, and the hydride exists everywhere in the analysis area [11]. However, there is no reported SIMS study which analyzed the hydrogen removal titanium. When a low content of hydrogen is measured by SIMS, it is important to decrease the background noise. The origin of the background noise are impurities in the original surface of the sample, and the suspended hydrogen ions or molecules in the vacuum chamber. In this study, the presence of a low hydrogen content in the CP-Ti is then clarified by SIMS using a method that cools the SIMS stage [27]. The cooling stage decreases the background noise because it increases the vacuum level and decreases the impurities in the vacuum chamber.

The material used in this study was a CP-Ti rod (JIS H 4650 class 2). Table 1 lists the chemical composition of the as-received material [3, 4]. It contains 20 ppm hydrogen. In

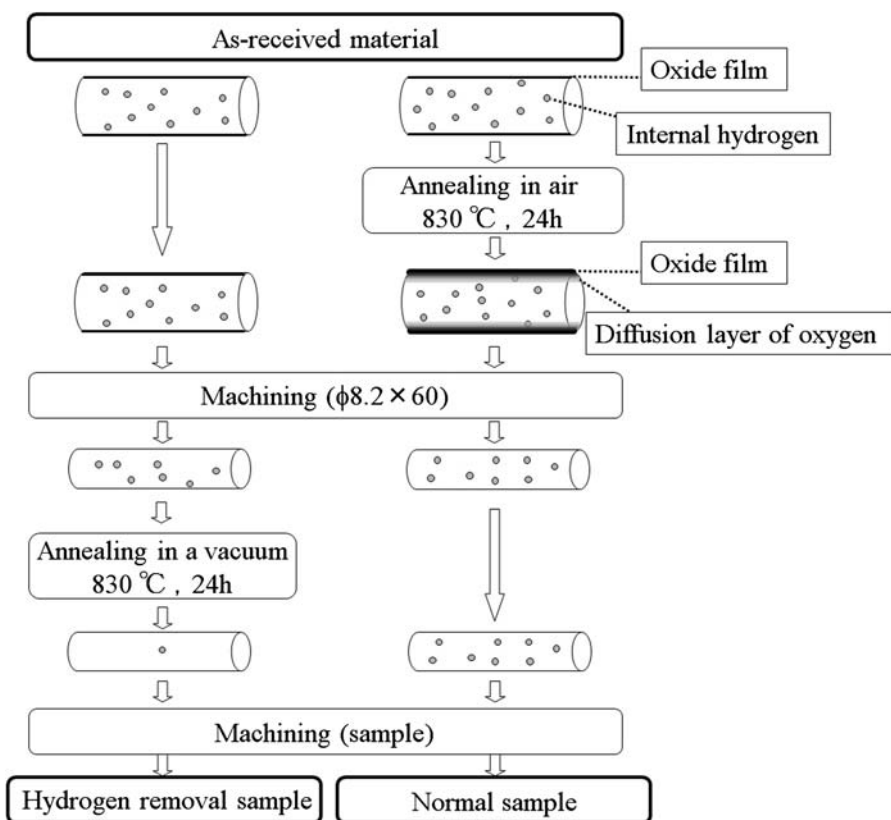
order to investigate the effect of the internal hydrogen on the fatigue behavior, two kinds of materials with different hydrogen contents were made from the as-received material. The amount of internal hydrogen was controlled by changing the annealing conditions, i.e., in air or in a vacuum [3, 4]. Figure 1 shows the sample preparation procedure for the SIMS analysis [3, 4]. It is the same as for the already mentioned fatigue test. The annealing conditions in both environments were 830 °C for 24 h. Figure 2 shows the thermal desorption spectrometer (TDS) profiles of hydrogen for the two annealed samples [3, 4]. Disk plates for the TDS measurement were cut from the original stock. The disk plate was 8 mm in diameter and 0.8 mm in thickness. The material annealed in air contains 34 ppm hydrogen, while the material annealed in a vacuum contains 2.7 ppm hydrogen. The hydrogen contents of the “normal sample” and “hydrogen removed sample” were 34 ppm and 2.7 ppm, respectively. The average grain size of both materials are the same, i.e., about 300 μm. There are acicular precipitates that seem to be hydrides in the normal sample. These materials were then analyzed by SIMS.

Figure 3 shows the sample preparation procedure for the SIMS analysis. The sample for the SIMS analysis was taken from the longitudinal section of the samples. The sample was 12 mm in length, 6 mm in width, and 1 mm in thickness. The sample surface was emery-polished to

Table 1 Chemical composition (mass%) [3, 4]

C	Si	Cr	Fe	Ni	N	O	H	Ti
0.008	0.007	0.008	0.058	0.009	0.005	0.116	0.002	bal.

