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SIMS Analysis of Hydride in Commercially Pure Titanium

by

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Abstract

Commercially pure titanium (CP-Ti) usually contains a few tens of ppm hydrogen. In order to clarify the fatigue behavior of CP-Ti, it is important to know the distribution of such hydrogen. In this study the distribution of hydrogen formed as hydride was analyzed by secondary ion mass spectrometry (SIMS). The hydrides could be detected interior the grain and at the grain boundaries. On the basis of the results, the points to be paid attention for the investigation of fatigue strength are discussed.

Keywords: Commercially pure titanium, Hydrogen, Hydride, SIMS

1. Introduction

Because of their excellent specific strength and environmental resistance, titanium and its alloys have been widely used for 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. The effects of these components on the mechanical properties of commercially pure titanium (CP-Ti) have been long investigated. On the basis of the results, the hydrogen content in CP-Ti is controlled so as not to exceed 150 ppm[1)]. It is considered that the internal hydrogen exists partially in the solution state but mostly as hydrides[2)]. Hydrogen is known to have detrimental effects on the strength of many metallic materials not forming any hydride. In the case of fatigue, such hydrogen may exert the complex effects on the fatigue behavior through the presence of solution-state hydrogen and hydride. In order to clarify the effects of such hydrogen on the fatigue behavior of CP-Ti, it is important to know the distribution of hydrogen in the material. Secondary ion mass spectrometry (SIMS) is a very useful instrument for analyzing such hydrogen.

In this study, the distribution of hydrogen formed as hydrides in CP-Ti is analyzed by SIMS. Then the points to be paid special attention for the investigation of fatigue behavior are discussed on the basis of the analyses. .

2. The Material and SIMS Analysis Procedure

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2.1 Material and SIMS sample

The material used in this study was a CP-Ti rod (JIS H 4650 class 2) with a diameter of 14 mm. **Table 1** lists the chemical composition of the material as-received. It contains 20 ppm hydrogen. In order to investigate the effects of internal hydrogen on the fatigue behavior, two kinds of material with different hydrogen contents were made from the material as-received. The amount of internal hydrogen was controlled by changing the annealing conditions: in air or in a vacuum. Annealing condition in both environments was 830℃ for 24 hours.

Table 1 Chemical composition (mass%).

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.

Figure 1 shows thermal desorption spectrometer (TDS) profiles of hydrogen for two kinds of annealed material. Disk plates for TDS measurement were cut out from the materials. The disk plate has a diameter of 8 mm and a thickness of 0.8mm. The material annealed in air contains 34 ppm hydrogen but the material annealed in a vacuum contains 2.7 ppm hydrogen.

Figure 2 shows photographs of microstructure of annealed materials. The average grain sizes of both kinds of materials are the same: about 300 μm. There are acicular precipitates that seem to be hydrides in the high hydrogen material. This material was analyzed by SIMS.

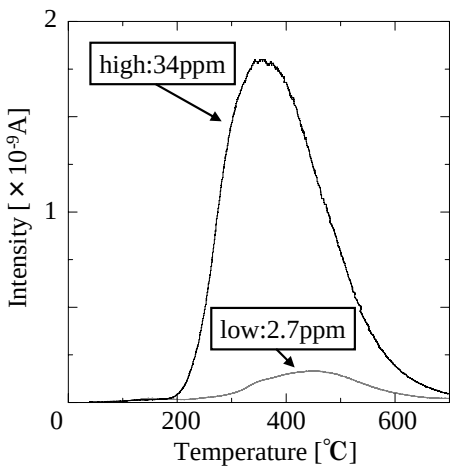
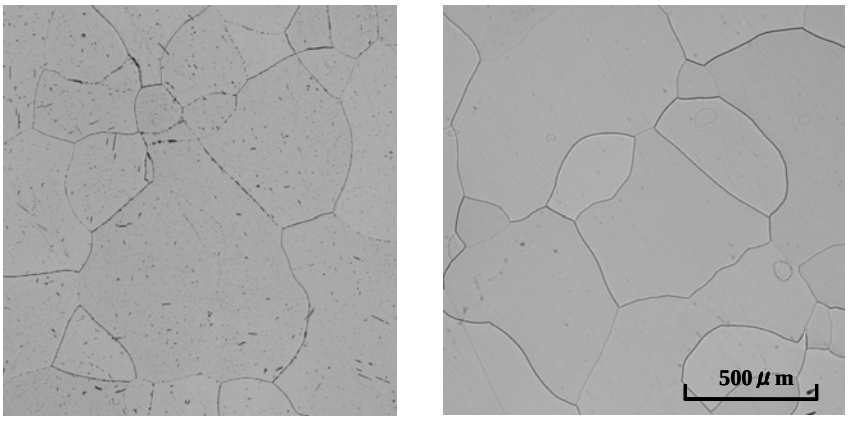


Fig. 1 TDS profiles for both materials. High: higher hydrogen content material. Low: lower hydrogen content material. Rate of temperature rise is 0.17℃/s.



(a) Higher hydrogen content material (b) Lower hydrogen content material

Fig. 2 Microstructure of materials.

