Effects of the Hydrogen Absorption Conditions on the Hydrogen Embrittlement Behavior of Ni–Ti Superelastic Alloy

Ken’ichi YOKOYAMA,1)* Akira NAGAOKA2) and Jun’ichi SAKAI2,3)

1) Department of Materials Science and Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu, 804-8550 Japan. E-mail: yokkken@post.matsc.kyutech.ac.jp  2) Department of Materials Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo, 169-8555 Japan.  3) Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo, 169-8555 Japan.

(Received on June 23, 2011; accepted on August 15, 2011)

The present study has investigated whether the hydrogen embrittlement behavior of Ni–Ti superelastic alloy can be changed by modifying the hydrogen absorption conditions. Upon immersion in H2SO4 or H3PO4 solution, the stress plateau due to the stress-induced martensite transformation becomes unclear and forms a gentle slope. In addition, the superelastic strain decreases with increasing immersion time. The peripheral part of the fracture surface of the immersed specimens is flat as usual, whereas the center part of the fracture surface is rough compared with that under other hydrogen absorption conditions reported previously. For the specimens immersed in H3PO4 solution, hydrogen thermal desorption tends to be observed at higher temperatures compared with the specimens immersed in H2SO4 solution. Moreover, for a longer immersion time, a second peak of hydrogen desorption is observed at a high temperature, indicating that the hydrogen states change with the hydrogen absorption conditions. The results of this study suggest that changing the hydrogen embrittlement behavior by modifying the hydrogen absorption conditions may enable the determination of the embrittlement mechanism of the alloy.

KEY WORDS: nitinol; shape memory alloy; martensite; corrosion; hydrogen absorption; hydrogen embrittlement.

1. Introduction

The hydrogen embrittlement of Ni–Ti superelastic alloy is affected by not only the hydrogen content but also the hydrogen states, which include diffusive hydrogen, hydrogen trapped at defects, hydrogen in a solid solution and hydrides.1–9) This is supported by the fact that the hydrogen embrittlement behavior of the alloy is not always the same for the same amount of absorbed hydrogen.10–12) In particular, the martensite transformation is sensitively affected by the hydrogen states.1–12) However, the mechanisms underlying the effects of hydrogen states on the martensite transformation are complicated and remain unclear. The hydrogen states are often reflected in the hydrogen thermal desorption behavior.13–19) Therefore, as a first step, investigating the relationship between the hydrogen desorption behavior and the hydrogen embrittlement behavior is important to elucidate the mechanism of hydrogen embrittlement.

The hydrogen thermal desorption behavior of Ni–Ti superelastic alloy changes with the hydrogen absorption conditions, such as the solution in which it is immersed. Upon immersion in acidulated phosphate fluoride (APF) solutions,10,20) hydrogen desorption is observed as a single peak at approximately 400–500°C. In contrast, upon immersion in methanol containing hydrochloric acid,11) a second peak at approximately 200°C is observed with increasing amount of absorbed hydrogen. In the case of immersion in ethanol solution containing hydrochloric acid,12) the hydrogen desorption behavior is characterized by double peaks at approximately 150 and 350°C. Under cathodic charging in 0.9% NaCl aqueous solution,6,21–23) hydrogen desorption over a wide range of temperatures from room temperature to 400°C is observed. However, the tensile behavior of the alloy, particularly the stress plateau due to the stress-induced martensite transformation and the fractographic features, only slightly depends on these variations of the hydrogen desorption behavior, although the critical stress for the martensite transformation increases or decreases.10–12) Hence, it is difficult to elucidate the relationship between hydrogen desorption behavior and hydrogen embrittlement behavior. If the tensile behavior including the stress-induced martensite transformation can be changed by modifying the hydrogen absorption conditions, i.e., hydrogen states, it will be a key to understanding the mechanism of hydrogen embrittlement.

The objective of the present study is to find hydrogen absorption conditions under which the hydrogen embrittlement behavior of Ni–Ti superelastic alloy becomes different from those in previous studies.6,10–12,21–23) Most previous studies on hydrogen embrittlement were conducted under similar conditions of hydrogen charging. It is desirable that hydrogen embrittlement is studied under the same hydrogen absorption conditions, because the obtained results can be compared among researchers. However, analysis under var-
ious hydrogen absorption conditions will be essential for determining the mechanism of hydrogen embrittlement. In the future, studies involving various hydrogen absorption conditions will be needed.