Fig. 1 Hydrogen controlling method [3, 4]



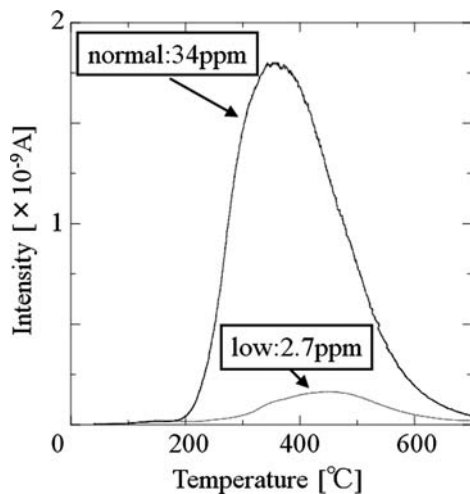


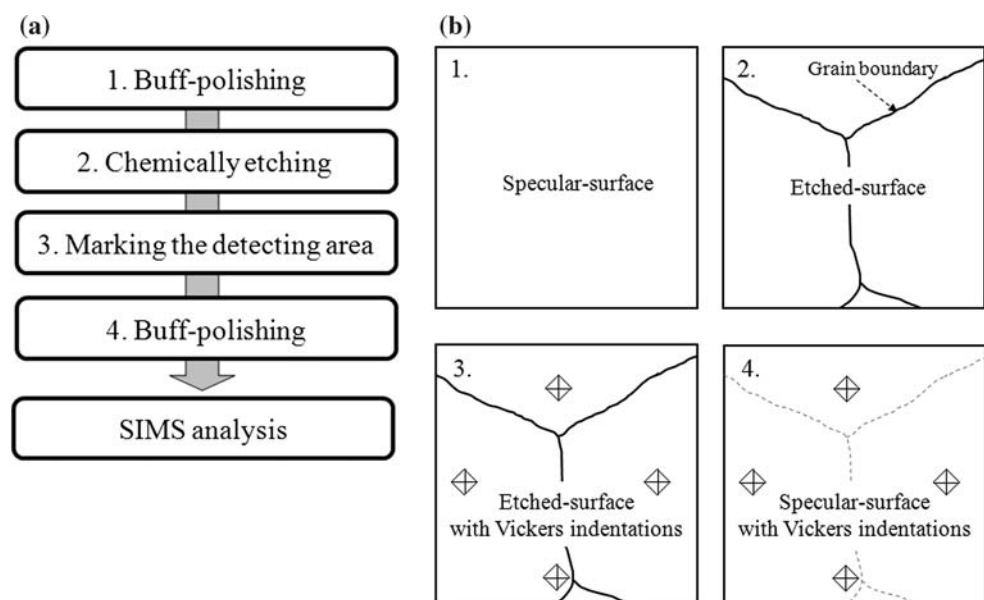
Fig. 2 TDS profiles for both materials. normal: normal sample (34 ppm), low: hydrogen removal sample (2.7 ppm). Rate of temperature rise is 0.17 °C/s [3, 4]

remove the work-hardened layer. Buffing was then performed on the surface, followed by chemical etching in a stirrer 3 mass% HF, 10 mass% HNO₃, and distilled water solution for 15 s to reveal the grain boundaries. These chemical etchings may favor the absorption of H in the near surface of the sample. The main SIMS analyses are performed after the removal of the thin etching effected film. After etching, Vickers indentations were marked to identify the analysis area on the sample surface. The surface condition as etched may lead to an inaccurate detection because of a micro-step at the grain boundary, asperity, and contaminated layer. Therefore, the surface of the sample was buff-polished to flatten the surface and minimize the effect of the surface conditions.

The instrument used in this study is a sector-type SIMS (Cameca IMS 7f). The cesium ion was used as the primary ion source. For the hydrogen analysis, the SIMS detection limit is very low, typically 1 ppm [28], so a high signal-to-noise ratio (S/N ratio) is required. A high primary ion density could lead to a high S/N ratio. There are two methods to obtain a high-density primary ion beam. One is to increase the primary current value, the other to reduce the beam size. However, these are not compatible, because a high-density primary ion beam makes it difficult to precisely focus the ion beam and the small raster size enhances the crater edge effect. In addition, the sputtering yield changes based on the incident angle of the ion beam to the sample surface. Therefore, it is necessary for the sample surface to be smooth and flat. Thus, the sputtering conditions are determined at the incident angle of 24.6°, an acceleration voltage 15 kV and a primary ion value of 16 nA. In order to remove the oxide thin film, the etching effected film and impurities from the surface, depth analyses were carried out using a 150 μm square raster and 100 μm circle analyzed area. Immediately after the depth analysis, the secondary ion image analysis was performed using resistive anode encoder (RAE) [29] in the same area. The measured ¹H secondary ion counts are normalized by the steady ⁴⁸Ti secondary ion count measured at the same time. Moreover, to reduce the background noise, special cooling equipment using liquid nitrogen was attached to the back side of the sample holder [27]. The temperature of the back side of the holder was kept below 120 K. Due to this equipment, the vacuum at the holder was kept below 4×10^{-8} Pa during the analyses.

