Reduction of hydrogen content in pure Ti

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Abstract. Pure Ti is adopted as a material for ducts and bellows at the proton accelerator 3 GeV-RCS in J-PARC project, because of its small residual radioactivity. In the particle accelerator, the H₂ outgassing due to ion impact is often the dominant source of gas release. As the reduction of hydrogen content will probably suppress ion induced desorption, we attempted to reduce the hydrogen content in the Ti by in-situ vacuum baking. First, thermal desorption behavior and the change in hydrogen content after the heat treatment were investigated. Vacuum firing at temperatures higher than 550°C was effective in reducing the hydrogen content in the Ti. At the same time, the mechanical properties were monitored because grain growth leads to decrease in mechanical strength. Even after treatment at 750°C for 12 hr, the decreases in tensile and yield strength were so small (~10%) that we have no anxiety about the reduction of mechanical strength. Based upon the results of this study, vacuum firing has been applied to reduce the hydrogen content in the Ti bellows and ducts of the RCS machine.

1. Introduction
Japan Atomic Energy Agency and High Energy Accelerator Research Organization are now constructing a high intensity proton accelerator (J-PARC), which consists of a 400 MeV linac, a 3 GeV rapid cycling synchrotron (3 GeV RCS), and a 50 GeV synchrotron[1]. The 3 GeV RCS aims to accelerate a proton beam of 0.333 mA to 3 GeV, and to supply the beam both to a neutron source generator and to the 50 GeV ring. Operation with 25 Hz repetition rate leads to 1 MW output. Some of the circulating protons diffuse and collide with the vacuum wall, so that secondary particles such as neutrons and gamma rays are generated. The radiation dose due to those secondary particles is estimated to be 100 MGY during 30 years of operation.

To minimize the radiation exposure during maintenance work, pure Ti has been adopted as the material for beam transfer ducts and bellows because of its small residual radioactivity. To reduce the radiation exposure more efficiently, it is important to suppress the outgassing during beam operation, as deviation of the high energy protons from their orbit is due mainly to their collision with gas species,
after which they impact the vacuum wall. Reduction of outgassing during beam operation is also essential to suppress pressure instability.

Some researchers have recently investigated the outgassing characteristics of Ti which have been given various surface treatments[2]: However, there are few studies dealing with the outgassing mechanism of the hydrogen (the main residual gas species) in the Ti bulk. As the main outgassing process during the beam operation is ion induced desorption, reducing the hydrogen content in the Ti will certainly be effective. Thus, we attempted to decrease the hydrogen content by in-situ vacuum baking, in hopes of applying this in-situ process to the RCS machine. The reduction of H-content by vacuum firing was experimentally verified, paying attention to the change in mechanical strength after the heat treatment. Based upon this study, vacuum firing has been applied to reducing the hydrogen content in the Ti bellows and ducts. The details are given in this paper.

2. Preparation of the sample

In this experiment pure Ti (Japanese industrial standards grade 2) was used. The impurities included in the Ti plate were measured, and are shown in Table 1. As the primary investigation should be focused on the interstitial hydrogen in the bulk and study of the absorbed gas species should be done separately, the surface of the samples should be given sophisticated treatment. Fortunately, Mizuno et al. have recently reported the characteristics of the outgassing of Ti which have been given various types of surface treatment [2]. Some mechanical surface treatments make the surface very smooth but also produce a modified surface layer of about 100 nm. On the other hand, chemical polishing (CP) produces a very thin oxidized layer. Therefore, all the samples in this experiment are prepared as followed except for the samples in section 4.2: 1) The surface of the rectangular Ti plate 10cm wide and 20cm long was buff-polished with # 400 emery paper and then was chemically polished with a mixed liquid consisting of 60% HNO₃ solution and 46% HF solution exactly for 1 min. 2) Then, the surface was rinsed ultrasonically with distilled water, and cut into pieces. The roughness Ra of the surface was found to be less than 0.02 µm by a stylus profilometer. The measured length was 1 mm. Surface composition was also analyzed by AES. As shown in Fig. 1, the oxidized layer on the sample

| H  | O  | N  | Fe | C  | Ti |
|----|----|----|----|----|----|
| 0.001 | 0.09 | 0.01 | 0.05 | 0.01 | balance |

Table 1. Chemical composition (wt. %) of pure Ti (JIS grade 2).

