Effect of Hydrogen Partial Pressure on the Hydrogen Embrittlement Susceptibility of Type304 Stainless Steel in High-pressure H₂/Ar Mixed Gas

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Slow strain rate testings (SSRTs) were carried out on Type304 stainless steel (Type304SS) in room temperature mixed gasses controlled to various pressure levels of up to 75 MPa, and the variation of embrittlement susceptibility of the tested steel under various hydrogen partial pressure was measured. Regardless of gas composition and at a hydrogen partial pressure level of 0.3 MPa or more in the gasses, elongation as well as relative reduction of area lowered, and brittle fracture surfaces appeared with accompanying quasi-cleavage. The critical $P_{H2}$ at which Type304SS embritles in a room temperature inert gas environment with mixed hydrogen is inferred to be between 0.05 and 0.1 MPa. From a conservative judgment it is concluded that hydrogen embrittlement fractures would be unlikely to occur to members made of Type304SS when $P_{H2}$ is around one tenth of the atmospheric pressure or lower (i.e. 0.05 MPa).

KEY WORDS: hydrogen embrittlement; hydrogen partial pressure; type304 stainless steel; H₂/Ar mixed gas.

1. Introduction

Austenitic stainless steel is widely used as material for high pressure industrial gas equipment and piping, on account of its cold-workability and high corrosion resistance. The representative types of austenitic stainless steel are Type304 (UNS S30400) SS and Type316L (UNS S31603) SS. While there is a problem with the anti-corrosive strength of weld heat-affected zones in a chloride solution, Type304SS has the advantages of being less expensive and of having more strength after cold-working than Type316LSS. Due to concerns about hydrogen embrittlement⁵ of Type304SS, however, Type316LSS is more often used as material for hydrogen gas equipment.

Mechanical properties of Type304SS deteriorate greatly in room temperature hydrogen gas.⁶ For example, the percentage elongation after fracture of Type304SS in room temperature hydrogen gas of 75 MPa decreases to around 30% of that in air⁶ while the percentage elongation after fracture of Type316LSS in the same hydrogen gas is equal to that in air.⁶ As Type304SS is semi-stable austenitic stainless steel, its austenitic phase ($γ$ phase) areas are transformed into strain-induced martensitic phase ($α′$ phase) when exposed to strong plastic deformation strength. It is considered that the embrittlement of Type304SS in hydrogen gas is caused by interactions between hydrogen and transformed areas, including $α′$ phase section, formed in the plastic region at the tip of a crack.⁶ Type316LSS, being stable austenitic steel which is not subject to strain-induced transformation under room temperature, is not believed to embrittle due to hydrogen, except when exposed to a condition equivalent to being under extreme high pressure⁷ such as cathodic charge in a solution.

From a cost-perspective, Type304SS is preferred as austenitic stainless steel material for equipment to handle hydrogen-free high pressure air and inert gas. For equipment with the possibility of hydrogen being mixed into air or inert gases, due to dispersion through a permeable membrane or by erroneous operation, Type304SS is still considered usable if the concentration of hydrogen mixed in these cases is expected to be low. In this case, however, in order to guarantee the safety of equipment there is a need to consider critical hydrogen partial pressure under which no embrittlement occurs, and to consider acceleration and control of embrittlement due to mixed inert gases.

As an initial approach to the study of this area, we measured the variation of embrittlement susceptibility of Type304SS under hydrogen partial pressure by conducting SSRTs in 5%H₂-Ar mixed gas at room temperature, controlled at various pressure levels of up to 75 MPa. We also carried out SSRTs using pure hydrogen gas and nitrogen-mixed gas. A thermal desorption method was used to analyze the concentration and conditions of hydrogen adsorbed on the surfaces of, and occluded in the near surface part of, the test pieces (surface hydrogen), in order to make use of such data in consideration of the embrittlement mechanism.
2. Tests

Sample materials were pieces of 5 mm thick Type304SS which had been solution-heat-treated in 1050°C for 24 hours. Similarly heat-treated pieces of Type316LSS sheet were also used. Table 1 shows the chemical composition, Ni$_{eq}$ and Md$_{30}$ of both materials. From these sample materials, flat tensile test pieces were made, corresponding to the dimensions given in Fig. 1. After machining, the test pieces were heat-treated at 10$^{-2}$ Pa and 1050°C for 2 hours for degassing and elimination of machining distortion. The parallel parts of test pieces were dry-polished with emery polishing paper of up to #600 and washed with acetone.