Figure 4a, b show a SIMS map and an optical microscope image for hydrogen near a grain boundary of the

Fig. 3 Sample preparation procedure for the SIMS analysis. **a** Sample preparation; **b** Schematic illustration of sample procedure surface



normal sample, respectively [30]. The distribution pattern detected a large number of counts on the SIMS map of ^1H corresponding to the distribution pattern of black needles and the grain boundary in the optical microscope image. This implies that the needles in the grain are hydrides [21]. On the other hand, hydrogen existences in the grain boundaries are also observed. This implies two possibilities: (i) The hydride may also exist in the grain boundaries; and (ii) the β -phase titanium may exist in the grain boundaries, because the solid solubility limit of the β -phase

titanium is higher than α -phase titanium, and as pointed out by Yan et al. [11], the β -phase titanium is predominantly located at the grain boundaries in the CP-Ti.

Figures 5 and 6a, b show a SIMS map and an optical microscope image for hydrogen near a grain boundary of the hydrogen removal sample, respectively. The distribution pattern detected a large number of counts on the SIMS map of ^1H corresponding to the distribution pattern at the grain boundary in the optical microscope image. Therefore, the hydrogen is mostly located in the grain boundaries. The

Fig. 4 Images near the grain boundary of the normal sample (34 ppm) [30]. **a** SIMS analysis for ^1H . **b** Optical microscope

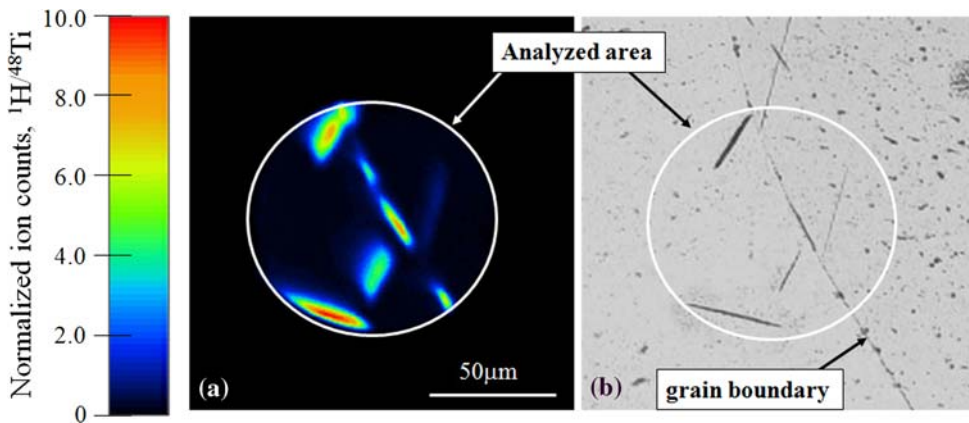


Fig. 5 Images near the grain boundary of the hydrogen removal sample (2.7 ppm). **a** SIMS analysis for ^1H . **b** Optical microscope

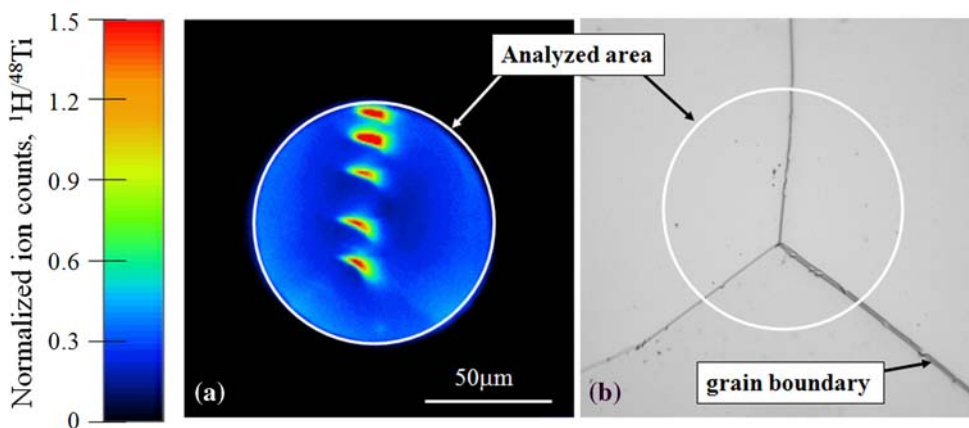


Fig. 6 Images near the grain boundary of the hydrogen removal sample (2.7 ppm). **a** SIMS analysis for ^1H . **b** Optical microscope

