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Effect of aging at room temperature on hydrogen embrittlement behavior of Ni-Ti superelastic alloy immersed in acidic fluoride solution

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Abstract

Background: It is important to investigate the mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloy in acidic fluoride solutions so that the reliability and safety of the alloy as a dental device can be improved. The purpose of the present study is to investigate the effect of aging at room temperature on the hydrogen embrittlement behavior of Ni-Ti superelastic alloy immersed in acidic fluoride solution.

Methods: Specimens were immersed separately in 50 mL of 0.2 % acidulated phosphate fluoride (APF) solution with pH 5.0 at room temperature for 16 h. The hydrogen-charged specimens were aged for various periods at room temperature in air to adjust the hydrogen distribution.

Results: The specimen that was tested immediately after immersion in 0.2 % APF solution fractured near the critical stress for martensitic transformation without martensitic transformation. The tensile strength of the immersed specimen was partially recovered by aging at room temperature for 24 h. In addition, the tensile strength of the specimen immersed in 0.2 % APF solution was completely recovered by aging at room temperature for 240 h.

Conclusions: After aging at room temperature for 24 h, the tensile strength of the immersed specimen was partially recovered. In addition, the tensile strength of the specimen immersed in 0.2 % APF solution was completely recovered by aging at room temperature for 240 h. These results indicate that the mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloys aged at room temperature after immersion in 0.2 % APF solution is dependent on the aging time.

Keywords: Ni-Ti; Hydrogen embrittlement; Corrosion; Aging

Background

Corrosion and fracture of Ni-Ti superelastic alloys used as dental devices in the oral cavity are serious problems (Yokoyama et al. 2001; Wang et al. 2007). Fluoride contained in toothpastes and prophylactic agents has a cariostatic effect, and it has been reported that the corrosion resistance of Ni-Ti alloys is lost in fluoride solutions (Huang 2007; Lee et al. 2009; Li et al. 2007; Mirjalili et al. 2013; Schiff et al. 2002; Schiff et al. 2004). Furthermore, it has been demonstrated that degradation of the mechanical properties of Ti, Ti alloys, and Ni-Ti alloys occurs in acidic and neutral fluoride solutions (Yokoyama et al. 2003a; Yokoyama et al. 2004a; Yokoyama et al. 2004b; Kaneko

et al. 2003; Yokoyama et al. 2005). Ni-Ti alloys absorb substantial amounts of hydrogen from acidic fluoride solutions, thereby causing hydrogen embrittlement of the alloys (Yokoyama et al. 2003a; Yokoyama et al. 2004a). Therefore, it is important to investigate the mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloy in acidic fluoride solutions so that the reliability and safety of the alloy as a dental device can be improved.

The reduction in the tensile strength of Ni-Ti superelastic alloy in 0.2 % acidulated phosphate fluoride (APF) solution with pH 5.0 has been confirmed when the total amount of absorbed hydrogen exceeds 200 mass ppm (Yokoyama et al. 2003a). However, the total amount of hydrogen obtained in that study (Yokoyama et al. 2003a) was the average value of the entire specimen. Thus, the distribution of absorbed hydrogen in Ni-Ti superelastic alloy immersed in 0.2 % APF solution has not yet been

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evaluated quantitatively, although the hydrogen distribution can influence the hydrogen embrittlement behavior of the alloy. It has been suggested that changes in the distribution and state of hydrogen due to aging at room temperature dominate the tensile properties of cathodically hydrogen-charged Ni-Ti superelastic alloy (Yokoyama et al. 2007). In addition, the cathodically hydrogen-charged Ni-Ti superelastic alloy was reported to contain diffusive hydrogen, hydride, hydrogen in a solid solution, and trapped hydrogen (Yokoyama et al. 2007). Aging at room temperature caused diffusive hydrogen to diffuse out, and hydrogen in a solid solution, weakly trapped hydrogen, and hydrogen generated by the dissociation of hydride diffused into the center of the Ni-Ti superelastic alloy. The hydrogen state in the cathodically hydrogen-charged Ni-Ti superelastic alloy varies significantly by aging at room temperature; therefore, the mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloy aged at room temperature has not yet been clarified sufficiently.

The hydrogen states in Ni-Ti superelastic alloy are often reflected in the hydrogen thermal desorption behavior and change with the hydrogen-charging conditions such as the type of solution used for an immersion test (Yokoyama et al. 2003b; Ogawa et al. 2005a; Ogawa et al. 2006; Yokoyama et al. 2012). For immersion of Ni-Ti alloys in 0.2 % APF solution, the presence of diffusive hydrogen was not observed (Yokoyama et al. 2003a; Yokoyama et al. 2004a; Yokoyama et al. 2004b). Therefore, by focusing on hydrogen that diffuses into the center of the Ni-Ti superelastic alloy, the effect of aging at room temperature on hydrogen embrittlement behavior of Ni-Ti superelastic alloy can be evaluated after immersion in 0.2 % APF solution. The purpose of the present study is to investigate the effect of aging at room temperature on the hydrogen embrittlement behavior of Ni-Ti superelastic alloy immersed in acidic fluoride solution.