Figure 1. AES depth profile on Ti surface for CP treatment. The depth is evaluated with the Ar ion sputtering rate for SiO₂.

Figure 2. TDS spectra of H₂ from the chemically polished Ti. The dotted lines show the deconvolution.
was estimated to be ~7 nm thick by the half value of O peak of the AES depth profile. There were carbon impurities less than 2 nm thick on the surface. This may be ascribed to the carbon monoxide absorbed on the surface which came through the air vent, because carbon monoxide was observed at about 200°C in the TDS spectra.

3. Observation by TDS
To get an overview of the temperature dependence of outgassing from a material, it is useful to observe the desorption behavior upon thermal desorption spectroscopy (TDS). The sample is mounted on a quartz stage, which guides infrared light applied for heating to the rear surface of the sample. The temperature was controlled by a WRe5%-WRe26% thermocouple (T/C) which was attached on the sample surface opposite the stage.

Typical TDS data from the Ti sample are shown in Fig. 2. Here, the temperature was ramped up to about 900°C at the rate of 0.2 K/sec. There are two peaks of H₂ desorption: a major peak and a rather small one. The deconvolution of the spectra is shown in Fig. 2. The main component starts at about 400°C, peaks at 620°C, and ends at about 850°C. This peak is attributable to the diffusible interstitial hydrogen, because the Ti surface after CP treatment is covered by TiO₂ thin film which hinders the hydrogen desorption but decomposes at temperatures above 400°C[3]. The dependence of the peak temperature on the ramp rate and on the shape of the peak also reflects simple diffusion behavior[4]. A sub-component starts at about 250°C and peaks at about 350°C. Then, it seems to end at 450°C. The amount of the hydrogen under the sub-component increases with decrease in the processing time of the chemical polishing. Therefore, this peak may be ascribed to the hydrogen trapped in the modified layer formed by buffing process. In either case, vacuum firing over 550°C is effective to reduce the hydrogen content in the Ti. Then, we investigated the hydrogen introduced through the CP treatment. Here we used samples which were completely degassed by pre-heating at 850°C for 4 hr (“850°C-4hr” samples). Typical TDS spectra both from the basic 850°C-4hr sample and from the chemically polished one are shown in Fig. 3. It is clear that the CP treatment carries the hydrogen into the bulk of Ti and that the behavior of this introduced hydrogen is the same as the interstitial hydrogen. From the area under the H₂ curve above 600°C, the amount of the introduced hydrogen is estimated to be ~1 \times 10^{16} \text{ atoms/cm}^2. Finally, the peak around 300°C is ascribed to the hydrogen absorbed on the surface which came through the air vent, because this peak cannot be observed in the subsequent TDS observations where there was no air vent.

4. Change in H content and mechanical strength after heat treatment

4.1 Change in H content after heat treatment
In order to determine the vacuum firing conditions for the Ti, the isothermal behavior was examined in detail. The samples are heated in a vacuum furnace with less than 10⁻⁵ Pa. Then, the hydrogen content was measured by the argon carrier fusion thermal conductivity method and/or integration of the TDS spectra. As the resolution of the thermal conductivity method is about 1 ppm weight, the content was estimated utilizing the TDS spectra when the H content was less than 1 ppm. Here we may reasonably presume that the H content is proportional to the integrated H₂ outgassing curve up to 900°C in TDS spectra. In fact, when the H content is over 1 ppm, the ratio of the integration value to the H content measured by the argon carrier fusion thermal conductivity method is almost constant. However, the area under the peak around 300°C should be eliminated in calculating the H content, because this peak is due to absorbed hydrogen as mentioned above. Thus, the H content can be estimated from the integration of the H₂ curves.

