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Hydrogen Absorption Behaviors of Titanium in High Pressure Gaseous Hydrogen

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Titanium and its alloys having high strength and light weight are very attractive for hydrogen energy systems if their durability against hydrogen is in acceptable level in high pressure hydrogen gas. To investigate the hydrogen absorption behaviors of titanium materials in the actual operation circumstances of high pressure hydrogen gas systems, hydrogen content distribution from the surface was examined in JIS Class-2 commercially pure titanium and a beta titanium alloy, Ti-3Al-8V-6Cr-4Zr-4Mo, after exposed in 45MPa hydrogen gas at 54 and 95°C for up to 1500h. In commercially pure titanium, hydrogen absorption seems not to be serious in the circumstances investigated and it was at most 40ppm in the surface area, which is far lower than the upper limit specified in the conventional codes and standards. In the beta alloy, considerable amount of hydrogen was absorbed. However, the maximum content of hydrogen absorbed in the circumstances investigated is considered to be around 200ppm, and any brittle hydride was not observed. It is considered that the alloy can fully be used as a structural material if 200ppm solid solution hydrogen does not degrade mechanical properties.

Keywords: commercially pure titanium, beta titanium alloy, hydrogen, high pressure, hydrogen absorption, hydride

1. Introduction

A Japanese national project "Establishment of Codes & Standards for Hydrogen Economy Society" is now ongoing to establish clean hydrogen societies featuring fuel cell vehicles in the very near future. The project started in 2005 after taking over the previous national projects "the Development for Safe Utilization and Infrastructure of Hydrogen" (2003-2005) and " International Clean Energy Network Using Hydrogen Conversion" (WE-NET program) (1993 to 2003).

In those projects, quite a wide range of technologies related to hydrogen such as hydrogen generation, hydrogen utilization, hydrogen transportation and storage have been investigated. In the WE-NET project, liquid hydrogen was considered as the most effective energy carrier and storage medium, and mechanical properties of various materials were investigated actually in liquid hydrogen at 20K using the specially designed mechanical testing facilities, which were installed in R&D Center of Nippon Steel in 1997[1)-4)]. Meanwhile, the recent two projects extensively examined properties in high pressure gaseous hydrogen using two facilities to characterize mechanical properties in gaseous hydrogen at up to 100MPa pressure, which were designed and installed in 2005 and 2007 in R&D Center of Nippon Steel[5)].

In hydrogen circumstances, austenitic stainless steels and aluminum alloys are considered to attractive structural materials from the viewpoints of mechanical properties, durability against hydrogen and low temperature in case of liquid hydrogen, availability, etc., and evaluation has been conducted mainly for those materials[6),7)]. Titanium and its alloys are also very attractive if their durability against hydrogen is acceptable because they have excellent mechanical properties from cryogenic temperature to ambient temperature and are widely available. In particular, high strength/weight ratio of titanium is expected to contribute considerable weight reduction and fuel efficiency in transportation systems and pumping systems. In this respect, tensile properties of ASTM grade 2 commercially pure titanium and Ti-6Al-4V ELI were evaluated in liquid hydrogen and their excellent properties were confirmed[8)]. In gaseous hydrogen, hydrogen embrittlement is one of the concerns for titanium because it is generally believed that titanium is vulnerable against hydrogen and may subject to hydrogen embrittlement when some amount of hydrogen is absorbed during long time use. To confirm the hydrogen absorption behaviors in the conditions close to the actual operation circumstances of high pressure hydrogen gas systems, commercially pure titanium and a beta titanium alloy, which is believed to have highest resistance against hydrogen embrittlement, were exposed in hydrogen gas at 45MPa at 54 and 95°C for up to 1500h, and hydrogen content distribution from the surface was examined. 45MPa is the maximum pressure specified for the 35MPa-class on-board hydrogen fuel systems, which may be heated to 54 - 95°C in hot summer and at opportunities of refueling.

2. Experimental Procedure

Materials used were JIS Class-2 commercially pure titanium (CP-2) bars of 13mm in diameter and Ti-3Al-8V-6Cr-4Zr-4Mo (Ti-38644) bars of 24mm in diameter. Ti-38644 is one of the conventional beta type titanium alloys. Chemical compositions of the materials used are listed in Table 1. Both materials have fully recrystalized grains and no alpha phase was observed in the matrix of Ti-38644 although small amount of silicide precipitates were contained as shown in Figure 1.