2.2 SIMS analysis procedure

The instrument used in this study is a sector type secondary ion mass spectrometer (SIMS; Cameca IMS 7F). Cesium ion was used for the primary ion source.

In the case of hydrogen analysis, a detection limit in SIMS is very severe, typically 10ppm, so high signal to noise ratio (S/N ratio) is required. High primary ion density could lead to high S/N ratio. There are two methods to obtain the high-density primary ion beam. One is to increase the primary current value, the other to reduce the raster size. However, these are not compatible, because high-density primary ion beam cause difficulty to precisely focus ion beam and small raster size enhanced a crater edge effect. In addition, the sputtering yield changes by an 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 as an incident angle of 24.6 degrees, an acceleration voltage 15kV and a primary ion value 16nA. In order to remove the oxide thin film and impurities from the surface, depth analyses was carried out in the condition of 150 μm raster and 100 μm analyzed area. Immediately after depth analysis the secondary ion image analysis was performed using RAE at the same area.

Moreover, to reduce the background noise, the special cooling equipment by liquid nitrogen was attached to the back side of the sample holder. The temperature of the back side of the holder was suppressed below about 120K. Due to this equipment, the degree of the vacuum at the holder was kept below 4×10^{-8} Pa during analyses.

3. Results

3.1 SIMS analyses

The sample for SIMS analysis was taken from the longitudinal section of the higher hydrogen content material. The sample has a length of 12mm, a width of 6mm and a thickness 1mm. The sample surface was emery-polished to remove the work-hardened layer. After that, the surface was buff-polished, then chemically etched in stirred 3 mass % HF, 10 mass % HNO_3 and distilled water solution for 15 seconds to reveal the grain boundaries. After etching, Vickers indentions were marked to identify the analysis area on the sample surface. Surface condition as etched may lead to

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 surface conditions.

Figure 3 shows the relationship between the indentations and the positions of the detection area. **Figure 4** shows depth profiles for ^{1}H and ^{48}Ti obtained by SIMS. Secondary ion counts of ^{1}H and ^{48}Ti reached the steady state after 1,000 seconds. Therefore, it was considered that the contamination layer of the sample had been sufficiently removed. Then the two-dimensional distribution of hydrogen was analyzed in the same area.

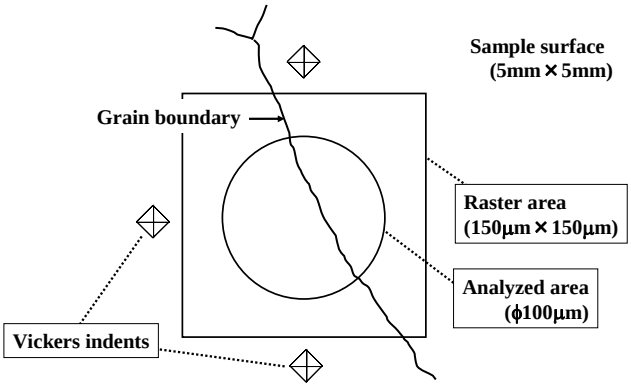


Fig.3 Illustration of detection area for SIMS.

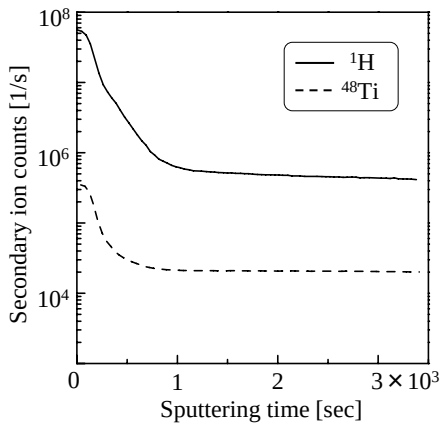
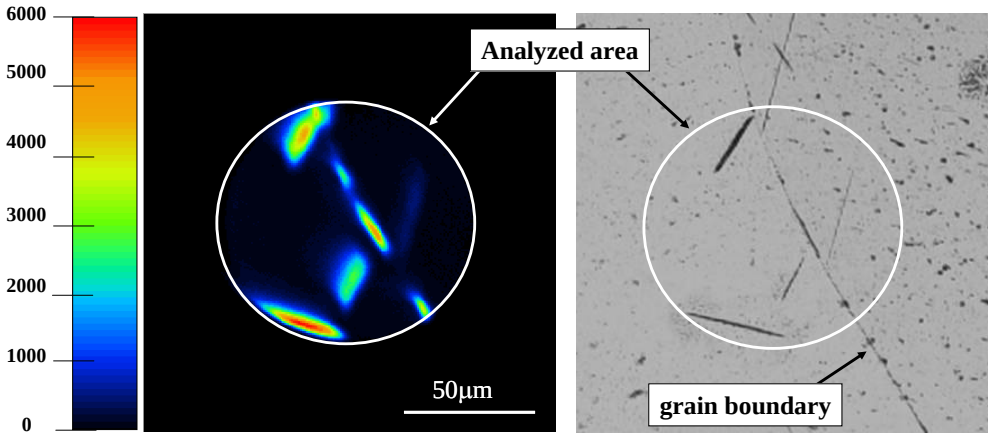


