

# Correlation between susceptibility to environment-assisted cracking of super-elastic TiNi alloy and the states and their amount of hydrogen in it

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## **Abstract**

Susceptibility to environment-assisted cracking (EAC) of super-elastic TiNi alloy has been correlated with the states and their amount of hydrogen in the material. The TiNi alloy specimen was immersed in sulfate solutions at a given pH, and a giving cathodic potential was applied to it for 13 ks to absorb hydrogen into it. The specimen was subjected to X-ray diffraction (XRD) test to detect hydride, and to thermal gas desorption spectroscopy (TDS) test to determine the state and its amount of hydrogen in it. In the case that a potential of  $-0.5 V_{Ag/AgCl}$  was applied to the specimen in the solution of pH 3, the XRD detected no hydride on it. Whereas, application of  $-1.5 V_{Ag/AgCl}$  was induced formation of hydride. The TDS indicated that the specimen treated at  $-0.5 V_{Ag/AgCl}$  involved hydrogen desorbing around 810 K, and the one at  $-1.5 V_{Ag/AgCl}$  involved hydrogen desorbing around 500 as well as 810 K. Therefore, it was suggested that the hydrogen desorbing at lower and higher temperatures obtained by the TDS were of hydride state and solid-solution state, respectively. The specimens treated under various conditions were analyzed by the same way as mentioned before, and an amount of the hydrogen in each state as well as a cathodic charge density applied to the specimen were obtained to be correlated. A logarithm of the amount of the hydrogen in the each state increased almost linearly with an increase in a logarithm of a charge density. Susceptibility to the EAC of the material suddenly increased around a charge density of  $0.025 MC \cdot m^{-2}$ , and the charge density was considered to induce the amounts of hydrogens in hydride and solid-solution state of 10 and 100 mass ppm, respectively.

## 1. **Introduction**

TiNi alloy demonstrates unique mechanical properties such as shape memory or super-elasticity. In addition, the alloy is known to show excellent corrosion resistance in dilute aqueous solutions. Therefore, the alloy has been widely employed in various industrial, dental, and medical applications. It has been reported in the dental field, however, that some parts composed of TiNi alloy fracture. For example, orthodontic arch wires and stents made of the alloy have broken down in oral cavities and in vivo, respectively [1,2]. It has been proposed that the reason for failure is environment-assisted cracking (EAC) in relation with hydrogen absorption, and many studies have been conducted to understand this mechanism [3-6]. The electrochemical hydrogen absorption technique has been widely employed in these studies to determine the relation between the EAC susceptibility of the alloy and the amount of hydrogen absorbing into it. However, it is also necessary to understand how the hydrogen absorption process depends on electrochemical and circumstantial conditions, such as potential, current density, solute of solution, and solution pH. Our group previously investigated the EAC behavior of TiAl intermetallic alloy as a function of the electrochemical potential and the solution pH, and successfully produced an EAC map of the alloy based on potential and pH [7,8]. In the map, the most severe EAC conditions were located in lower pH and around  $-1.0 V_{Ag/AgCl}$ , almost  $Ti^{3+}$  stable region. Extensively, the effects of the electrochemical potential and the solution pH on the EAC susceptibility of TiNi alloy with super-elastic property was investigated [9] and it was found that the EAC susceptibility was significantly enhanced for lower potentials as well as lower pH values, quite different EAC map against that of TiAl. The investigation on EAC of TiNi additionally revealed that the EAC had possibility to be affected by hydride and/or hydrogen as solid-solution state. This research, therefore, aimed to understand the changes in the amounts of hydride and hydrogen with hydrogen absorption conditions, and to discuss the relation between the two amounts and the EAC susceptibility of TiNi.

## 2. **Material and experiments**

Material was a Ti-50.85 at% Ni alloy and was heated at 673 K for 3.6 ks to have super elastic property. A 1.1 mm thick alloy plate was machined into specimens with a size about  $15 \text{ mm}^L \times 3 \text{ mm}^W$ . The specimen surfaces were mechanically polished with dry emery paper to #6/0 (corresponding to about #800) immediately before hydrogen absorption treatment described below.