Table 1. Chemical composition of the material used. (mass %)

	Al	V	Cr	Zr	Mo	Fe	Ni	Si	C	O	N	H
CP-2	-	-	0.008	-	-	0.058	0.009	0.007	0.008	0.116	0.005	0.0013
Ti-38644	3.70	8.1	6.24	3.81	4.15	0.061	0.011	0.058	0.004	0.081	0.008	0.0080

Cylindrical specimens of 4mm in diameter were taken from the bars and surfaces were finished by polishing with #1000 abrasive papers. After cleaning in acetone, specimens were placed in autoclaves and hydrogen gas with 7N purity was introduced after cleaned with nitrogen gas and evacuated. After pressurized to 45MPa, one of the autoclaves was heated to 54°C and the other was heated to 95°C. After exposed in high pressure hydrogen gas for 750h, specimens were taken from the autoclaves and subject to the analyses. The same procedure was applied and specimens were taken from the autoclaves in 1500h of exposure time. Specimens were stored in liquid nitrogen at -196°C before analyses after taken out from the autoclaves to avoid desorption of hydrogen. Hydrogen content distribution was measured with the following procedure: cylindrical specimens of 4mm in diameter were cut to several pieces and some were ground to smaller diameter, 2, 2.5, 3 and 3.5mm. Total hydrogen contents were measured in accordance with JIS H 1619 for the cut samples of 2 to 4mm in diameter, and average hydrogen contents in the areas from the surface to 0.25mm in depth, 0.25 to 0.5mm, 0.5 to 0.75, 0.75 to 1, and 1 to 2 were calculated by taking geometrical positions of the ground samples into account.

Microstructure observations were also conducted for transver se sections of specimens. In addition, TDS (Thermal Desorption Spectroscopy) analyses were conducted for the specimens hydrogen charged at 95°C for 750h. In TDS analyses, specimens were heated to 1000°C at heating rate of 1.67°C/min in vacuum of $5x10^{-6}$Pa initially.

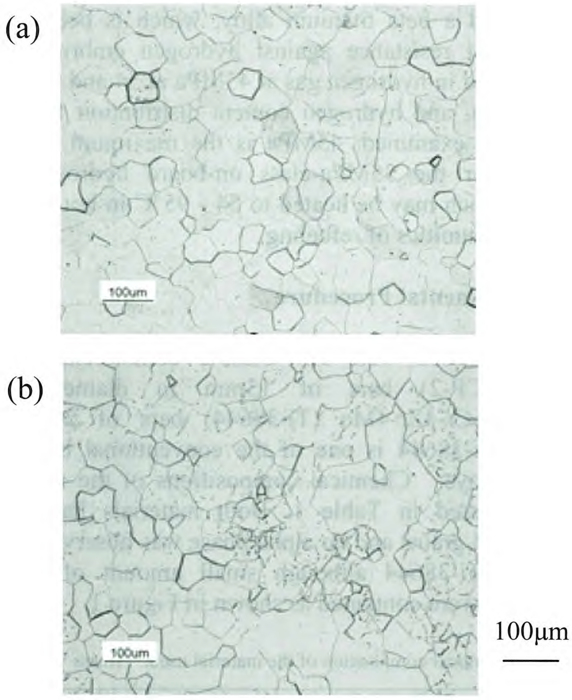

Figure 1. Microstructures of center portion of the transverse sections of the materials used. (a) JIS Class-2 commercially pure titanium, (b) Ti-3A1-8V-6Cr-4Zr-4Mo.

3. Experimental Results and Discussion

Hydrogen content distribution in CP-2 is shown in Figure 2. Exposure at 54°C (Figure 2(a)) for 750h, clear increase in hydrogen content was recognized in the area between 0 and 1mm in depth from the surface, while hydrogen content was the same level as that before the exposure inside the specimen from 1 to 2mm in depth from the surface. In 1500h of exposure time, hydrogen content in this area was slightly increased. However, further hydrogen diffusion into the matrix was not clearly observed. At 95°C (Figure 2(b)), hydrogen content was considerably higher than that exposed at 54°C. Hydrogen content was increased in the center portion of the sample after the exposure for 750h and more than 40ppm hydrogen was enriched in the surface area from 0 to 0.75mm in depth after the exposure for 1500h. It should be noted that the hydrogen contents were constant in the area between 0 to 0.75mm in depth from the surface. This area probably corresponds to the alpha + hydride two phase area at 95°C while hydrogen in the inner area (1 to 2mm in depth from the surface) probably exists in the form of solid solution.