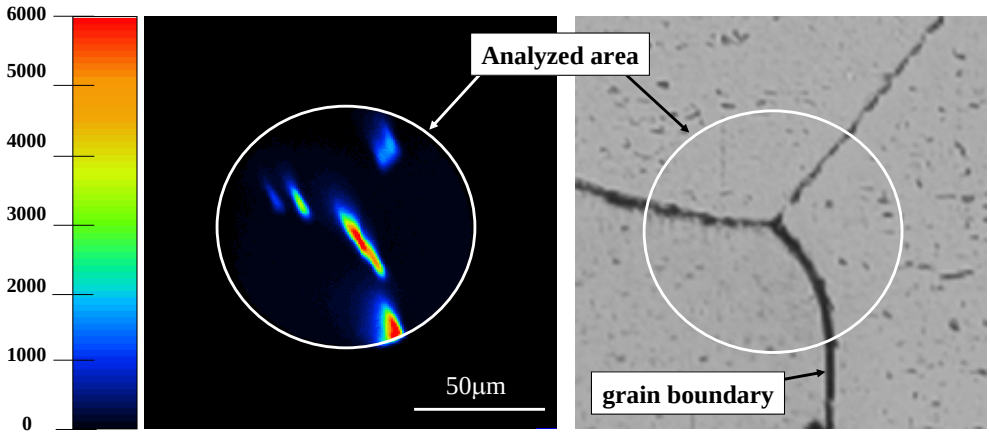
Fig.4 SIMS depth profile for H and Ti.

Figures 5 (a) and (b) show an optical microscope image and an SIMS map for hydrogen near a grain boundary, respectively. The distribution pattern detected a large number of counts on the SIMS map of ^{1}H 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 γ hydrides[9]. **Figures 6** (a) and (b) show similar images to **Fig. 5**, but hydrides detected only at the boundaries. **Figures 7** (a) and (b) show optical microscope images of the observation area before and after SIMS analysis shown in **Fig. 5**, respectively. The sputter rates of two adjacent grains seemed to be different from each other. However, **Fig. 7** (c) shows that the step of the grain boundary is small and the intensity of ^{1}H along the grain boundary is not constant. In addition, the solubility of hydrogen into titanium is low. On any case, the intensity of edge effects is not very high. Therefore, high-intensity sites along the boundary are also thought to be hydrides.



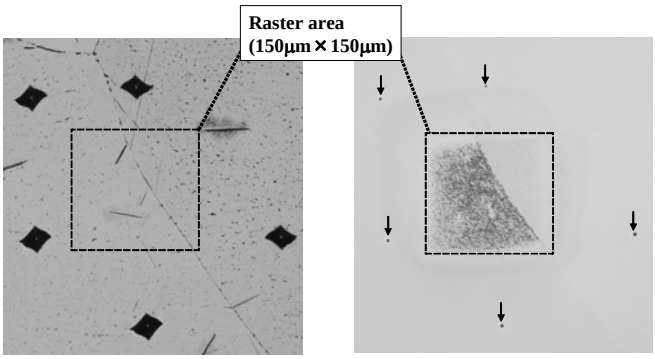
(a) SIMS image (b) Optical microscope image

Fig. 5 SIMS analysis of higher hydrogen content material.

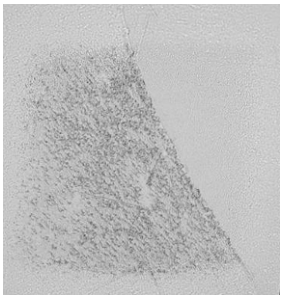


(a) SIMS image (b) Optical microscope image

Fig. 6 SIMS analysis of higher hydrogen content material.



(a) Marked SIMS sample (b) After SIMS analysis of polished sample of (a)



(c) Enlargement the raster area in (b)

Fig. 7 Change in surface morphology near the grain boundary before and after SIMS analysis. Arrows indicate Vickers indents after polishing sample in (a).

3.2 Discussion for fatigue investigation

Hydride is reported to be brittle, and harder than the base material[4]. In addition, expansion during hydride formation[5] causes the stress in base material. Hydrides shown in **Fig. 5** and **6** are considered to inhibit slip inside the grain and near the grain boundary.

It was reported that fatigue crack of CP-Ti is mainly initiated from slip-bands inside the grain [6), 7)]. However, it is considered that the situation is different with higher mean stress or higher amounts of hydride, which cause the cracking of hydride. There is possibility that hydride has detrimental effects on the fatigue strength acting as defects in material. In addition, hydrides in the grain boundary are hard to identify with microscope. Therefore, there is possibility that such hydride was overlooked.

Hydride melt at 100-200℃ and get into the base material as the solution state hydrogen. Therefore in the case of rather higher temperature, the effect of solid-solution hydrogen on the fatigue behavior should be considered.

Conclusion

(1) Internal hydrogen usually contained in CP-Ti can be visualized. The hydrogen exists as hydride along grain boundary and interior the grain.

(2) Points to be paid special attention for the investigation of fatigue behavior are pointed out on the basis of SIMS analyses.

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