Role of Dynamic Interactions between Hydrogen and Strain-induced Martensite Transformation in Hydrogen Embrittlement of Type 304 Stainless Steel

Yuma YOSHIOKA,1) Ken’ichi YOKOYAMA1)* 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.
2) Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo, 169-8555 Japan.
3) Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, 2-8-26, Nishiwaseda, Shinjuku-ku, Tokyo, 169-0051 Japan.

(Received on March 6, 2015; accepted on April 30, 2015)

The role of the dynamic interactions between hydrogen and the strain-induced martensite transformation in the hydrogen embrittlement of type 304 stainless steel has been investigated by fractographic observations after a modified hydrogen charging. The modified charging is cathodically conducted in 3.5% NaCl solution at 80°C under aerated conditions while preventing the dissolution of chlorine and oxygen gases evolving on the platinum counter electrode, thus increasing the amount of hydrogen thermally desorbed at low temperatures. Upon tensile testing at 160°C, plastic deformation of the austenite phase in the stainless steel occurs, but no strain-induced martensite transformation occurs. The fracture surface of the hydrogen-charged specimen exhibits the double-cup mode and consists of microscopic shallow dimples. Upon tensile testing at 25°C, the martensite transformation and plastic deformation both occur and are intricately related; a brittle area is observed on the outer part of the fracture surface that exhibits both transgranular and intergranular fracture. At −196°C, the martensite transformation increases, but the amount of plastic deformation decreases and the amount of intergranular fracture increases. It is found that, when the martensite transformation occurs before hydrogen charging, the amount of intergranular fracture decreases. Moreover, when charged hydrogen is trapped in defects in the austenite phase, the amount of intergranular fracture also decreases. The present study indicates that the dynamic interactions between hydrogen and the martensite transformation play an important role in the hydrogen embrittlement of type 304 stainless steel.

KEY WORDS: stainless steel; martensite; hydrogen embrittlement; fractography.

1. Introduction

Hydrogen embrittlement is related to the interactions between hydrogen and dynamic changes in the crystalline structure such as plastic deformation.1) When a metastable austenitic stainless steel such as type 304 is subjected to tensile deformation below the martensitic deformation temperature (a hundred and several tens °C), a strain-induced martensite transformation and plastic deformation of the austenite and/or martensite phases occur, which are intricately related.2,3) However, the hydrogen embrittlement of stainless steel has been mainly studied by investigating strain localization4–6) or the embrittlement of the martensite phase itself.7–9) The dynamic interactions between hydrogen and the martensite transformation should also be examined. Recently, Zhang et al.10,11) have reported that the dynamic martensite formed during deformation contribute to hydrogen embrittlement more than prior martensite formed by prestraining.

We have demonstrated that the interactions between hydrogen and the stress-induced martensite transformation markedly affect the hydrogen embrittlement behavior for Ni–Ti superelastic alloy.12–15) For this alloy, the martensite transformation occurs with almost no plastic deformation. The hydrogen solubility and diffusion constant in the martensite phase (B19’) are larger than those in the parent phase (B2).15,16) Hence, during the martensite transformation, hydrogen readily moves from sites in the parent phase to sites in the martensite phase or to trap sites such as vacancies and dislocations, although many defects are induced by the interactions between hydrogen and the martensite transformation. The state of the hydrogen that interacts directly with the martensite transformation is probably an unstable state such as diffusible hydrogen or hydrogen in a solid solution. When hydrogen is trapped in defects, the interactions between hydrogen and the martensite transformation decrease.15)

For metastable austenitic stainless steel, the strain-induced martensite transformation is accompanied by plastic...
deformation of the austenite phase, making it difficult to separate the effects of the martensite transformation and the deformation process. In addition, the solubility of hydrogen in the martensite phase is less than that in the austenite phase,\(^{10,17}\) although hydrogen diffusion in the martensite phase is faster than that in the austenite phase.\(^{18,19}\) Accordingly, during the martensite transformation, hydrogen appears to preferentially move from sites in the austenite phase such as octahedral site to trap sites such as dislocations and boundaries rather than to sites in the martensite phase such as tetragonal site. In this case, a large number of defects may be induced by interactions between hydrogen and the martensite transformation. However, an experimental method to demonstrate the role of the interactions between hydrogen and the martensite transformation in the hydrogen embrittlement of metastable austenitic stainless steel has not been established.