Methods

Commercial Ni-Ti (Ni, 55 mass%; Ti, balance) superelastic alloy wires with a diameter of 0.50 mm were used. Percent in this paper indicates mass percent, unless otherwise stated. The specimens were cut into 50-mm lengths, polished with 600-grit SiC paper, and then ultrasonically cleaned in acetone for 5 min. The critical stress of martensitic transformation and the tensile strength of the Ni-Ti alloy are 630 and 1453 MPa, respectively.

Specimens were immersed separately in 50 mL of 0.2 % acidulated phosphate fluoride (APF; 0.048 M NaF + 0.018 M H_3PO_4) solution with pH 5.0 at room temperature (25 ± 2 °C) for 16 h. Hydrogen charging of some specimens was conducted by cathodic electrolysis using a 0.9 % NaCl aqueous solution at a current density of 10 A m^{-2} for 6 h at room temperature. The hydrogen-charged specimens were aged for various periods at room temperature in air to adjust the hydrogen distribution.

Tensile tests of the non-immersed and immersed specimens were conducted at room temperature with a strain rate of 8.33 × 10^{-4} s^{-1} within a few minutes after removal of the specimens from the test solution. The gauge length of each specimen was 10 mm. Vickers microhardness tests were performed at room temperature on the non-immersed and immersed specimens from the surface to the center of the cross-section of the wire at 50-μm intervals. Measurements were performed under an applied load of 0.98 N with an applied time of 15 s. Standard deviations of the tensile strength and Vickers microhardness were calculated from the results obtained from five specimens.

The fracture surface of the tensile-tested specimens was observed using scanning electron microscopy (SEM). Corrosion products and hydrides on the surface of the specimens were examined using X-ray diffraction (XRD) analysis with Co Kα radiation (λ = 0.178897 nm; 40 kV and 20 mA) in the 2θ range from 10° to 100°.

Hydrogen thermal desorption analysis (TDA) was performed under vacuum at 10^{-6} Pa using a quadrupole mass spectrometer. Sampling was conducted at 30-s intervals at a constant heating rate of 100 °C h^{-1} up to 600 °C. TDA was started within 30 min after removal of the specimens from the test solution. The total amount of desorbed hydrogen is defined as the integrated peak intensity.

Results

Figure 1 shows the side surfaces of the non-immersed and immersed specimens. Scratches due to SiC paper polishing are observed in the non-immersed specimen (Fig. 1a, b), whereas the scratches are removed by general corrosion in the immersed specimen (Fig. 1c, d). In addition, granular corrosion products were observed on the immersed specimen.

Figure 2 shows hydrogen thermal desorption curves for the non-immersed specimens and those immersed and aged at room temperature after immersion. The amount of desorbed hydrogen in Fig. 2 indicates the mean value of the entire specimen. For the immersed specimen, the main peak of hydrogen desorption is approximately 450 °C and the amount of desorbed hydrogen is approximately 800 mass ppm. The hydrogen desorption behavior of the specimens aged for 24 and 240 h at room temperature is quite similar to that of the immersed specimen.

Figure 3 shows representative stress-strain curves for the non-immersed, immersed, and aged after immersion specimens. The immersed specimen fractures near the critical stress for martensitic transformation without martensitic transformation (Fig. 3b). In contrast, the specimen aged for 24 h at room temperature after immersion fractures after martensitic transformation (Fig. 3c). Furthermore, the tensile strength of the specimen aged for 240 h at room temperature after immersion is larger than that of the non-immersed specimen (Fig. 3a, d).

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Fig. 1 Representative SEM micrographs of side surfaces of **a** non-immersed specimen, **b** magnified view of **a**, **c** specimen immersed in 0.2 % APF solution, and **d** magnified view of **c**
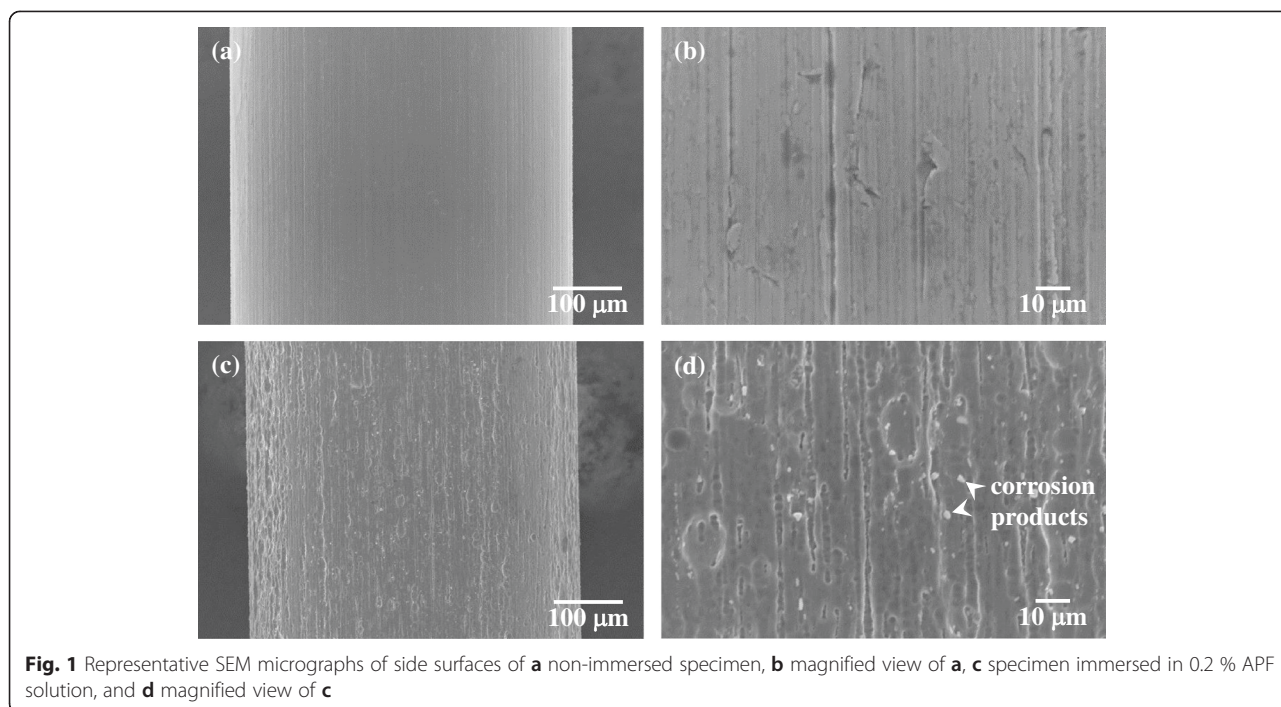
Figure 4 shows that with cathodic hydrogen charging, recovery of the tensile strength of the hydrogen-charged Ni-Ti superelastic alloy by aging at room temperature was partial (Yokoyama et al. 2007). On the other hand, the tensile strength of the specimen immersed in 0.2 % APF solution is completely recovered by aging at room temperature.