SSRTs were conducted in 5 vol% H$_2$-Ar mixed gas using a device as described in Fig. 2. After setting a test piece on a jig in the pressure vessel, the vessel was pressurized up to 3 MPa using nitrogen gas and the pressure was then released, with this cycle being repeated three times. The same cycle was then repeated three times using the mixed gas. Following this, using a compressor we introduced test gas from a gas cylinder into the pressure vessel until the prescribed pressure was attained. It took approximately one hour from the setting of a test piece to the attainment of test pressure. SSRTs were started as soon as the test pressure was reached. For the purpose of comparison, we carried out the same procedure using pure H$_2$ gas and 50 vol%H$_2$-N$_2$ mixed gas. In the latter test, we mixed hydrogen and nitrogen gasses within the pressure vessel instead of using a cylinder of ready-mixed gasses. First, hydrogen gas was introduced into the pressure vessel until the inside reached half the test pressure, then the cylinder connected to the pressure vessel was replaced with a nitrogen cylinder, to introduce nitrogen gas into the vessel until the test pressure was attained. Pure hydrogen gas with a purity of 99.99999% or more was used in both tests. Table 2 lists the types of gasses used, the levels of internal pressure in the pressure vessel and the corresponding hydrogen partial pressure applied in SSRTs.

In all SSRTs, strain rate was set at 8 × 10$^{-6}$ s$^{-1}$. We regarded the elongation of the whole test piece as that of its parallel part, and shifted the cross-head of the testing device in the tensile direction at a speed of 0.2 mm/s. Crack susceptibility of test pieces in each testing environment was evaluated using the ratio of relative reduction of area and the percent brittle fracture in each test piece after fracture. The ratio of relative reduction of area was defined as the ratio ($\phi_{env}/\phi_{air}$) between the reduction of area in the testing environment ($\phi_{env}$) and the reduction of area in air with the same strain rate and temperature ($\phi_{air}$). The $\phi_{env}/\phi_{air}$ value becomes smaller as the embrittlement susceptibility of test pieces under the testing environment increases. We observed the whole area of one of the two fracture surfaces using a scanning electron microscope (SEM), and obtained

![Fig. 1. Shape and dimensions of the tensile specimen.](image1)

![Fig. 2. Schematic diagram of a slow strain rate testing (SSRT) apparatus at high pressure environments.](image2)

| Table 1. Chemical compositions of the materials (in mass%), and their Ni$_{eq}$ and Md$_{30}$. |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Ni | Cr | Mo | N | Ni$_{eq}$ | Md$_{30}$ |
| Type 304 SS | 0.05 | 0.39 | 0.81 | 0.026 | 0.005 | 8.10 | 18.09 | 0.13 | 0.048 | 21.6 | 30.4 |
| Type 316L SS | 0.02 | 0.62 | 0.90 | 0.023 | 0.001 | 12.10 | 17.21 | 2.10 | 0.017 | 26.8 | −6.7 |

Ni$_{eq}(\text{mass%}) = Ni + 0.65Cr + 0.98Mo + 1.05Mn + 0.35Si + 12.6C$

Md$_{30}(\text{°C}) = 413 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 9.5Ni - 18.5Mo

| Table 2. List of the SSRT condition; the types of gasses used, the levels of internal pressure in the pressure vessel and the corresponding hydrogen partial pressure applied in SSRTs. |
|---|---|---|
| Types of gasses used | Levels of internal pressure in the pressure vessel | Partial pressure ($P_{H_2}$) |
| 5% H$_2$-Ar | 70 MPa | 3.5 MPa |
| | 6.0 MPa | 0.30 MPa |
| | 1.1 MPa | 55 kPa |
| | 0.1 MPa | 5 kPa |
| pure-H$_2$ | 75 MPa | 75 MPa |
| | 10 MPa | 10 MPa |
| | 1.1 MPa | 1.1 MPa |
| | 0.6 MPa | 0.6 MPa |
| | 0.1 MPa | 0.1 MPa |
| 50% H$_2$-N$_2$ | 70 MPa | 35 MPa |
the percent brittle fracture from the area ratio between the brittle fracture surface area and the whole fracture surface area.