Treatment of hydrogen absorption into the specimens was conducted by electrochemical method. The treatment solutions were aqueous sulfate solutions prepared with distilled water and reagents of  $H_2SO_4$ , NaOH, and  $Na_2SO_4$ . The sulfate concentration was fixed at  $9.85 \times 10^{-3} \text{ kmol}\cdot\text{m}^{-3}$  and the pH was controlled from 3 to 11. The solutions were used at room temperature (about 298 K) and

deacrated with N<sub>2</sub> gas from 1.8 ks before to the end of the tests. In the treatment, an Ag/AgCl (3.3 kmol·m<sup>-3</sup> KCl, room temperature) reference electrode, a Pt counter electrode and a potentiostat were employed. A given cathodic potential from -2.0 to -0.5 V<sub>Ag/AgCl</sub> was applied to the specimen in the solution of a given pH for 13 ks.

In 1.2 ks after the hydrogen absorption treatment, X-ray diffraction (XRD) test and thermal gas desorption spectroscopy (TDS) test were carried out for detecting hydride and amount of hydrogen, respectively. The X-ray emission conditions for the XRD test with a Cu-K $\alpha$  (wavelength: 0.154 nm) excitation source were 50 kV and 130 mA. The following is an outline of the TDS test: A schematic illustration of the system is shown in **Fig.1**. The specimen was placed in a quartz chamber under ultra-high vacuum (10<sup>-6</sup> to 10<sup>-7</sup> Pa) conditions and was heated gradually at 5.6 x 10<sup>-2</sup> K·s<sup>-1</sup> from room temperature to 900 K. A desorption rate of hydrogen out of the specimen during the heating process was determined as a function of the specimen temperature using a quadrupole mass spectrometer.

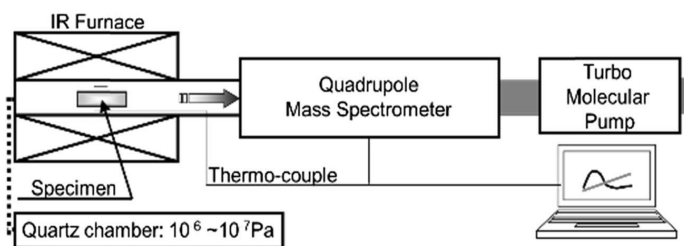


Fig.1 Schematic illustration of an apparatus for thermal desorption gas spectroscopy (TDS).

### 3. Results and discussion

The hydrogen absorption treatment was carried out for the specimen in the solution of pH 3 under the potentials of -0.5 and -1.5 V<sub>Ag/AgCl</sub>. The specimens were then subjected to the XRD test, and it was found that the specimen treated at -0.5 V<sub>Ag/AgCl</sub> consisted of main TiNi and slight Ti<sub>2</sub>Ni, identical to the specimen without the treatment. On the other hand, an XRD pattern of the specimen treated at -1.5 V<sub>Ag/AgCl</sub> involved additional peaks attributing to its hydride of TiNiH<sub>1.4</sub>.

The two treated specimen were then subjected to the TDS test. **Figure 2** shows the TDS profile of the specimen treated at -0.5 V<sub>Ag/AgCl</sub>. A TDS profile is a change in hydrogen desorption rate of the specimen with the specimen temperature. It was found in this figure that a hydrogen desorption started at about 600 K, increased with a rise in a temperature, rapidly increased from about 720 K, reached a maximum at around 810 K, and decreased with a rise in a temperature. The profile included almost one peak. Whereas, the TDS profile of the specimen treated -1.5 V<sub>Ag/AgCl</sub> showed that a hydrogen desorption rate started at about 400 K, increased with a rise in a temperature, reached a peak

around 500 K, decreased, again increased from about 680 K, reached a maximum around 810 K, and decreased with a rise in a temperature. The profile included two peaks. In comparison of the results of the XRD with those of the TDS tests, the followings were suggested: Since the specimen treated at  $-0.5 V_{Ag/AgCl}$  had no hydride but involved hydrogen desorbing at higher temperature around 810 K, the hydrogen desorbing at the higher temperature may be hydrogen in solid-solution state in the specimen. The result was mainly found in the test solution of higher pH and under a higher potential. On the other hand, the hydrogen desorbing at lower temperature around 500 K may be hydrogen decomposed from hydride, because the specimen treated at  $-1.5 V_{Ag/AgCl}$  had hydride and involved additional hydrogen desorbing at the lower temperature. The result was mainly found in the test solution of lower pH and under a lower potential. In addition, an amount of hydrogen in the each state was determined by integration of the each peak of the TDS profile with a measuring time.