2. Experimental Procedures

Commercially available Ni–Ti (Ni: 55 mass%, Ti: balance) superelastic alloy wires with a diameter of 0.50 mm were used. The specimens were carefully finished with 600-grit SiC paper and ultrasonically cleaned with acetone for 5 min. The mechanical properties of the specimens are listed in Table 1. From the stress-strain curves obtained by a tensile test, the critical stress for the martensite transformation and the tensile strength were 633 and 1601 MPa, respectively. The tensile-test data were measured at room temperature (25 ± 2°C) using an Instron machine at a strain rate of 8.33 × 10⁻⁴/s. The gauge length of specimen was 10 mm. The standard deviation was calculated from the results of at least five specimens.

The specimens were immersed separately in 50 ml of 3.25 M H₂SO₄ or 5.0 M H₃PO₄ solution at 60°C for various periods. These concentrations and the temperature of the solution were carefully predetermined so that the same amount of hydrogen was absorbed in the same immersion time. At higher concentrations or temperatures, the corrosion loss was very large, whereas at lower concentrations or temperatures, the hydrogen absorption rate was too low. Tensile or cyclic tensile tests on the immersed specimens were carried out within a few minutes after removing the specimens from the test solutions. The fracture surface was examined by scanning electron microscopy (SEM).

Hydrogen thermal desorption analysis (TDA) was performed in vacuum at 10⁻⁶ Pa using a quadrupole mass spectrometer (ULVAC, Kanagawa, Japan). Sampling was conducted at 30 s intervals at a constant heating rate of 100°C/h up to 600°C. TDA was started 30 min after hydrogen charging. The amount of desorbed hydrogen was defined as the integrated peak intensity.

The side surface of specimens immersed in the solutions was observed by SEM. Corrosion products or hydrides on the surface of the specimens were examined 60 min after hydrogen charging and were carried out on a transverse cross section from the periphery to the center of the wire at 0.05 mm intervals. Measurements were performed under an applied load of 0.98 N for 15 s. The average value of hardness and standard deviation were calculated from the results of at least eight indentations.

3. Results

Figures 1(a) and 1(b) show tensile stress-strain curves of the specimens immersed in H₂SO₄ and H₃PO₄ solutions for various periods, respectively. Upon immersion, the critical stress for the martensite transformation often increased, particularly in the case of specimens immersed in H₃PO₄ solution. In the case of immersion for more than 3 h, the alloy fractured without necking. Note that the behavior of the stress plateau due to the stress-induced martensite transformation changed with increasing immersion time. For instance, the start and finish of the martensite transformation became unclear and the stress plateau became a gentle slope. Moreover, the superelastic strain decreased with immersion time.

Figures 2(a) and 2(b) show cyclic tensile stress-strain curves of the specimens immersed in H₂SO₄ and H₃PO₄ solutions for various periods, respectively. With increasing immersion time, the slope of the stress plateau became more distinct, and with increasing number of cycles, the slope became steep. The number of cycles to fracture decreased with increasing immersion time irrespective of the solution type. In the case of immersion time for 24 h, the specimens fractured before the cyclic test. The tensile and cyclic stress-strain curves are not necessarily the same for the specimens immersed in H₂SO₄ and H₃PO₄ solutions for the same immersion time. For example, the decrease in the superelastic strain of the specimen immersed
in H₂SO₄ solution tended to be larger than that for the specimen immersed in H₃PO₄ solution.

Representative fractographs of the non-immersed specimen and specimens immersed in H₂SO₄ and H₃PO₄ solutions for various periods obtained by the tensile test are shown in Fig. 3. The fracture surface of the non-immersed specimen was ductile and characterized by double cup morphologies, as shown in Fig. 3(a); it consisted of deep dimples. The reduction in area was approximately 33% (Table 1). For specimens immersed in solutions for more than 3 h, no reduction in area was observed, as shown in Figs. 3(b)–3(g). This is consistent with the stress-strain curves (Fig. 1). There was not much difference between the characteristics of the fracture surface of specimens immersed in H₂SO₄ solution and that of specimens immersed in H₃PO₄ solution, although the characteristics were not necessarily the same. For longer immersion times, the outer part of the fracture surface was flat, whereas the center part was composed of shallow dimples or quasi-cleavage. The width of the flat area of the fracture surface increased with immersion time. For example, for 18 and 24 h immersion, the maximum widths of the flat area were approximately 30–40 and 60–70 μm, respectively. It should be noted that the center part of the fracture surface was rougher than those for specimens immersed in other solutions, such as APF solutions and alcohol solutions reported previously. The roughness of the center part decreased with increasing immersion time.