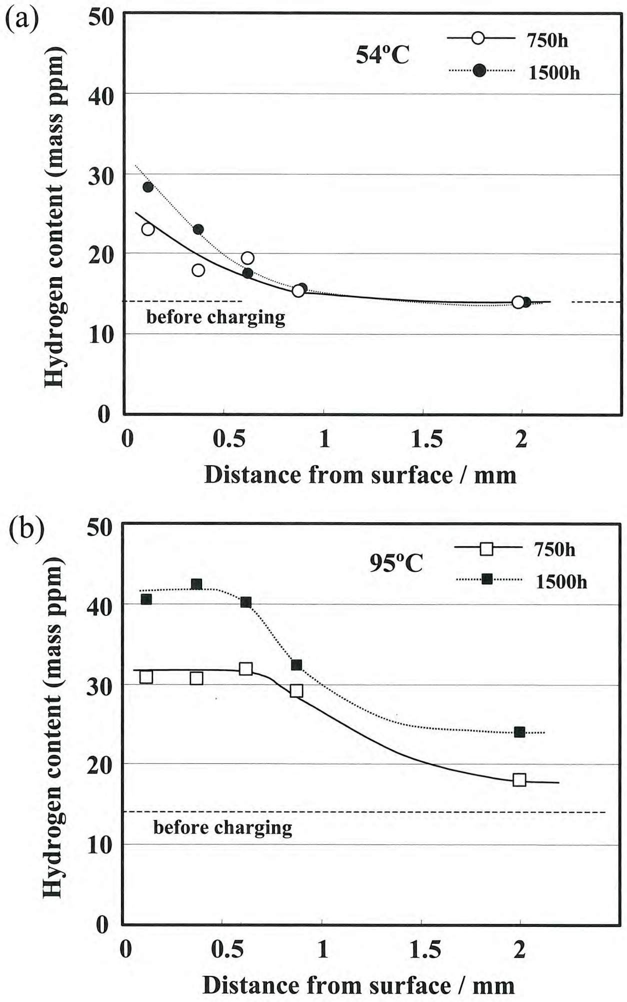

Figure 2. Hydrogen content distribution from the surface in JIS Class-2 CP titanium exposed in hydrogen gas at 45MPa for long time. (a) Exposed at 54°C for 750 and 1500h, (b) Exposed at 95°C for 750 and 1500h.

Microstructures of the sample exposed at 95°C for 750h are shown in Figure 3. Hydride (etched in black) was observed in the area near the surface (Figure 3(a)). In the very surface of about 50µm in depth from the surface, hydride density was very high and it indicates that hydrogen content in this area is far higher than that shown in Figure 2. Meanwhile, in the center area, no hydride was observed as shown in Figure 3(b). The microstructures are corresponding to the hydrogen content distribution in Figure 2 except the area of 50µm in depth from the surface : the surface area in which hydrogen content is constant is the one containing hydride and the inner area having gradient in hydrogen content distribution corresponds to the area that hydrogen is contained in the form of solid solution at 95°C.

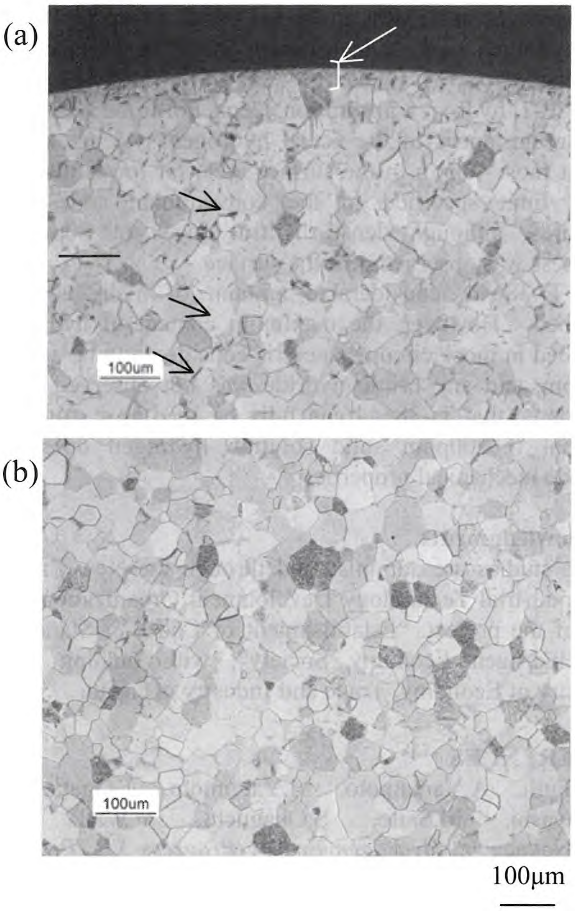

Figure 3. Microstructures of the transverse section of JIS Class-2 CP titanium exposed in 45MPa gaseous hydrogen at 95°C for 750h. (a) near the surface, (b) center portion of cylindrical specimens of 4mm in diameter. Arrows indicate hydride.