Fig. 2 Hydrogen thermal desorption curves for the non-immersed specimen, specimen immersed in 0.2 % APF solution, and specimens aged for 24 and 240 h at room temperature in air after immersion
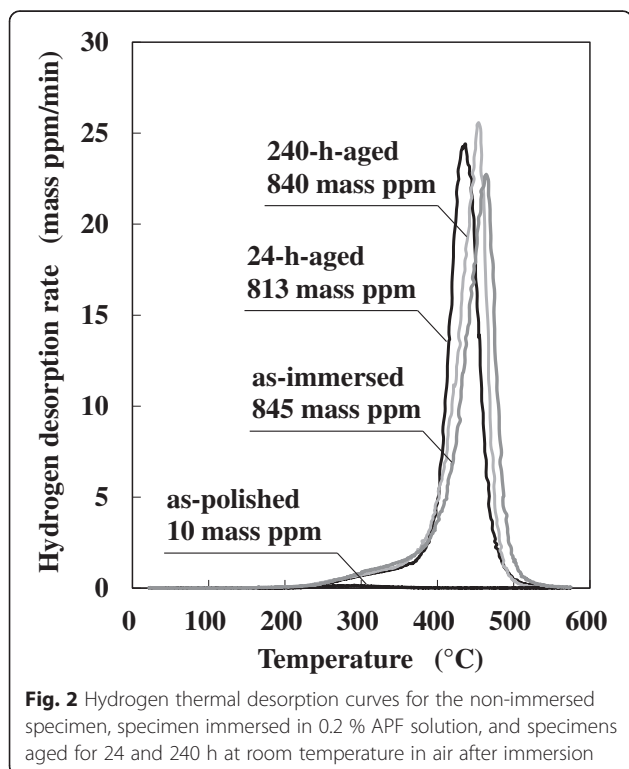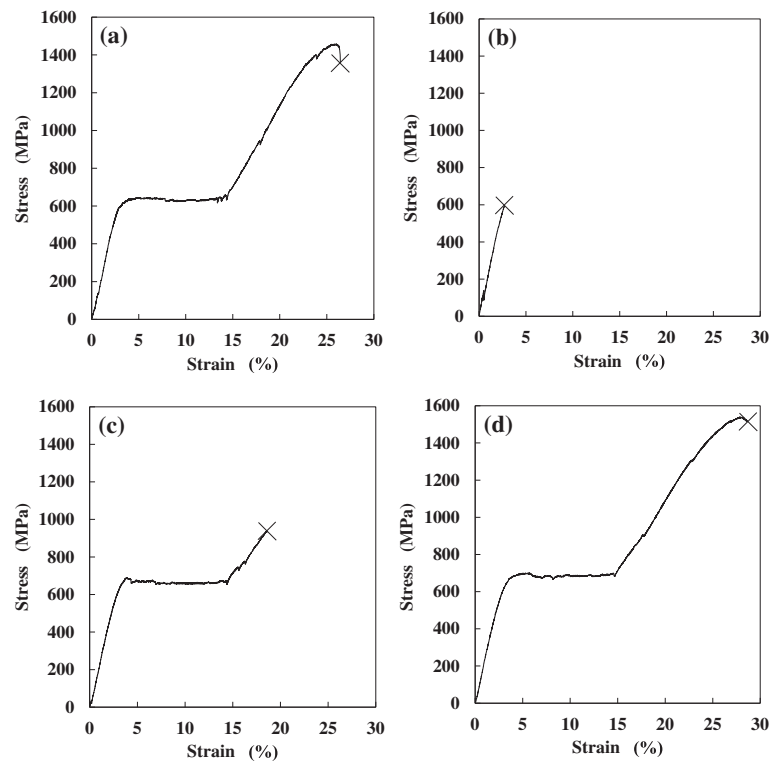
Figure 5 shows fractographs of the non-immersed, immersed, and aged after immersion specimens. The fracture surface of the non-immersed specimen is ductile and characterized by cup-cone morphologies (Fig. 5a). In addition, the fracture surface of the non-immersed specimen consists of the primary and secondary dimples in the central part (Fig. 5b) and shear dimples in the outer part (Fig. 5c). For the immersed specimen, no reduction in area is observed (Fig. 5d), and the central part of the fracture surface is composed of shallow dimples (Fig. 5e), while the outer part is flat (Fig. 5f). For the specimen aged for 24 h at room temperature, although no reduction in area is observed (Fig. 5g), the central part of the fracture surface consists of primary and secondary dimples (Fig. 5h), while the outer part is flat (Fig. 5i). The flat area in the outer part of the fracture surface of the specimen aged for 24 h at room temperature is narrower than that of the immersed specimen. Figure 5j–l shows that the fracture surface morphologies of the specimen aged at room temperature for 240 h are quite similar to those of the non-immersed specimen.