Figures 4(a) and 4(b) show hydrogen thermal desorption curves for the specimens immersed in H₂SO₄ and H₃PO₄ solutions for various periods, respectively. The hydrogen desorption behavior of the specimens immersed in H₂SO₄ solution was different from that of specimens immersed in H₃PO₄ solution. The hydrogen thermal desorption of the specimens immersed in H₂SO₄ solution was observed from 300 to 550°C, and the primary peak temperature was approximately 450°C. In contrast, for the specimens immersed in H₃PO₄ solution for a longer time, the shoulder of hydrogen desorption was also observed at high tempera-
tures, although the primary peak temperature was almost the same as that for specimens immersed in H$_2$SO$_4$ solution. Moreover, upon immersion in H$_3$PO$_4$ solution for 24 h, a second peak of hydrogen desorption was clearly observed at 350°C. The wide range of desorption temperature indicates the existence of a variety of hydrogen states.

The progress of hydrogen entering the alloy was denoted by an increase in the total amount of desorbed hydrogen, defined as the integrated peak intensity, relative to the immersion time. The total amount of hydrogen desorbed from room temperature up to 600°C is shown as a function of immersion time in Fig. 5. The amount of hydrogen absorbed during immersion can be calculated by subtracting the amount of hydrogen desorbed from a non-immersed specimen, that is, predissolved hydrogen content (3 mass ppm), from the amount of hydrogen desorbed from an immersed specimen. The amount of desorbed hydrogen, that is, the amount of hydrogen absorbed during immersion, increased with immersion time, although the hydrogen absorption rate in the early stage of immersion was slightly higher than that in the later stage of immersion. The amounts of absorbed hydrogen for the specimens immersed in H$_2$SO$_4$ solution were almost the same as those of the specimens immersed in H$_3$PO$_4$ solution for the same immersion time because of the predetermined concentration and temperature of the solutions. For example, the amounts of absorbed hydrogen in the case of 18 and 24 h immersion were approximately 950 and 1200 mass ppm, respectively.

Scratches due to SiC paper polishing were observed on the side surface of the non-immersed specimen, as shown in the SEM micrographs in Figs. 6(a) and 6(b). The specimens immersed in H$_2$SO$_4$ (Figs. 6(c) and 6(d)) and H$_3$PO$_4$ (Figs. 6(e) and 6(f)) solutions for 18 h exhibited general corrosion, but the corrosion morphologies were not necessarily the same. No corrosion products were observed on the surface of the immersed specimens irrespective of the solution type and immersion time.

Figure 7 shows representative results of X-ray diffraction (XRD) analysis of the side surface of the non-immersed specimen and specimens immersed in H$_2$SO$_4$ and H$_3$PO$_4$ solutions for 18 h. For the immersed specimens, peaks of the hydride TiNiH (tetragonal; a = 0.6221 nm, c = 1.2363 nm)$^{24,25}$ were confirmed. These hydride peaks were confirmed for specimens immersed for the other immersion times. The peaks of NiTi (B2) shifted to a slightly lower angle upon immersion, implying an increase in the lattice constants resulting from the absorption of hydrogen atoms at the interstitial sites.$^{26}$ Furthermore, an unknown peak near the peak of (110)$_{\text{NiTi}}$ (B2) was detected for specimens immersed in the solutions. It is unlikely that this peak is
related to corrosion products on the surface of the specimens on the basis of the results of SEM observation.

Vickers microhardness values along a diameter of a cross section of the non-immersed specimen and specimens immersed in H2SO4 and H3PO4 solutions for 18 h are shown in Fig. 8. For the immersed specimens, the hardness slightly increased toward the center part of the specimen regardless of the solution type. This increase is probably caused by the presence of hydrogen including solid-solution hydrogen, although such an increase is not always related to hydride formation.27)

4. Discussion

One noteworthy finding in the present study is that the stress plateau due to the stress-induced martensite transformation becomes unclear and forms a gentle and short slope depending on the hydrogen absorption conditions. Since this finding is unprecedented, the detailed mechanisms of the martensite transformation upon changing the hydrogen absorption conditions remain unclear. Nevertheless, some clues can be obtained by a comparison with previously reported results, and such a comparison will be a key to understanding the mechanism of hydrogen embrittlement.