The results are shown in Fig. 4. The data for the plates 4 mm thick are also plotted in this figure. Temperature dependency of the residual hydrogen is consistent with the observations by TDS. In addition, we experimentally confirmed that the H content decreases with increase in the processing time.
Table 2. Change in mechanical strength after heat treatment at 750°C for Ti plates 4 mm thick.

| Processing time (h) | Tensile strength (MPa) | 0.2% yield strength (MPa) | Elongation (%) |
|---------------------|------------------------|--------------------------|----------------|
| 0                   | 418                    | 333                      | 33.8           |
| 2                   | 377                    | 297                      | 38.0           |
| 4                   | 379                    | 298                      | 37.8           |
| 8                   | 378                    | 298                      | 39.2           |
| 12                  | 378                    | 299                      | 36.6           |

Then, we evaluated the activation energy of diffusion by parameter fitting. If the diffusion process is reasonably modelled, the evacuated amount of hydrogen is easily calculated. In an infinite plate with the thickness of \( d \), the H content distribution is simply expressed when the surface concentration of hydrogen is zero. As a result, the residual hydrogen \( Z \) after processing time \( t \) is expressed by the following:

\[
\frac{Z}{Z_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} (2n+1)^2 \exp\left\{-\frac{(2n+1)^2 \pi^2}{d^2}Dt\right\}. \tag{1}
\]

Here, the \( Z_0 \) refers to the initial hydrogen content. The diffusion coefficient \( D \) is determined from a pre-exponential term \( D_0 \), the activation energy \( E \), and the firing temperature \( T \) by the equation \( D = D_0 \exp\{-E/kT\} \). In turn, \( E \) and \( D_0 \) are determined by fitting the following experimental data to the equation (1). Here, there is no need to modify the nominal values of the firing temperature \( T \) and the duration time \( t \), since all of the samples were ramped up from 500°C to the planned temperatures within 5 min and cooled down from the nominal temperatures less than 500°C within 10 min. For the experimental data set which consist of the ratio of residual hydrogen to the initial content, the equation (1) was fitting as a model function using the least squares method: \( E=0.64 \) eV, and \( D_0=0.0003 \) cm²/s for a plate 1 mm thick and 0.005 cm²/s for one 4 mm thick.

The fitted curves are also shown in Fig. 4. These curves are in close agreement with the experimental data. However, the pre-exponential term \( D_0 \) is strongly dependent on the thickness. This may imply that the boundary condition at the surface is not so simple and that the recombination of hydrogen atoms approaching the surface from the bulk should be taken into consideration[5].

Fig. 3. TDS spectra of H₂ from the completely degassed sample and from the chemically polished “850°C-4hr” one.

Fig. 4. Residual H content after the heat treatment as a function of the heating temperature.
4.2 Change in mechanical strength after heat treatment

It is well known that the heat treatment at high temperature leads to the growth of grains and thus decreased mechanical strength of the metal. Therefore, we investigated the change in mechanical strength. As shown in Table 2, the change in mechanical strength is quite small even after heat treatment at 750°C for 12 hr. The tensile and 0.2% yield strength decrease by ~10%. On the contrary, the elongation is enhanced by ~10%. The thin plates were also found to have sufficient mechanical strength even after treatment at 650°C for 8 hr. Thus we have no anxiety about the reduction of mechanical strength after heat treatment.

Based on the results given in sections 4.1 and 4.2 here, the Ti bellows (0.3 mm thick) and ducts (4 mm thick) for the RCS have been vacuum-fired at 650°C for 8 hr and at 750°C for 8 hr, respectively.

5. Conclusions

To suppress the ion induced desorption of hydrogen from pure Ti, the hydrogen content can be reduced through heat treatment in a vacuum. The reduction of H content was examined in detail as a function of heating temperature, paying attention to the change in mechanical strength. The following conclusions can be drawn:

1) Study of residual H content shows that the interstitial hydrogen in the bulk diffuses with an activation energy of 0.64 eV. Vacuum firing at temperatures higher than 550°C is effective in reducing the hydrogen content in the Ti.

2) The change in mechanical strength is quite small even after heat treatment at 750°C for 12 hr; the tensile and 0.2% yield strength decrease by 10%. The elongation is enhanced by 10%.

3) Surface treatments such as chemical polishing introduce a small amount of hydrogen (~1 × 10¹⁶ atoms/cm²) into the bulk. This introduced hydrogen behaves like the interstitial hydrogen.

Based on the above results, to reduce the hydrogen content, the Ti bellows and ducts for the RCS have been vacuum fired at 650°C for 8 hr and at 750°C for 8 hr, respectively. The outgassing behavior during the beam operation of the RCS will be reported on in the near future.

References

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