Figure 6 shows the Vickers microhardness along the diameter of the cross section of the hydrogen-charged specimens and the specimens aged for 24 and 240 h after hydrogen charging. For the Ni-Ti alloys, an increase in hardness due to hydrogen absorption has been confirmed (Yokoyama et al. 2003b; Ogawa et al. 2005a). Hence, the distribution of hardness shown in Fig. 6 corresponds to the hydrogen distribution in the cross section of the specimens. The hydrogen concentrations in the vicinity of the surface of the cathodically hydrogen-charged specimen and the specimen

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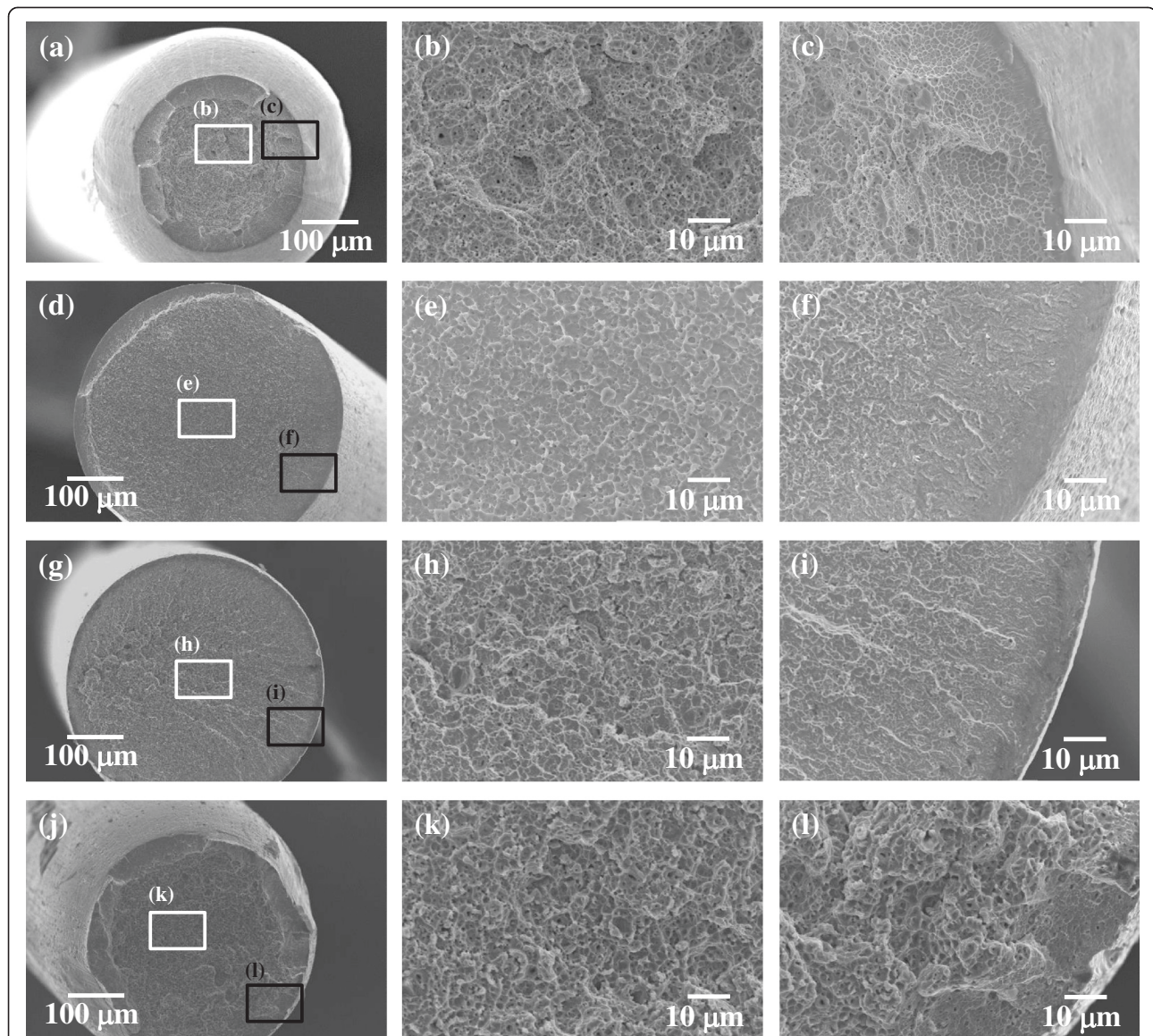
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Fig. 3 Typical stress-strain curves for the **a** non-immersed specimen, **b** specimen immersed in 0.2 % APF solution, and specimens aged for **c** 24 h and **d** 240 h at room temperature in air after immersion
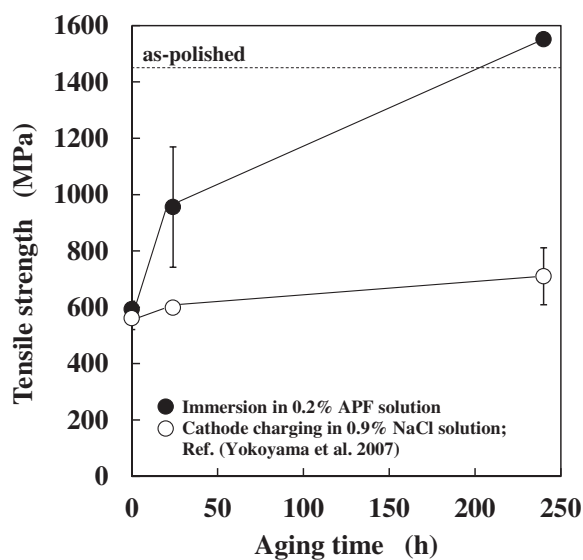
Fig. 4 Tensile strength for specimens immersed in 0.2 % APF solution and cathodically hydrogen-charged specimens as a function of aging time

