NECESSARY CONDITION FOR DELAYED FRACTURE OF METASTABLE 304 STAINLESS STEEL WITH STRAIN-INDUCED MARTENSITE

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Abstract

In order to reveal the necessary condition for shot-peened 304 stainless steel strips to cause delayed fracture, we monitored AE signals during stepwise strain increasing (SSI) tests of the hydrogen-charged strips in flexure and also during hydrogen charging of the bent strips. During the strain holding in the SSI test, we detected less than ten AE signals from the cracks produced in martensite-bearing surface layer. Numbers of AE signals and cracks agreed. This test showed no need for dynamic straining to cause the delayed fracture when sufficient hydrogen is supplied to martensite-bearing layer. Cracks did not propagate beyond the martensite-bearing surface layer of 150-200 µm. We also detected AE signals from the bent strips exposed to hydrogen charging, and estimated apparent diffusion coefficient of hydrogen in martensite-bearing layer from both the charge time for first AE detection and hydrogen diffusion length. It was estimated to be $10^{-9}$ cm$^2$/s for austenite layer with strain-induced martensite of 10 mass %.

Introduction

Susceptibility of austenitic stainless steels (SS) to delayed fracture is generally low. However, some types of the stainless steels show susceptibility when they are exposed to wet hydrogen environment. These SS are metastable 300-series (typ. Fe-18Cr-8Ni) and dual phase SS (50% ferrite-50% austenite phase). Also susceptible are high nickel alloys such as Inconel and Hastelloy with nickel content higher than 40%. Dual phase SS was demonstrated to show high susceptibility to the delayed fracture [1].

This paper deals with the delayed fracture of shot-peened 304 SS and as-received dual phase SS. 304 SS produces martensite when it is shot-peened at room temperature. Here, the martensite formation temperature of this steel is calculated as 30 ºC (303 K) according to the Md30 formulation. The Md30 temperature means the temperature at which half of austenite phase at plastic strain of 30% is transformed to ferritic phase. The 304 SS shot-peened by partially stabilized zirconia (PSZ) shots produces up to 10% martensite, depending on the peening intensity.

Delayed fracture of the 304 SS with strain-induced martensite were studied by some researchers [2, 3]. Carpenters group [4, 5] utilized AE technique to study the delayed fracture of sensitized 304 SS under dynamic straining or constant extension rate testing (CERT) in charging solution. They reported that the intergranular (IG) cracking occurs when hydrogen charging was continued till the maximum tensile load, and that AE signals were produced by grain boundary separation. They proposed a hydrogen transport model by moving dislocations. This model implies that both the fast and sufficient supplies of hydrogen to the martensite are possible by gliding dislocations accompanying hydrogen.

We also monitored AE signals from hydrogen related brittle cracking of sensitized 304 and 316 SS [6]. We monitored much AE signals from the 304 SS when it is exposed to both the
dynamic plastic deformation (CERT) and hydrogen charging, simultaneously. AE emission rate increased during plastic loading at higher crosshead speed. No emission from 316 SS suggested that brittle cracking occurs when martensite is formed during dynamic plastic straining. Results by Carpenter and our group suggest that hydrogen-assisted cracking or grain boundary separation occurs when sufficient hydrogen is transported to the martensite by dynamic straining or gliding dislocations. It is noted that the CERT tests in Carpenter study were completed within 1,800 s (30 minutes) and those in our group were 20,000 s (6.6 hrs).

Purpose of this research is to study whether the gliding dislocation is necessary condition for delayed fracture of non-sensitized 304 SS with strain-induced martensite using AE technique. Here, the martensites less than 10% were produced by shot peening at room temperature. We also monitored AE signals from duplex SS under hydrogen charging and estimated apparent diffusion coefficient of hydrogen in the shot-peened 304 stainless steel.