In the case of a cyclic deformation test without the hydrogen charging of Ni–Ti superelastic alloy reported by Miyazaki et al.,28) the stress plateau due to the stress-induced martensite transformation often became a gentle slope after 10 cycles. The internal stress formed by slip deformations is considered to assist the formation of stress-induced martensite, thereby resulting in the gentle slope. Under our previous hydrogen absorption conditions,10–12,29,30) the stress plateau did not become unclear, inclined and short, although the critical stress for the martensite transformation did vary. However, in the present study, the slope was distinct after only a few cycles or even a single cycle in the case of a longer immersion time. This result suggests that the hydrogen absorbed in H2SO4 and H3PO4 solutions readily induces internal stress. The decrease in superelastic strain also appears to be supported by the generation of internal stress.28) Asaoka et al.4) suggested that a small amount of hydrogen charged cathodically in NaOH solution at room temperature for 1 h interacts with dislocations, leading to the local formation of stress-induced martensite. The hydrogen absorbed in H2SO4 and H3PO4 solutions probably forms special hydrogen states. In fact, as shown in Fig. 4, the hydrogen desorption behavior was unprecedented, particularly for specimens immersed in H3PO4 solution. These special hydrogen states may assist the stress-induced martensite transformation.

Another origin of the gentle slope of the stress plateau is considered to be a change in the hydrogen distribution in the specimens. The temperature at which hydrogen absorption was investigated was 60°C in the present study, whereas it was 25 or 37°C in our previous studies.10–12,29,30) The hydrogen diffusion rate usually increases with temperature. Moreover, the immersion time, i.e., diffusion time, was not always the same among the various experimental results. Hence, the hydrogen distribution in the specimens in the present study may not necessarily correspond to those in the previous studies.10–12,29,30) even for the same amount of absorbed hydrogen. However, in our previous studies,29,30) no effects of the hydrogen distribution on the slope of the stress plateau were confirmed for specimens subjected to homogenization by aging at room temperature after hydrogen charging. In addition, upon immersion at 37°C for a longer time (more than 120 h),12) a gentle slope was not observed. Therefore, it is likely that a change in the hydrogen distribution is not necessarily essential to change the
stress-induced martensite transformation behavior, although it was required under the present hydrogen absorption conditions.

A change in the hydrogen absorption temperature from 25 to 60°C does not greatly affect the hydrogen desorption behavior under cathodic hydrogen charging in NaCl solution.\(^{31}\) In the case of different desorption behavior, we can conclude the existence of different hydrogen states. However, in the case of similar hydrogen desorption behavior, we must consider that the hydrogen states are not always the same, because the hydrogen desorption behavior does not always reflect all hydrogen states.\(^{29}\) Hence, it appears that an effect of the hydrogen absorption temperature on the hydrogen states cannot altogether be ruled out at present. For example, hydrogen absorbed at a high temperature may be trapped at different sites.

When the amount of absorbed hydrogen exceeds approximately 50–200 mass ppm, Ni–Ti superelastic alloy readily fractures in association with the stress-induced martensite transformation from our previous studies.\(^{10–12,29,30}\) However, fractures in association with the stress-induced martensite transformation appears to be affected by the hydrogen absorption conditions.

For the specimens immersed in H\(_3\)PO\(_4\) solution for a longer immersion time, hydrogen desorption was observed at higher temperatures (550 to 600°C) than those of specimens immersed in H\(_2\)SO\(_4\) solution or in other solutions reported previously.\(^{6,10–12,20–23,29,30}\) Moreover, a second peak was observed at a high temperature. Upon immersion in 1 M HCl solution at 60°C,\(^{34}\) similar hydrogen desorption is often observed to that at a high temperature, although a second peak of hydrogen desorption is not observed. The hydrogen desorption at high temperatures is considered to be associated with the stable states of hydrogen, such as hydrogen strongly trapped in defects. For high-strength steels,\(^{18,19}\) hydrogen desorption at low temperatures, i.e., diffusive hydrogen, is considered to greatly affect hydrogen embrittlement behavior compared with that at high temperatures. The present result for specimens immersed in H\(_2\)SO\(_4\) solution indicates that the hydrogen desorbed at high temperatures does not always directly result in the obscurity, gentle slope and shortening of the stress plateau due to the stress-induced martensite transformation. However, the role of hydrogen desorbed at high temperatures should also be considered for Ni–Ti superelastic alloy because of the following reasons.