Hydrogen content distribution in Ti-38644 is shown in Figure 4. Exposure at 54°C (Figure 3(a)) for 750h, increase in hydrogen content was very small and it is limited in the area between 0 and 1 mm in depth from the surface. After the exposure at 54°C for 1500h, hydrogen content was slightly increased not only in the surface area but also in the center portion, and hydrogen content was almost constant from the surface to the center. It indicates that the hydrogen content almost reached the equilibrium one which is determined with hydrogen pressure (45MPa) and temperature (54°C) according to what is called Sieverts low9). At 95°C (Figure 3(b)), hydrogen content was considerably higher than that exposed at 54°C. In the center portion of the sample, hydrogen content increased to around 120ppm from 80ppm and the hydrogen content distribution had gradient from the surface to the center. It indicates that hydrogen was contained as a solid solution element and diffused toward the center of the sample. After the exposure for 1500h, increase of hydrogen content near the surface became small while it was hydrogen content is approaching to the equilibrium one at 95°C, 45MPa, and the equilibrium hydrogen content is considered to be around 200ppm in this condition.

As described above, distribution of hydrogen content in the surface area had gradient and any plateau, observed in CP-2 in Figure 2(b), was not observed. It suggests that hydrogen was involved in the beta matrix in the form of solid solution and hydride was not formed. This can be confirmed in the microstructures shown in Figure 5. Any hydride was not observed in the optical micrographs.

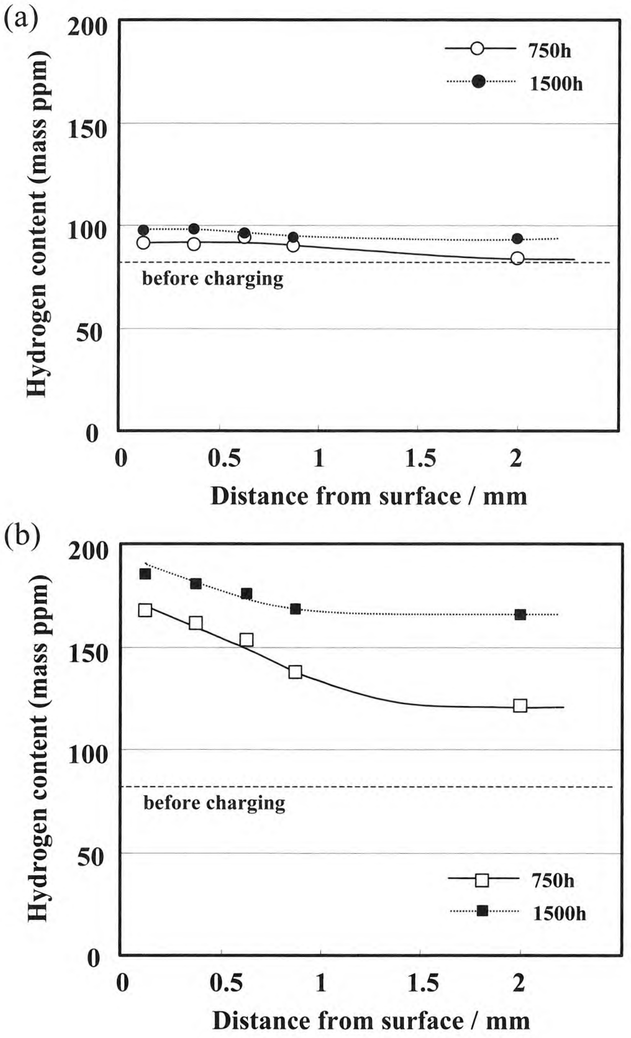

Figure 4. Hydrogen content distribution from the surface in Ti-3A1-8V-6Cr-4Zr-4Mo exposed in hydrogen gas at 45MPa for long time. (a) Exposed at 54°C for 750 and 1500h, (b) Exposed at 95°C for 750 and 1500h.