Fractography is an effective method for investigating the hydrogen embrittlement mechanism. Since the fracture surface reflects fracture processes including the plastic deformation and/or martensite transformation, an evidence of the interactions between hydrogen and the martensite transformation is presumably observed as the variation of the fracture surface. For type 304 stainless steel charged with hydrogen, however, the surface fractured under a tensile test generally exhibits dimples or transgranular fracture including flat facets irrespective of the tensile test conditions such as the test temperature.\(^{20}\) It has been difficult to investigate hydrogen embrittlement from the variation of the fracture surface obtained by the conventional hydrogen charging. To clarify the variation of the fracture surface induced by the interactions between hydrogen and the martensite transformation, the modification of hydrogen charging is required. In fact, for Ni–Ti superelastic alloy, upon modifying the conditions of hydrogen absorption, hydrogen states often change, thereby affecting the martensite transformation.\(^{21–28}\) If the modification of hydrogen charging can clarify the relationship between the fracture surface and the martensite transformation, it may help reveal the hydrogen embrittlement mechanisms of stainless steel.

The purpose of the present study is to investigate the role of dynamic interactions between hydrogen and the strain-induced martensite transformation in the hydrogen embrittlement for type 304 stainless steel by the observation of fracture surfaces, using a modified method of cathodic hydrogen charging.

### 2. Experimental Procedures

#### 2.1. Materials

A commercially available type 304 metastable austenitic stainless steel wire with a diameter of 0.50 mm was used. The side surfaces of specimens were finished with 600-grit SiC paper and ultrasonically cleaned with acetone for 5 min. The chemical composition and mechanical properties of the specimens at room temperature (25±2°C) are shown in Tables 1 and 2, respectively. Tensile tests were conducted using an Instron-type machine. The gauge length of the specimens was 10 mm. The strain was calculated from the elongation (displacement of cross head) and initial gauge length. The strain rate in all the tensile tests in the present study was 8.33×10\(^{-4}\) s\(^{-1}\) unless otherwise stated. The mean value and standard deviation were calculated from the results of at least four specimens.

An optical micrograph of the side surface of a specimen is shown in Fig. 1. The side surface of the specimen was mechanically polished and etched with aqua regia (mixed solution of HCl and HNO\(_3\)). The grain size was approximately 17 μm and the grains were polygonal in shape. Figure 2 shows the X-ray diffraction (XRD) pattern obtained from the side surface of a specimen examined using an X-ray diffractometer operated at 45 kV and 200 mA with Cu K\(_\alpha\) radiation of wavelength λ=0.1541862 nm. Only peaks corresponding to the austenite phase were detected.

#### 2.2. Hydrogen Charging Conditions

Hydrogen was cathodically charged in 200 ml of 3.5% NaCl aqueous solution at 80°C with a current density of 100 A/m\(^2\) for 96 h under aerated conditions. A platinum

---

#### Table 1. Chemical composition of type 304 stainless steel (mass%).

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.33</td>
<td>1.03</td>
<td>0.033</td>
<td>0.005</td>
<td>9.06</td>
<td>18.06</td>
<td>bal.</td>
</tr>
</tbody>
</table>