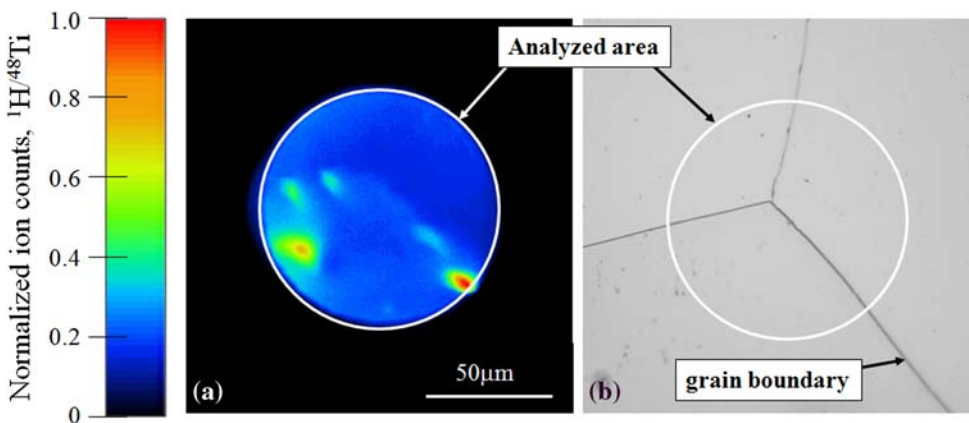
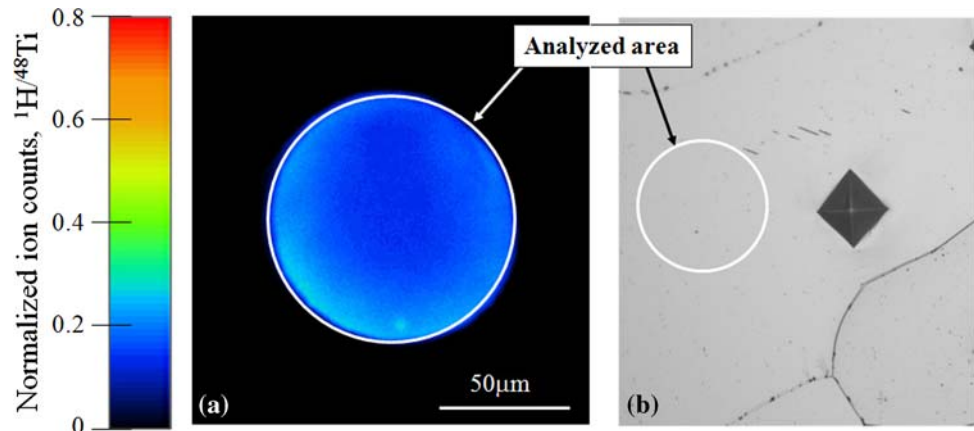


Fig. 7 Images of grain interior of the hydrogen removal sample (2.7 ppm). **a** SIMS analysis for ^1H . **b** Optical microscope



hydride or the β -phase titanium may exist in the grain boundaries.

Figure 7 shows the interior of a grain. It implies that the hydrogen count is extremely lower than that of Figs. 5 and 6, and there is a uniform hydrogen distribution in the grains. It was found that the presence of hydrogen in the Ti with the 3.4 ppm hydrogen level is not a solid solution, but in the localized state at the grain boundary as a hydride or β -phase titanium [11].

We conclude as follows:

- (1) Internal hydrogen in the CP-Ti was visualized by the SIMS technique. For the normal sample with the hydrogen content of 34 ppm, hydrogen exists as a hydride inside the grains and along the grain boundaries, and for the hydrogen removal sample with the hydrogen content of 2.7 ppm, the hydrogen exists as a hydride along the grain boundaries.
- (2) The presence of hydrogen in Ti with 2.7 ppm hydrogen is not a solid solution, but in the localized state at the grain boundary as a hydride or β -phase titanium.

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