Test Specimen and Test Procedure

Specimens are as-received 304 SS and duplex (0.03C-4.95Ni-21.6Cr) SS with 2-mm thickness, 19-mm width and 76-mm length. One side of the 304 SS strips was shot-peened with 0.6-mm diameter PSZ shots by direct compressed air. Peening strength (expressed by the arc height of Almen strip A, or in mmA) was changed from 0.3 mmA to 0.8 mmA by changing the air pressure and peening time. All specimens were peened so as the coverage is higher than 100% except one sample (#31) with coverage of 40%. The Md₃₀ temperature of the 304 SS is calculated as 30 °C. As shown in Fig. 1, temperature of the strip increases rapidly just after the peening starts, and reaches 50 to 60 °C. Thus the martensite is mainly produced during early time of the peening. Amount of the martensite in the peened strips was measured by a magnetic-type ferrite meter, and found to be from 0.5 % to 10 %. Figure 2 shows transverse microphotograph of the peened type-304 SS strip (0.6 mmA) with martensite from 5 to 7.5 %. Here, the martensite (black portion) was revealed by etching in the surface layer up to 0.12 mm.

![Fig. 1. Change of back surface temperature of the Type-304 SS strip during shot peening.](image)
Fig. 2. Transverse structure of peened 304 SS strip.

Fig. 3. Comparison of hardness profiles of 304 SS plate shot-peened by PSZ and cast-steel shots at 20°C.

Fig. 4. $2\theta$ peak angle vs. $\sin^2\Psi$ for shot peened ($\varepsilon = 0$) and three point bent strips.
Figure 3 compares the hardness profiles in the depth of peened 304 SS. Here the steel strips were peened by 0.6-mm PSZ shot or cast steel shots. Peening intensity reaches 0.7mmA for the PSZ peening but that by cast steel shot only to 0.25mmA. Higher peening intensity by PSZ shots appears to be due to its high fracture toughness ($K_{IC} = 12 \text{ MPa}\sqrt{\text{m}}$) and hardness. The strain induced martensite exists in the hardened layer with hardness higher than 430 Hv. This implies that the 304 SS peened by cast steel shots does not show susceptibility to the hydrogen cracking with less martensite.

We next measured surface stress of as-peened and three-point bent 304 SS strips since the strips were hydrogen charged while being bent. X-ray diffraction method was used. The stresses were calculated by the $\sin^2 \Psi$ method. Figure 4 shows changes of slopes in $2\theta$ vs. $\sin^2 \Psi$ relation. Here, the negative slope indicates compressive stresses and the positive slope tensile stresses. It can be seen that the outer fiber stress of the as-peened 304 SS strip ($\varepsilon = 0$) and bent strips with strain $\varepsilon$ lower than 0.58% are compressive, while the strips bent at strain higher than 0.66% show tensile stresses. As the delayed fracture occurs under tensile stresses, we bent the strips so that the surface strain, measure by strain gage, is higher than 0.66%. Outer fiber stresses, calculated from the slopes in Fig. 4, are shown in Fig. 5. The stresses increased nonlinearly with bending strain. In most experiments, we applied 500 MPa by giving strips 0.8% strain.

![Fig. 5 Change of outer fiber stresses of three point bent strips.](image)

Next we measured the depth distribution of tensile stress using a modified hole-drilling method [7]. In this modified method, stress distribution in depth was calculated from the slope of the released strain by hole drilling. Figure 6 shows depth distribution of residual stresses of peened strip (dashed line) and actual stresses of the bent strip. Axial stresses (blue data) of the bent strip at 0.8% strain are higher than 200 MPa in the surface layer of 0.15 mm, and transverse stresses are compressive. It is noted that the delayed cracks occur, as shown later, in the surface layer less than 0.15 mm thick.

Hydrogen charge and AE monitoring methods are the same as used in our previous study [8]. Bent strips were hydrogen charged using a 20-mm diameter glass cell attached on the convex plane. Cathode charging is performed by direct current at density of 0.6 mA/cm$^2$ in a 1 N boric acid solution with 0.033 mol/l KCl and 0.02 mol/l thiourea. The thiourea accelerates the hydrogen permeation into the strips by reducing the combination of adsorbed hydrogen ions (H$^+$) to
hydrogen gas (H₂). AE signals were monitored by two resonant type sensors (PAC Pico) mounted on the concave plane at 18 mm and 36 mm from the center of the glass cell. Outputs of the sensors were amplified 40 dB and acquired as digital data. In addition to in-situ AE monitoring, we used a step-wise strain increasing (SSI) method to detect hidden cracks underneath the surface [7]. It is noted that the strips are hydrogen charged under a statically bent strain. Thus, dislocation gliding during hydrogen charging is less compared to that by the dynamic straining method or the CERT. Hydrogen charge was continued for 2,000 hrs at room temperature.