#### Table 2. Mechanical properties of type 304 stainless steel at 25°C.

<table>
<thead>
<tr>
<th>0.2% proof strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Reduction in area (%)</th>
<th>Vickers hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>247±9</td>
<td>680±3</td>
<td>88±1</td>
<td>169±2</td>
</tr>
</tbody>
</table>
wire was used as the counter electrode. The counter electrode was enclosed with a glass tube with a porous bottom to prevent the dissolution of chlorine and oxygen gases, which evolved on the counter electrode, into the solution. This method is referred to as modified charging in the present study. During modified charging, the pH of the solution increased from 5.3 to 12.2, as shown in Fig. 3(a). In contrast, during hydrogen charging without enclosing the counter electrode with the glass tube, that is, conventional hydrogen charging, the pH of the solution increased from 5.3 to 8.6. The potential during hydrogen charging with the glass tube rapidly shifted in the less noble direction and then gradually shifted to $-1.55 \text{ V vs. SCE}$, as shown in Fig. 3(b). The potential during hydrogen charging without the glass tube rapidly shifted to $-1.45 \text{ V vs. SCE}$ and then stabilized.

2.3. Hydrogen Thermal Desorption Analysis

Hydrogen thermal desorption analysis (TDA) was conducted using a gas chromatograph at a constant heating rate of $100^\circ \text{C/h}$ from room temperature to $600^\circ \text{C}$, and the sample gas was analyzed at 5 min intervals using Ar as the carrier gas. TDA was started 15 min after the end of hydrogen charging. The amount of desorbed hydrogen was defined as the integrated peak intensity. The amount of desorbed hydrogen for the noncharged specimen was less than detection limit.

2.4. Tensile Tests after Hydrogen Charging

Tensile tests were performed at 160, 100, 25 and $-196^\circ \text{C}$ within 15 min after the end of hydrogen charging. The amount of hydrogen desorbed during the tensile tests was negligible. The fracture surfaces were examined by scanning electron microscopy (SEM).

2.5. Effects of Prestraining on Hydrogen Embrittlement Behavior

To investigate the effects of the martensite phase and/or defects such as vacancies and dislocations on the fracture surface, three specimens were prepared by tensile deformation under different prestrain conditions. A specimen subjected to 10% prestrain at $-196^\circ \text{C}$ was prepared to introduce a large amount of the martensite phase, a specimen subjected to 30% prestrain at $160^\circ \text{C}$ was prepared to introduce defects without the martensite phase, and a specimen subjected to 70% prestrain at $25^\circ \text{C}$ was prepared to introduce both the martensite phase and defects. The prestrained specimens were charged with hydrogen in the manner described above, i.e., modified charging, and then tensile tests were performed at $-196^\circ \text{C}$.

3. Results and Discussion

3.1. Effects of Tensile Test Temperature on Hydrogen Embrittlement Behavior

Figure 4 shows the hydrogen thermal desorption curves for the specimens subjected to modified charging. For comparison, this figure also includes the curve for the specimen subjected to conventional charging. The amount of desorbed hydrogen (absorbed hydrogen) for the modified charging was $324 \pm 24 \text{ mass ppm (n=3)}$; the amount of scatter was at most 30–50 mass ppm. The amount of desorbed hydrogen for the modified charging was 25% larger than that for the conventional charging. Hydrogen desorption was observed from room temperature to approximately $400^\circ \text{C}$. The desorption peak temperature was approximately $200^\circ \text{C}$. It should be emphasized that, for the modified charging, the amount of hydrogen desorbed at low temperatures (room temperature to $200^\circ \text{C}$) was greater than that for the conventional charging, although at high temperatures ($250^\circ \text{C}$ to $400^\circ \text{C}$) the amount of desorbed hydrogen was the same. The hydrogen desorbed at low temperatures is expected to be an unstable state of hydrogen such as diffusible hydrogen, although details of the hydrogen states cannot necessarily be explained by only a simple comparison of thermal desorption behavior. The amount of unstable states of hydrogen

Fig. 3. Changes in (a) pH of solution and (b) potential of specimen during modified and conventional charging.

Fig. 4. Hydrogen thermal desorption curves for specimens subjected to modified and conventional charging. The numerical values are the amounts of desorbed hydrogen.
in the modified charging is probably larger than that in the conventional charging.