immersed in 0.2 % APF solution are almost the same, as shown in Fig. 6a. For the specimens aged at room temperature for 24 h, the hydrogen concentration in the surface of the specimen immersed in 0.2 % APF solution is larger than that of the cathodically hydrogen-charged specimen (Fig. 6b). In contrast, for the specimens aged at room temperature for 240 h, the hydrogen concentration in the surface of the specimen immersed in 0.2 % APF solution is smaller than that of the cathodically hydrogen-charged specimen (Fig. 6c).

Figure 7 shows the results for XRD analysis of the side surface of the non-immersed, immersed, and aged after immersion specimens. For the specimens measured immediately or aged at room temperature for 24 h after immersion, peaks of the hydride TiNiH (tetragonal; a = 0.6221 nm, c = 1.2363 nm) (Noréus et al. 1985; Soubeyroux et al. 1993) are confirmed. After aging at room temperature for 240 h after immersion, no hydride peaks are detected, due to hydride dissociation. In all the specimens, no peaks that correspond to corrosion products are confirmed. Figure 8 shows the results for XRD analysis of the side surface of specimens aged at room temperature for 50 h after hydrogen charging. No hydride peaks are detected, due to hydride dissociation in the specimen immersed in 0.2 % APF solution (Fig. 8a), whereas hydride peaks are detected in the cathodically hydrogen-charged specimen (Fig. 8b).

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Fig. 5 SEM micrographs of typical fracture surfaces of the **a** non-immersed specimen, magnified views of **b** center and **c** outer parts in **a**, **d** specimen immersed in 0.2 % APF solution, magnified views of **e** center and **f** outer parts in **d**, **g** specimen aged for 24 h at room temperature in air after immersion, magnified views of **h** center and **i** outer parts in **g**, **j** specimen aged for 240 h at room temperature in air after immersion, and magnified views of **k** center and **l** outer parts in **j**
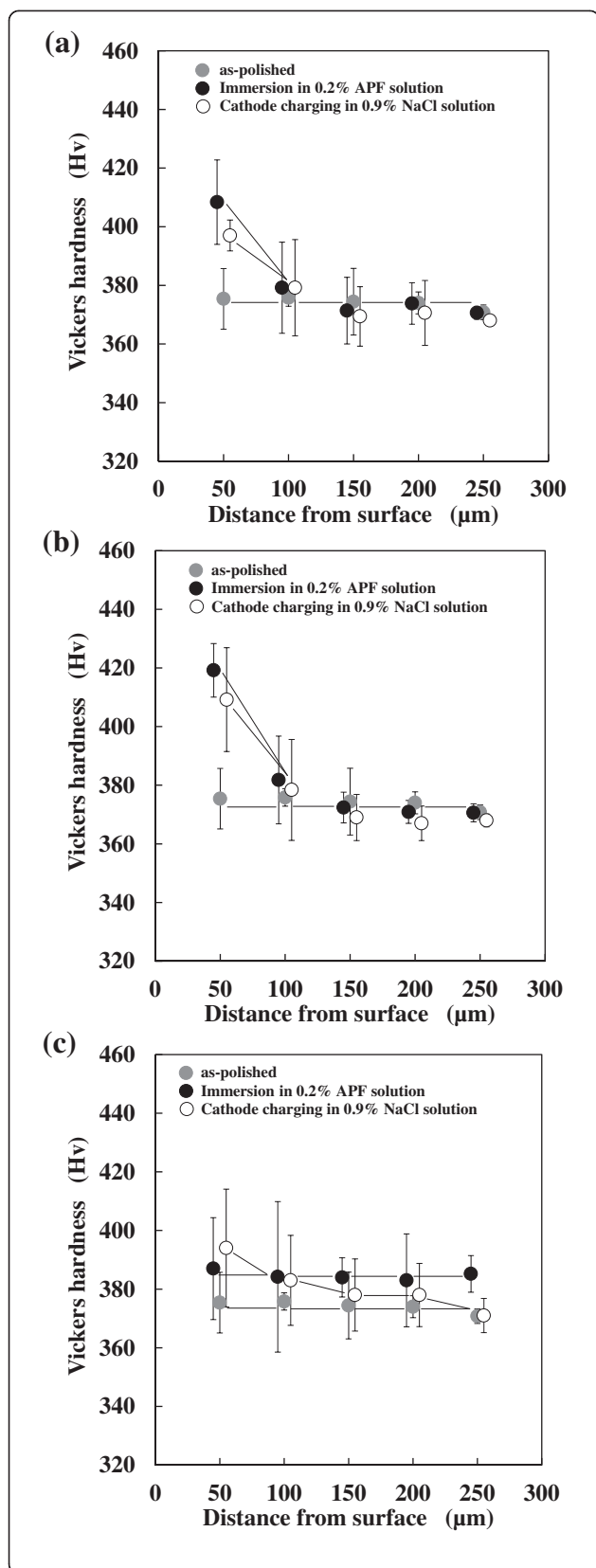
Discussion