Test Results

Results of the shot-peened 304 SS strips
Test result is summarized in a diagram (Fig. 7) of charge time (H⁺ amount) vs. martensite content of peened strips. The samples that suffered delayed cracks are represented by red solid lines with crack number and length, while the samples free from delayed crack are by black dotted line. Sample-31, out of the plot area, designates the sample with peening coverage of 40%. This sample showed short cracks of less than 100 µm in peened craters. Thus, the sample -31 is located in crack zone. Blue slant line represents a tentative boundary between crack/no-crack regions. Characteristic feature of delayed cracks of samples-1, -2, -3, -11 and -14 are shown below.

For sample-1 with martensite of 7.5-10% with bending strain of 1%, we could not observe any open crack after being charged for 170 hours, as shown in top photo of Fig. 8. However after the SSI test up to strain of 2.2%, we observed several fine cracks, as shown in the bottom photo. Figure 9 shows a relation between step-wise strain and AE generation during the SSI test of sample-1. We detected five events during the first strain increase from 1% to 1.45 %. This indicates that the crack produced by hydrogen charging under static strain is buried underneath the surface, and dynamic straining is needed for opening the closed crack. Transverse microphotograph of this sample is shown in Fig. 10. We observed 9 short transverse cracks less than 0.2 mm long.
Fig. 7. Tentative boundary for crack/non-crack region in peened strips as function of amounts of martensite and hydrogen charge.

Fig. 8. Surface appearance of sample-1 after being charged for 170 hours (top) and after the SSI test with fine cracks (bottom).

Capturing of short cracks by specimen sectioning to reveal the crack distribution density is generally very difficult work. Successful results for samples-2 and-3 are shown in Fig. 11. Here the central loading point is at 3 mm. Seven cracks were generated over 5 mm width for sample-2,
Fig. 9. Relation between step-wise strain and AE generation during the SSI test of sample-1.

Fig. 10. Nine TG-cracks at transverse section of sample-1 around maximum applied strain. Martensite amount = 8%, charge amount: \(Q = 540 \text{ C/cm}^2\).

and over 2 mm for sample-2. Surface crack length after the SSI test of sample-3 were from 80 \(\mu\) m to 330 \(\mu\) m except one long crack of 8.1 mm. Figure 12 shows SEM of delayed cracks observed in sample-2. Curved and branched cracks were observed. This is in contrast to delayed cracks in high strength ferritic steel, which are generally straight without any branching. Thus, the zigzag and branched cracks in Fig.12 are unique crack observed only for austenitic steel with
martensite. The branching is due to complex distribution of the martensite as shown in Fig. 2 and is indicative of the strain-induced martensite being a path for hydrogen diffusion and crack site.

Fig. 11. Distribution of micro-cracks for samples-2 and -3.

Fig. 12. Some transverse cracks for sample-2.
While small hidden cracks were produced during static charging, we next studied whether AE can be detected during static charging. Figure 13 represents a result for sample-14 with 5-7.5% martensite. We first detected only noise by hydrogen gas bubbles, but after 40 hours, we detected three signals. After 95 hours, intermittent AE signals were emitted. The AE signal from crack generation possesses dispersive Lamb-wave characteristics, while that from gas bubbles is composed of single frequency, as shown in Fig. 14. Though we could not detect any crack by sectioning of this sample, this sample was classified as the sample in cracking zone of Fig. 4 owing to AE signals. Another example for sample-18 with 5-7.5% martensite is shown in Fig. 15. We detected three strong AE signals at 88 hours. Sectioning revealed one crack with 150-µm depth.