As shown in Fig. 3, during the modified charging, the pH of the solution increased and the potential shifted in the less noble direction. As a result, the solution properties or hydrogen overvoltage changes during the modified charging. These variations often lead to a change in the hydrogen absorption rate or the hydrogen states. For Ni–Ti superelastic alloy, the hydrogen absorption rate and hydrogen states were found sensitive to small variations in the solution or the electrochemical potential. In the present study, the variations of the amount of absorbed hydrogen and hydrogen states may be attributed to a similar phenomenon. The relationship between charging conditions and hydrogen absorption rate or hydrogen states should be investigated for type 304 stainless steel in future.

Figure 5 shows representative tensile stress-strain curves at various test temperatures for a noncharged specimen and the specimens subjected to modified or conventional charging. The fracture surfaces of each type of specimen after the tensile test at each temperature are shown in Figs. 6 to 8. The fracture surfaces of the noncharged specimens exhibited a macroscopic double-cup mode and were composed of microscopic dimples irrespective of the test temperature, although the reduction in area slightly decreased at −196°C. This result indicates that the motion of dislocations is suppressed at −196°C.

In the tensile test at 160°C, the fracture strain was slightly increased by hydrogen charging. By examining the fracture surfaces, it was found that the reduction in area was slightly decreased by modified and conventional charging, although the macroscopic and microscopic features exhibited the double-cup and dimple modes, respectively. The reduction in area for modified charging was smaller than that for conventional charging. The shallowing of dimples was observed for both types of charging. The reason for the slight increase in the fracture strain may be that hardly any necking of the
hydrogen-enhanced strain-induced vacancy (HESIV)\textsuperscript{29–32}) or austenite phase should be considered. For example, the interactions between hydrogen and the plastic deformation of the austenite phase appear to dominate the hydrogen embrittlement behavior. The fracture strain for the specimen subjected to conventional charging increased. For the modified charging, it is likely that the increase in the amount of hydrogen desorbed at low temperatures enhances the interactions between hydrogen and the plastic deformation and/or martensite transformation, thereby causing brittle fracture surface.

In the tensile test at $25^\circ C$, it appears that the plastic deformation of the austenite phase and the strain-induced martensite transformation occur in the early stage of the tensile deformation, and the plastic deformation of the martensite phase starts in the middle stage of the tensile deformation. In general, the pronounced hydrogen embrittlement of metastable austenitic stainless steels is considered to occur at temperatures from $-150^\circ C$ to $80^\circ C$, although the greatest embrittlement is observed at approximately $-73^\circ C$ to $-53^\circ C$.\textsuperscript{9,37–39} In this temperature range, hydrogen probably interacts with not only the martensite transformation but also the plastic deformations of the austenite and/or martensite phases, thereby generating a synergetic effect. As shown in Fig. 5(c), the 0.2% proof strength was substantially increased by hydrogen charging. For the conventional charging, only brittle transgranular fracture including flat facets was observed as shown in Fig. 8(c). These fracture modes are frequently observed in the hydrogen-related fracture of various types of austenitic stainless steels.\textsuperscript{6,9–11,20,37–44} The brittle transgranular fracture surface is considered to result from fracture along martensite lath\textsuperscript{39,40} or deformation twins.\textsuperscript{45} The flat facets have been reported to originate from twin-boundary fracture\textsuperscript{38} or to be composed of the \{111\} $\gamma$ plane and $\alpha'$ martensite.\textsuperscript{43} On the other hand, for modified charging, intergranular fracture was observed in some areas on the outer part of the fracture surface along with brittle transgranular fracture including flat facets (Fig. 7(c)). The intergranular fracture generally exhibits the three-dimensional nature of grains. For the modified charging, because the amount of hydrogen desorbed at low temperatures increases, the interactions between hydrogen and the martensite transformation and plastic deformation probably increase.