One noteworthy finding in the present study is that the tensile strength of the Ni-Ti superelastic alloy immersed in 0.2 % APF solution fully recovered by aging at room temperature in air. In contrast, the recovery of tensile strength for the cathodically hydrogen-charged Ni-Ti superelastic alloy under the same aging conditions was only partial (Yokoyama et al. 2007). Therefore, these results indicate that the mechanism for the recovery of tensile strength by aging at room temperature is dependent on the hydrogen charging conditions.

Here, we discuss the mechanism for the recovery of tensile strength by aging at room temperature for different times.

Aging at room temperature for 24 h

The specimen aged at room temperature for 24 h after immersion in 0.2 % APF solution fractured after the martensitic transformation, which indicates that the tensile strength was partially recovered under this aging condition. In contrast, the tensile strength of the cathodically hydrogen-charged specimen was increased slightly by aging at room temperature for 24 h (Yokoyama et al. 2007). After

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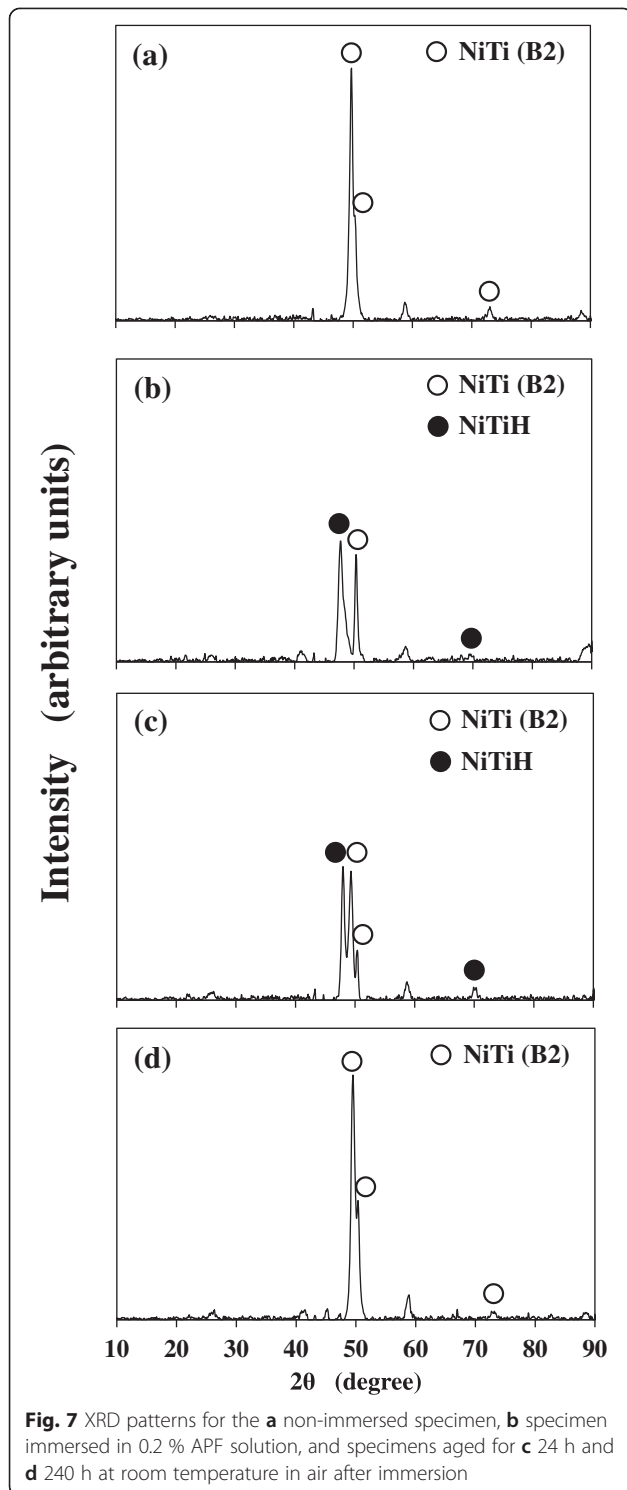
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(a)