Fig. 14. Typical waveforms from gas bubbles (the upper) and from internal crack.
Based on the fact that 1) the crack length of sample-2 is 100 µm after 70 hours charging, 2) crack length of sample-3 is 200 µm after 100 hours and 3) that of sample-11 is 150 µm after 88 hours, we estimated that hydrogen can diffuse in the martensite-bearing 304 SS up to 140 µm after 90 hours. Thus, apparent diffusion coefficient of hydrogen in martensite (7.5-10%) bearing 304 SS is of the order of $10^{-9}$ cm$^2$/s at room temperature.

*Results of the duplex stainless steel*

Duplex stainless steel with 50% ferrite phase is demonstrated to suffer the delayed fracture. Sensitization accelerates the delayed fracture. Our work revealed that the hydrogen could diffuse up to 2 mm ahead of the main crack using K-controlled CT specimen. However, the hydrogen-induced crack of the duplex SS strip at constant bending strain is smaller and different from that observed in the K-controlled CT specimen.

Figure 16 shows the transverse photo of the steel that was hydrogen charged for 40 hours. We see crack-like attack along grain boundary. It is noted that crack number is extraordinarily large, but cracks are shallow and at less than 100 µm. Due to numerous surface cracks, we detected a number of AE during hydrogen charge, as shown in Fig. 17. First AE signal was detected after approximately 10 hours of charging.
Fig. 17. Change of cumulative AE counts with charge time for the duplex SS at constant bending strain of 1.3%.

Fig. 18. Comparison of waveforms and amplitudes of AEs detected for two types of SS and high-strength ferritic steel.

Figure 18 compares waveforms and amplitudes of AE signals detected for two types of stainless steels and high-strength ferritic steel. Time scale of the bottom AE is expanded from top two, since it is cited from our previous data [7]. Amplitude or Vpp of the So-mode wave from martensite-bearing 304 SS is smallest among the three. The Vpp of 80 mV from duplex stainless steel is 3 times larger than 304 SS but 5 times smaller than Vpp (400 mV) from the high-strength ferritic steel. It is noted that the high-strength steel strip of 2 mm thickness completely fractured within 2 hours of charging.
Fig. 19. Transient hydrogen concentration at 1-mm distance from plate surface with different diffusion coefficients.

**Apparent hydrogen diffusion coefficient of martensite- or ferrite-bearing austenitic SS**

Diffusion coefficient of hydrogen in ferritic steels is reported as $10^{-6}$ cm$^2$/s that is $10^6$ times faster than in the austenitic SS with $10^{-12}$ cm$^2$/s. As shown in Fig. 19, hydrogen hardly diffuses in the austenitic steel within our test time of less than 2000 hours. This figure represents transient hydrogen concentration at mid-section of 2-mm thick plate, which absorbs hydrogen from both surfaces. We estimated above apparent diffusion coefficient of hydrogen in 304 SS with 10% martensite as $10^{-9}$ cm$^2$/s. This estimation is based on the average crack length and charge time. We can roughly estimate the crack time by equating the charge time to the crack time. However, we must remember that the delayed crack in the shot peened 304 SS does not progress beyond 200 µm within 1000 hours.

**Conclusion**

We studied delayed fracture of shot-peened 304 SS with strain-induced martensite less than 10%. AE technique was successfully utilized for the detection of small cracks during both hydrogen charging of bent strips and SSI test of hydrogen-charged strips. Results are summarized below.

1) 304 stainless steel with strain-induced martensite produces subsurface delayed cracks under constant tensile stress. The cracks are not straight, but zigzag and often branched. Neither the gliding dislocation nor sensitization is a necessary condition for the delayed crack of metastable austenitic stainless steel.

2) Shot-peening produces less than 10% martensite in the surface layer of 150-200 µm. Delayed cracks occur in the hardened surface layer and does not progress beyond the hardened layer.
3) Apparent diffusion coefficient of hydrogen in the shot-peened 304 SS with 10% martensite was estimated as $10^{-9}$ cm$^2$/s. Strain induced martensite appears to be the path for hydrogen diffusion.

References