From the results of the tensile test at $-196^\circ C$, the 0.2% proof strength was substantially increased by hydrogen charging. At this temperature, the strain-induced martensite transformation increases, but the plastic deformation of the austenite and martensite phases by the dislocation motion is less than that at other temperatures. Therefore, the effects of the interactions between hydrogen and the dynamic martensite transformation are revealed. Note that for the case of modified charging, marked decrease in the fracture strain was observed as shown in Fig. 5(d). In addition, the intergranular fracture was observed as shown in Fig. 7(d). The amount of intergranular fracture at $-196^\circ C$ was greater than that at $25^\circ C$. In the tensile test at $-196^\circ C$, the number of defects induced by plastic deformation was probably less than that at other temperatures. It is likely that because hydrogen only slightly moves from sites in the austenite phase to trap sites such as defects, hydrogen acts as an obstacle to the martensite transformation. Accordingly, the interactions between hydrogen and the martensite trans-
formation significantly affect the hydrogen embrittlement behavior. For the conventional charging, the fracture strain was slightly less than that for the noncharging, and dimples and transgranular fracture were observed on the outer part of the fracture surface (Fig. 8(d)). Thus, for the conventional hydrogen charging, the degree of hydrogen embrittlement at −196°C was less than that at 25°C, consistent with previous studies. For the conventional charging, it appears that because the amount of hydrogen in an unstable state is smaller than that for the modified charging, the interactions between hydrogen and the martensite transformation are limited. Furthermore, the effects of interactions between hydrogen and the plastic deformation on the hydrogen embrittlement behavior at −196°C are less than those at 25°C. As a result, it appears that the degree of hydrogen embrittlement at −196°C is less than that at 25°C.

The brittle area was observed on the outer part of the fracture surface. The width of brittle area of the specimen fractured at −196°C was approximately 90–120 mm. The center part of the fracture surface exhibited shallow dimples. The distribution of the hydrogen concentration was estimated by solving the circular cylinder model (Fick’s second law) using the pre-exponential factor ($D_0 = 4.41 \times 10^{-7} \text{m}^2/\text{s}$), the activation energy ($E = 53.51 \text{kJ/mol}$) for hydrogen diffusion into annealed type 304 stainless steel reported by Sakamoto and Katayama and the amount of charged hydrogen, as shown in Fig. 9. The hydrogen concentrations in the vicinity of the surface in the cases of modified and conventional charging were estimated to be approximately 900 mass ppm and 700 mass ppm, respectively. For modified charging, since the amount of absorbed hydrogen increases, the hydrogen concentration is larger than that for conventional charging. These values are in good agreement with that in a previous study. The calculated distances of hydrogen diffusion are almost consistent with the size of the brittle area. Intergranular fracture was observed on the outer part of the fracture surface up to a distance of approximately 70–80 μm from the surface. In this area, the hydrogen concentration was estimated to be at most 200 mass ppm. For the conventional charging (Fig. 8), no intergranular fracture was observed even for hydrogen concentrations of larger than 200 mass ppm. Moreover, when a specimen was charged by modified charging for shorter period than the present study, the amount of charged hydrogen was less than that for conventional charging, while intergranular fracture was observed on the fracture surface. Thus, these results indicate that hydrogen enrichment does not necessarily lead to intergranular fracture.

The 0.2% proof strength and tensile strength of the noncharged and hydrogen-charged specimens increased with decreasing temperature. In the tensile tests at 25°C and −196°C, the 0.2% proof strength of the hydrogen-charged specimens was much larger than that of the noncharged specimens, although the 0.2% proof strength of the charged specimens was almost the same or slightly larger than that of the noncharged specimens in the tests carried out at 160°C and 100°C. For Ni–Ti superelastic alloy, charged hydrogen obstructs the stress-induced martensite transformation, thereby increasing the critical stress required for the martensite transformation or causing fracture during the martensite transformation. In the present study, however, the cause of the marked increase in the 0.2% proof strength may not always be the direct interactions between hydrogen and the strain-induced martensite transformation, because both Ulmer and Alstetter and ourselves have confirmed similar increases in the 0.2% proof strength for type 316L and 310S stainless steels in which no martensite transformation occurs. Therefore, the increase in the strength appears to be attributable to the obstruction of the motion of dislocations by hydrogen. Nonetheless, for type 304 stainless steel, the obstruction of the motion of dislocations presumably affects the martensite transformation behavior.