(b)

(c)

Fig. 6 Vickers microhardness as a function of distance from the specimen surface **a** immediately after hydrogen charging and for specimens aged for **b** 24 h and **c** 240 h at room temperature in air after hydrogen charging

aging at room temperature for 24 h, the amounts of hydrogen in the cathodically hydrogen-charged specimen and the specimen immersed in 0.2 % APF solution were approximately 450 (Yokoyama et al. 2007) and 800 mass ppm, respectively. Furthermore, the hydrogen concentration in the surface of the cathodically hydrogen-charged specimen was less than that of the specimen immersed in 0.2 % APF solution (Fig. 6b). Therefore, it should be noted that the difference in the tensile strength of both specimens aged at room temperature for 24 h cannot be explained by the amount and distribution of absorbed hydrogen.
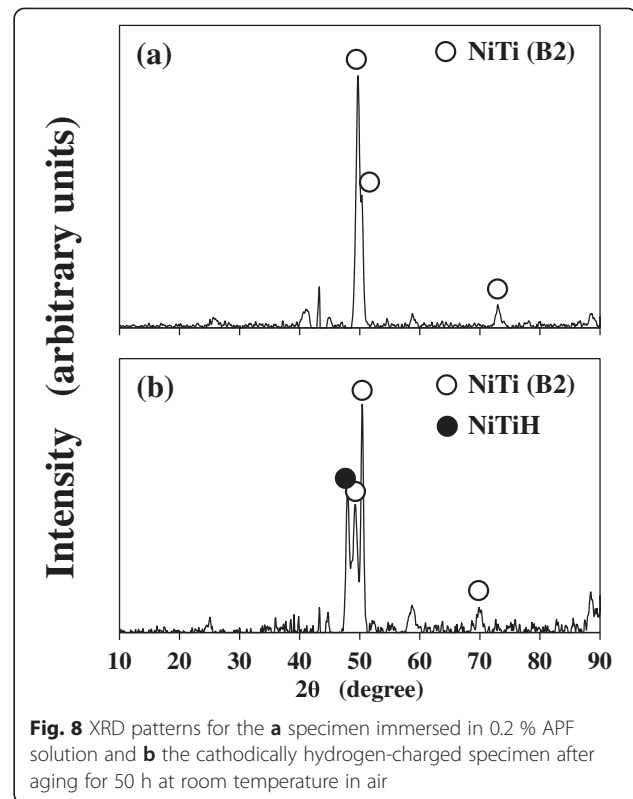
Here, we focus on the hydride (TiNiH) formed in both specimens after aging at room temperature for 24 h. However, after hydrogen charging and aging at room temperature for 50 h, while hydride peaks were also detected in the cathodically hydrogen-charged specimen, no hydride peaks were detected in the specimen immersed in 0.2 % APF solution (Fig. 8). It has also been reported that the hydride formed in Ni-Ti alloy can dissociate by aging at room temperature (Yokoyama et al. 2007; Leu et al. 2002). These results imply that the amount of hydride formed in the specimen by cathodic hydrogen charging is larger than by immersion in 0.2 % APF solution. In addition, after aging at room temperature for 24 h, it is likely that the amount of remaining hydride in the cathodically hydrogen-charged specimen is also larger than that in the specimen immersed in 0.2 % APF solution. Thus, it appears that the dominant factor for the tensile strength of the specimens aged at room temperature for 24 h is the amount of hydride formed in the specimens.

The role of hydride on the hydrogen embrittlement behavior of Ni-Ti alloy has been discussed by several authors (Yokoyama et al. 2007; He et al. 2004; Asaoka et al. 1992). He et al. (2004) suggested that the main reason for the hydrogen embrittlement of Ni-Ti shape memory alloy is a decrease of the intrinsic fracture toughness caused by the hydride. Asaoka et al. (1992) insisted that the main cause for the recovery of the mechanical properties of Ti-Ni shape memory alloy by aging in air after hydrogen charging was a small amount of charged hydrogen that did not form hydrides. These reports indicate that hydride plays an important role in the hydrogen embrittlement behavior of Ni-Ti alloy. Therefore, it can be considered that the tensile strength of the specimens aged at room temperature for 24 h after hydrogen charging in the present work is dependent on the amount of hydride formed in the specimens.