Figure 6 is the results of TDS analyses. In CP-2, hydrogen desorption was most active at around 540°C and only one peak was obtained. The peak is considered to correspond to solid solution hydrogen in the alpha phase matrix because hydride does not exist at those high temperatures and it should be dissolved during heating. In Ti-38644, hydrogen desorption was most active at around 500°C and again only one peak was obtained. Although diffusion coefficients of hydrogen in the alpha phase and the beta phase are considerably different, hydrogen desorption peak temperatures are not so different. It indicates that the solubility of hydrogen in the both phases is very large at those temperatures.

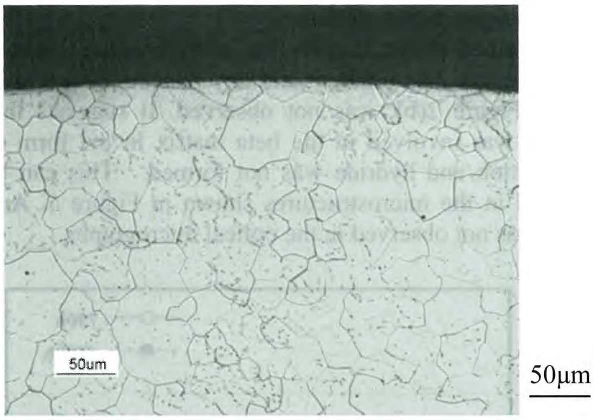

Figure 5. Microstructure near the surface of the transverse section of Ti-3A1-8V-6Cr-4Zr-4Mo exposed in 45MPa gaseous hydrogen at 95°C for 750h.

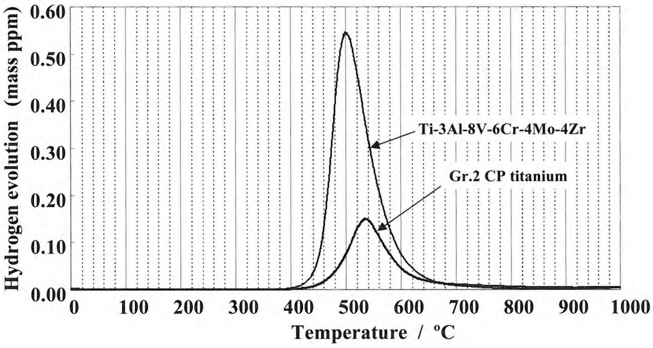

Figure 6. Temperature dependence of hydrogen evolution in TDS analyses for JIS class-2 CP titanium and Ti-3A1-8V-6Cr-4Zr-4Mo exposed in 45MPa gaseous hydrogen at 95°C for 750h.

As described in the "Introduction", the maximum hydrogen pressure specified for the 35MPa-class on-board hydrogen fuel systems and the corresponding refueling gas stands in Japan is 45MPa, and temperature at which those systems are exposed is at most 95°C. Experimental results for CP-2 suggest that hydrogen absorption is not serious in those circumstances because 40ppm hydrogen in the surface area is far lower than the maximum content specified in the JIS, ASTM and other codes and standards. In fact, hydride observed in the surface area was very limited except the area of 50µm in depth from the surface.

In case of a beta titanium alloy, Ti-38644, hydrogen absorption was enormous. However, the content of hydrogen to be absorbed in those circumstances is considered to be around 200ppm and any brittle hydride would not be formed. In this respect, Ti-38644 can fully be used as a structural material having 800MPa of tensile strength if 200ppm solid solution hydrogen does not degrade mechanical properties.

4. Summary

To confirm the hydrogen absorption behaviors of titanium materials in the operation circumstances of high pressure hydrogen gas systems including 35MPa-class on-board hydrogen fuel systems, JIS Class-2 commercially pure titanium (CP-2) and a beta titanium alloy, Ti-3A1-8V-6Cr-4Zr-4Mo (Ti-38644), were exposed in hydrogen gas at 45MPa at 54 and 95°C for up to 1500h, and hydrogen content distribution from the surface was examined.

In CP-2, hydrogen absorption seems not to be serious in the circumstances of the actual hydrogen systems, which was at most 4Oppm in the surface area, far lower than the upper limit specified in the conventional codes and standards, although dense hydride layer of 50µm in thickness was observed near the surface.

In Ti-38644, considerable amount of hydrogen was absorbed. However, the maximum content of hydrogen absorbed in those circumstances is considered to be around 200ppm, and any brittle hydride was not observed. It is considered that Ti-38644 can fully be used as a structural material if 200ppm solid solution hydrogen does not degrade mechanical properties.

Acknowledgments

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