One important finding of the present study is that the features of the fracture surface correlate with the temperature of the tensile test for the modified charging; thus, the evidence of the interactions between hydrogen and the strain-induced martensite transformation appears as the intergranular fracture due to the change in hydrogen states. The variation of fracture surface induced by the interactions between hydrogen and the martensite transformation appears as the intergranular fracture. In general, intergranular fracture is observed for various sensitized austenitic stainless steels. For aged AISI 316 stainless steel subjected to hydrogen charging with a current density of 500 A/m² in H₂SO₄ solution containing Na₂SO₄, intergranular fracture was observed by Hammen et al., although the interactions between hydrogen and the martensite transformation were not described. To our knowledge, no intergranular fracture has been observed for solution-annealed type 304 stainless steel. In fact, as shown in Fig. 8, no intergranular fracture was observed for the conventional charging. Details of the mechanism of intergranular fracture resulting from the interactions between hydrogen and the martensite transformation are not yet clear and their clarification is beyond the scope of the present study. Nevertheless, one of the reasons for intergranular fracture has been revealed to be the change in the hydrogen states.

3.2. Effects of Prestraining on Hydrogen Embrittlement Behavior

The microstructures of the side surface of the specimens

---

**Fig. 9.** Estimated distributions of hydrogen concentration for specimens subjected to modified and conventional charging.
subjected to 10% prestrain at −196°C, 30% prestrain at 160°C and 70% prestrain at 25°C before hydrogen charging are shown in Fig. 10. The XRD patterns corresponding to these specimens are shown in Fig. 11. For the specimens subjected to 10% prestrain at −196°C and 70% prestrain at 25°C, not only the austenite phase but also the martensite phase was observed. The amount of the martensite phase for the specimen subjected to 10% prestrain at −196°C appears to be larger than that for the specimen subjected to 70% prestrain at 25°C, as reported previously.51) However, the number of defects for the specimen subjected to 70% prestrain at 25°C was larger than that for the specimen subjected to 10% prestrain at −196°C. For the specimen subjected to 30% prestrain at 160°C, no martensite phase was detected.

Figure 12 shows hydrogen thermal desorption curves for the specimens subjected to modified charging after prestraining under three different conditions. The numerical values are the amounts of desorbed hydrogen.

For comparison, the representative curve in the case of modified charging without prestraining shown in Fig. 4 is reproduced. The amount of desorbed hydrogen (absorbed hydrogen) was increased by prestraining. It is likely that the increase in the amount of desorbed hydrogen for the specimens subjected to 10% prestrain at −196°C (473 mass ppm) and 70% prestrain at 25°C (769 mass ppm) is mainly caused by the increase in the martensite phase, because hydrogen diffuses through the martensite phase to the center part of the specimen, as reported previously.52) Additionally, the marked increase for the specimen subjected to 70% prestrain at 25°C appears to be attributable to the decrease in the diameter of the specimen induced by 70% prestrain (from 0.50 mm to 0.41 mm). The amount of hydrogen desorbed at high temperatures decreased for the specimens subjected to 10% prestrain at −196°C and 70% prestrain at 25°C. In particular, for the specimen subjected to 10% prestrain at −196°C, no hydrogen desorption was observed above 280°C. This is probably due to the effect of the martensite phase on hydrogen diffusion. Since hydrogen diffusion in the martensite phase is faster than that in the austenite phase,18,19) hydrogen readily diffuses to the center of the specimen or diffuses out
of the specimen. However, the hydrogen solubility in the martensite phase is less than that in the austenite phase,\textsuperscript{16,17} hence, most of the charged hydrogen probably dissolves in the retained austenite phase or is trapped in defects. For the specimen subjected to 70\% prestrain at 25\°C, the desorption of hydrogen at high temperatures may be explained by the trapping of hydrogen in defects. In contrast, for the specimen subjected to 30\% prestrain at 160\°C, the hydrogen desorption behavior was almost the same compared with that for the specimen without prestraining. The increase in the amount of desorbed hydrogen compared with the specimen without prestraining is probably caused by the increase in the amount of hydrogen trapped in defects in the austenite phase.\textsuperscript{53} In this case, part of the hydrogen states appear to change from diffusible hydrogen or hydrogen in a solid solution to hydrogen trapped in defects such as vacancies and dislocations.