The shift in hydrogen desorption to high temperatures is
probably explained by the formation of defects accompanied by hydrogen absorption. Birnbaum et al.35) reported that hydrogen enters aluminum accompanied by the formation of vacancies at the surface. In general, however, the vacancy is considered to be annihilated at a low temperature, although it plays an important role in hydrogen embrittlement.8,19,36–38) Hence, it is unlikely that the hydrogen trapped in a vacancy is directly related to the hydrogen desorption at high temperatures. Upon heating a previously immersed specimen to perform TDA, it is likely that the hydrogen diffuses and is strongly trapped in other defects, causing it to become stable. Since the number of defects increases with the amount of absorbed hydrogen, hydrogen desorption at high temperatures may increase with immersion time. For commercial pure titanium formed hydrde by the hydrogen absorption, we have proposed the above mechanism.39) In the present study, the hydride identified by XRD (Fig. 7) is not directly related to the hydrogen desorption at high temperatures, because for the hydrde formed in Ni–Ti superelastic alloy, dissociation occurs even at room temperature.29,30,40) However, hydrde formation and dissociation appear to be induced by stable defects in the alloy. Because these defects are considered to be only slightly annihilated, they may be indirectly connected with the shift of desorption. Regarding the effects of the hydrde on hydrogen embrittlement, we have recently elucidated that the dynamic change in hydrogen states accompanied by the stress-induced martensite transformation, rather than the hydrde, plays an important role in hydrogen embrittlement behavior.27) On the other hand, we have demonstrated that the shift of hydrogen desorption to a high temperature does not result from only a change in the hydrogen distribution in the specimens.29,30) Moreover, the corrosion products covering the surface of a beta titanium alloy sometimes shift hydrogen desorption to a high temperature.39) Presumably because they prevent the outdiffusion of hydrogen. In the present study, no corrosion products were observed on the surface of the specimens, as shown in Figs. 6 and 7; hence, the shift of hydrogen desorption is caused by a difference in hydrogen states. The hydrogen desorption behavior of Ni–Ti superelastic alloy should be analyzed carefully by comparison with those of steels.

From the above discussion, complex factors rather than a single factor among the hydrogen absorption conditions probably play an important role in changing the martensite transformation behavior, and it is likely that the primary origin of the difference in hydrogen desorption behavior is a difference in hydrogen absorption behavior. The hydrogen absorption behavior is closely related to the corrosion behavior. In fact, the side surface of the specimens immersed in H2SO4 and H3PO4 solutions are not necessarily absorbed in solution.39) Hence, it is unlikely that the hydrogen desorption behavior of Ni–Ti superelastic alloy, changing the type of solution seems to be more effective than changing the solution temperature, concentration, pH, charging current density or applied potential. Changing the type of solution possibly leads to a greater change in corrosion behavior.

The manufacturer’s serial number for the specimens used in the present study was different from those of specimens in our previous studies.6,10–12,21–23,29,30) It appears that metallurgical factors of Ni–Ti superelastic alloy, such as the microstructure, chemical composition, phase stability and strength, often affect hydrogen embrittlement behavior. In fact, we have revealed that the hydrogen desorption behavior of the alloy is affected by the heat treatment before hydrogen charging.30) Nevertheless, before carrying out the experiment in this study, we confirmed that the hydrogen embrittlement behavior of the present specimen was similar to those of previous specimens under the same hydrogen absorption conditions. Thus, the present findings are essentially due to changes in the hydrogen absorption conditions. A detailed discussion on the effects of metallurgical factors on hydrogen embrittlement behavior is beyond the scope of the present study but is an interesting topic from the standpoint of materials science.

5. Conclusions

We have demonstrated that the hydrogen embrittlement behavior of Ni–Ti superelastic alloy, such as the stress-induced martensite transformation behavior and fractographic features, can be changed markedly by modifying the hydrogen absorption conditions. Upon immersion in H2SO4 or H3PO4 solution, the stress plateau due to the stress-induced martensite transformation of the alloy becomes short and unclear, forming a gentle slope, and the center part of the fracture surface often becomes rough. The hydrogen thermal desorption shifts to a high temperature. For specimens immersed in H3PO4 solution, a second peak of hydrogen desorption is observed at high temperatures. Possible mechanisms have been discussed but further studies are needed to fully understand these phenomena. A study on the effects of hydrogen absorption conditions, particularly the type of solution used for immersion, on the hydrogen embrittlement behavior will probably contribute to elucidating the mechanism of hydrogen embrittlement of many alloys. Therefore, data on hydrogen embrittlement behavior under various hydrogen absorption conditions should be accumulated.

Acknowledgments

This study was supported in part by a Grant-in-Aid for Young Scientists (B) (20760473) and a Grant-in-Aid for Scientific Research (C) (18560702) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

10) K. Yokoyama, K. Kaneko, K. Moriyama, K. Asaoka, J. Sakai and M.