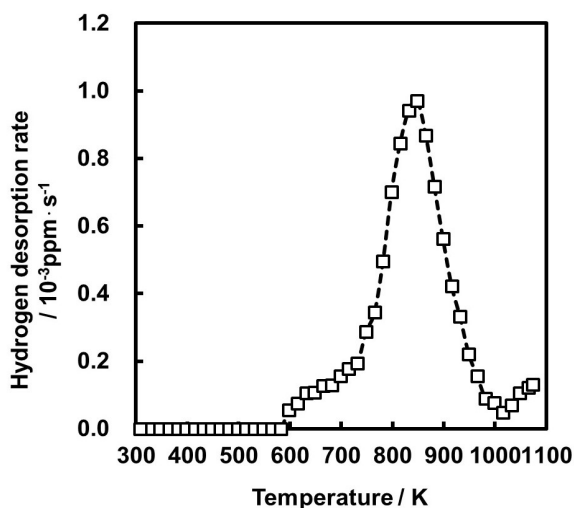


Fig.2 TDS profile of the specimen treated in the test solution of pH 3 at  $-0.5 V_{Ag/AgCl}$ .

In the previous research [9], it was found that the EAC susceptibility of the TiNi alloy increased with a decrease in pH as well as a fall in potential, and that the susceptibility was completely controlled by a cathodic charge density, not pH nor potential. A cathodic charge density is denoted as the value obtained by integrating a cathodic current density with time during the hydrogen absorption treatment. The results demonstrates that (1) the parent phase of TiNi ( $< 470 \text{ MPa}$ ) suffered no EAC even when the phase involved an amount of hydrogen corresponding to a cathodic charge density of  $100 \text{ MC} \cdot \text{m}^{-2}$ ; (2) the stress-induced martensitic phase ( $\geq 470 \text{ MPa}$ ) suffered almost no EAC and fractured at about 1600 MPa when the phase involved an amount of hydrogen corresponding to a cathodic charge density below  $0.025 \text{ MC} \cdot \text{m}^{-2}$ ; and (3) the stress-induced martensitic phase suffered EAC and fractured at a stress of 470 MPa, at which the phase transformation was completed. The tensile strength was independent of the amount of hydrogen (corresponding to a cathodic charge

density of more than  $0.025 \text{ MC}\cdot\text{m}^{-2}$ ). Hereafter, the hydrogen absorption treatments were conducted to the specimens in the solutions of various pHs under various constant potentials for a fixed treatment time of 13 ks, and the changes in an amount of hydrogen in each state with a cathodic charge density was realized. The amount of the hydrogen in solid-solution state increased with an increase in the charge density, and logarithm values of both the factors correlated linearly. The amount of the hydrogen was about 100 mass ppm when a charge density reached the critical value of  $0.025 \text{ MC}\cdot\text{m}^{-2}$  for the EAC induction. On the other hand, the amount of the hydrogen in hydride state increased with an increase in the charge density, and logarithm values of both the factors also correlated linearly. The amount of the hydrogen was about 10 mass ppm when a charge density reached the critical value of  $0.025 \text{ MC}\cdot\text{m}^{-2}$ .

#### 4. **Conclusion**

- The specimen involved the hydrogen in solid-solution state but less the one in hydride state by the hydrogen absorption treatment under higher pH and higher potential.
- The specimen involved the hydrogens in solid-solution state and in hydride state by the hydrogen absorption treatment under lower pH and lower potential.
- The amount of the hydrogens in both solid-solution state and hydride state increased with an increase in the charge density, and logarithm values of both the factors correlated linearly.
- Susceptibility to the EAC of the material suddenly increased around a charge density of  $0.025 \text{ MC}\cdot\text{m}^{-2}$ , and the charge density was considered to supply the amounts of hydrogens in hydride state and solid-solution state hydrogen of 10 and 100 mass ppm, respectively.

#### 5. **References**

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