Figure 13 shows tensile stress-strain curves obtained at −196\°C for the noncharged specimen and the specimens subjected to modified charging after prestraining under the three experimental conditions. The corresponding fracture surfaces are shown in Fig. 14. No reduction in area of all specimens was observed for the specimens subjected to modified charging. For the specimens subjected to 10\% prestrain at −196\°C and 70\% prestrain at 25\°C, the brittle area spread to the center of the fracture surface, indicating that the martensite phase induced by prestraining accelerates hydrogen diffusion.

Upon modified charging, the specimen subjected to 10\% prestrain at −196\°C fractured in the initial stage of plastic deformation before the martensite transformation. The 0.2\% proof strength substantially increased after prestraining. The fracture is probably only slightly affected by the interactions between hydrogen and the dynamic martensite transformation. In this case, hydrogen embrittlement appears to be responsible for the martensite phase itself rather than the martensite transformation. The fracture surface mainly consisted of a mixture of brittle transgranular fracture, flat facets and very small amount of intergranular fracture. Under this condition, since the martensite phase is formed in abundance by prestraining at −196\°C, the amount of the martensite transformation is probably small during the tensile test after the modified charging. Consequently, the intergranular fracture of the prestrained specimen may be less than that of the specimen without prestraining (Fig. 7(d)).

For the specimen subjected to 30\% prestrain at 160\°C, compared with the specimen without prestraining (Fig. 7(d)), the intergranular fracture was decreased by the modified charging, although the 0.2\% proof strength was almost the same for both specimens. The probable reason is this is as follows: Since hydrogen is trapped in defects induced by prestraining, the interactions between hydrogen and the martensite transformation decrease. For Ni–Ti superelastic alloy, upon hydrogen trapping in defects, the effect of the interactions between hydrogen and the martensite transformation on hydrogen embrittlement decreases.\textsuperscript{15} Thus, the hydrogen states interacting directly with the martensite transformation are hydrogen in the solid solution and diffusible hydrogen rather than hydrogen trapped in defects. The present results clearly indicate that a similar mechanism can be applied to type 304 stainless steel.

For the specimen subjected to 70\% prestrain at 25\°C, marked increases in the 0.2\% proof strength and anomalous transgranular fracture were observed upon modified
charging, but no intergranular fracture was observed. The probable origin of this is that the decrease in the amount of the martensite transformation and the increase in the amount of hydrogen trapped in defects result in the decrease in the interactions between hydrogen and the dynamic martensite transformation. In addition, hydrogen embrittlement of the martensite phase itself probably occurs. The results obtained for the specimens subjected to prestrain under the three experimental conditions do not contradict the idea of dynamic interactions between hydrogen and the martensite transformation.

4. Conclusions

We have demonstrated that the intergranular fracture for type 304 stainless steel increases with decreasing tensile test temperature (increasing amount of the strain-induced martensite transformation) by preventing the dissolution of chlorine and oxygen gases into the solution used for hydrogen charging, i.e., modified charging. Upon modified charging, the amount of hydrogen thermally desorbed at a low temperature, which is related to unstable states of hydrogen, increases. When the martensite phase or defects are induced by tensile strain before hydrogen charging, the amount of intergranular fracture decreases. The states of hydrogen interacting directly with the martensite transformation are probably unstable hydrogen such as diffusible or solid solution rather than hydrogen trapped in defects. We conclude that the dynamic interactions between hydrogen and the martensite transformation as well as plastic deformation play an essential role in the hydrogen embrittlement of metastable austenitic stainless steel.

Acknowledgments

This study was financially supported in part by the 21st ISIJ Research Promotion Grant and a Grant-in-Aid for Scientific Research (C) (24560885) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

48) Unpublished data.