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Fig. 7 XRD patterns for the **a** non-immersed specimen, **b** specimen immersed in 0.2 % APF solution, and specimens aged for **c** 24 h and **d** 240 h at room temperature in air after immersion

Fig. 8 XRD patterns for the **a** specimen immersed in 0.2 % APF solution and **b** the cathodically hydrogen-charged specimen after aging for 50 h at room temperature in air

Aging at room temperature for 240 h

The tensile strength of the specimen immersed in 0.2 % APF solution was completely recovered by aging at room temperature for 240 h, whereas that of the cathodically hydrogen-charged specimen was only partially recovered

by aging at room temperature for 240 h (Yokoyama et al. 2007). In the case of aging at room temperature for 24 h after hydrogen charging, the dominant factor that influences the tensile strength of the specimen is the amount of hydride. However, dissociation of the hydride by aging at room temperature for 240 h was confirmed in both specimens. Therefore, the difference in the tensile strength of both specimens aged at room temperature for 240 h cannot be explained by the amount of hydride.

The amounts of hydrogen in the cathodically hydrogen-charged specimen and the specimen immersed in 0.2 % APF solution after aging at room temperature for 240 h were approximately 450 (Yokoyama et al. 2007) and 800 mass ppm, respectively. Furthermore, the hydrogen concentration in the surface of the cathodically hydrogen-charged specimen was larger than that of the specimen immersed in 0.2 % APF solution. In the viewpoint of hydrogen concentration, there is a gradient of hydrogen concentration in the position from 50 to 100 μm from the surface of the cathodically hydrogen-charged specimen. In contrast, the hydrogen distributed homogeneously in the specimen immersed in 0.2 % APF solution. Hence, it is likely that the hydrogen concentration within 50 μm from the surface of the cathodically hydrogen-charged specimen was much larger than that of the specimen immersed in 0.2 % APF solution. On the other hand, for the aging at room temperature for 24 h, the hydrogen concentration in the vicinity of the surface of the cathodically hydrogen-charged

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specimen was smaller than that of the specimen immersed in 0.2 % APF solution. Therefore, after aging at room temperature for 240 h, the dominant factor that influences the tensile strength of the specimens is probably the hydrogen concentration in the vicinity of the surface of the specimens.

With respect to dissociation of the hydride, the hydride was still observed in the cathodically hydrogen-charged specimen after aging at room temperature for 50 h, whereas hydride dissociation was confirmed in the specimen immersed in 0.2 % APF solution after aging for the same time. After the aging at room temperature for 50 h, hydrogen generated by hydride dissociation can diffuse to the center of the specimen immersed in 0.2 % APF solution, whereas the remaining hydride cannot diffuse to the center of the cathodically hydrogen-charged specimen. Therefore, the difference in the amount of hydride in each specimen appears to be responsible for the difference in the hydrogen concentration in the vicinity of the surface of each specimen. In addition, the hydrogen diffusion obeys Fick's second law (Carslaw and Jaeger 1984) when the hydrogen concentration changes with the aging time. According to Fick's second law, the diffusion rate of hydrogen gradually decreases with the hydrogen concentration in the vicinity of the specimen surface. The hydrogen concentration in the vicinity of the surface of the cathodically hydrogen-charged specimen was less than that of the specimen immersed in 0.2 % APF solution after aging at room temperature for 24 h. Therefore, it is likely that the diffusion rate of hydrogen in the cathodically hydrogen-charged specimen was less than that in the specimen immersed in 0.2 % APF solution after aging at room temperature for 24 h.

The mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloy aged at room temperature after immersion in APF solution is dependent on the aging time. The effect of trap sites of absorbed hydrogen on the hydrogen embrittlement behavior of Ni-Ti superelastic alloy was not sufficiently taken into consideration in the present study. Gamaoun et al. (2011) reported that the hydrogen embrittlement of hydrogen-charged Ni-Ti superelastic alloy was detected after aging at room temperature for 24 h, and this damage may have been due to hydrogen diffusion throughout the entire specimen via weak activation energy trap sites. However, changes in the hydrogen thermal desorption behavior were not confirmed by aging at room temperature in the present study (Fig. 5). The hydrogen thermal desorption behavior reflects the state of hydrogen in metals (Choo and Lee 1982; Takai and Watanuki 2003; Takasaki et al. 1995; Ogawa et al. 2005b); therefore, it is unlikely that the complete recovery of tensile strength by aging at room temperature for 240 h is due to the changes of hydrogen trap sites due to hydrogen diffusion.

Conclusions

The effect of aging at room temperature on the hydrogen embrittlement behavior of Ni-Ti superelastic alloy immersed in 0.2 % APF solution was investigated.

The specimen that was immersed in 0.2 % APF solution fractured near the critical stress for martensitic transformation without martensitic transformation. However, after aging at room temperature for 24 h, the tensile strength of the immersed specimen was partially recovered. After immersion and aging at room temperature for 24 h, the dominant factor that influenced the tensile strength of the specimens was probably the amount of hydride formed in the specimens.

The tensile strength of the specimen immersed in 0.2 % APF solution was completely recovered by aging at room temperature for 240 h, where the dominant factor that influenced the tensile strength of the specimens was probably the hydrogen concentration in the vicinity of the specimen surface. Therefore, the mechanism for the hydrogen embrittlement of Ni-Ti superelastic alloy aged at room temperature after immersion in APF solution was confirmed to be dependent on the aging time.

Authors' contributions
TO drafted the manuscript. TO carried out the experimental work. KM and JS guided the entire research work and made vital discussions. All authors read and approved the final manuscript.

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