Using a thermal desorption method, we analyzed the concentration and conditions of hydrogen adsorbed on the surfaces of, and occluded in the near surface part of, the test pieces (surface hydrogen). The equipment described in Fig. 2 was used to strain the test pieces up to 20% in hydrogen gas under various pressure levels. For the purpose of comparison, we analyzed hydrogen of test pieces which had been pre-strained up to 20% in air and exposed to hydrogen gas for the same number of hours beforehand. The dimensions and strain rate were identical to those in SSRTs described above. In order to prevent hydrogen from escaping, the test pieces were stored in a minus 70°C freezer after being tested and until immediately before analysis. In analyses, sample pieces obtained from the parallel parts of test pieces were heated in vacuum from room temperature to 300°C at a temperature increase rate of 10°C/min, and the amount of hydrogen released from the samples at each temperature level was analyzed with a quadrupole mass spectrometer (ST-200P Special Model made by ULVAC, Inc.). The apparent hydrogen content was then obtained by dividing the integral of hydrogen desorption curve by the mass of each sample subjected to analyses.

3. Results

3.1. Stress-strain Curve

As examples of the stress-strain curve measured in SSRTs, Fig. 3 shows the results obtained in 5%H₂-Ar gas at 0.10 MPa and 70 MPa (with a hydrogen partial pressure of 5 kPa and 3.5 MPa respectively). Elongation decreased under high pressure conditions, and it is inferred that the material has embrittled due to the influence of hydrogen (hydrogen embrittlement).

3.2. Variation of Relative Reduction of Area due to Hydrogen Partial Pressure

The values of relative reduction of area measured in SSRTs under each condition were plotted as a function of hydrogen partial pressure in Fig. 4, as illustrated in Fig. 5. For the purpose of comparison, the relative reduction of area was measured in pure H₂ gas and in 50%H₂-N₂ gas, the results of which are also plotted as a function of $P_{H_2}$.

The relative reduction of area in 5%H₂-Ar gas varied greatly between when $P_{H_2}$ is 55 kPa (Plot $d$ in Fig. 4) and when $P_{H_2}$ is 0.30 MPa (Plot $b$ in Fig. 4). The relative reduction of area was 1.0 in each case when $P_{H_2}$ was 55 kPa or lower, and dropped to 0.5 or lower when $P_{H_2}$ was 0.30 MPa or higher.

The values of relative reduction of area both in pure H₂ gas and 50%H₂-N₂ gas with $P_{H_2}$ being 0.1 MPa or greater were generally plotted on the test curve of results obtained in 5%H₂-Ar gas. This means the relative reduction of area under the condition where hydrogen embrittlement is observed on the test pieces has become a function of $P_{H_2}$ regardless of gas composition.

3.3. Variation of Fracture Surface Configuration due to Hydrogen Partial Pressure

Shown in Fig. 5 are the general and enlarged views of fracture surfaces of test pieces after SSRTs conducted under $P_{H_2}$ of around 0.1 MPa, where a great variation of relative reduction of area took place. The views marked $a$ through $d$ in the figure are the fracture surfaces of those test pieces for which the relative reduction of area was measured (as illustrated in Fig. 4 with corresponding marks). $P_{H_2}$ at the time of measurement of fracture surfaces $a$ through $d$ are, therefore, 0.60, 0.30, 0.10 and 0.055 MPa respectively. However, pure hydrogen gas was used in the measurement of $a$ and $c$, and 5%H₂-Ar gas for $b$ and $d$.

As indicated in each figure within Fig. 5, the whole area of fracture surfaces $a$ and $b$ at a hydrogen partial pressure level of 0.1 MPa or more became brittle fracture surfaces with accompanying quasi-cleavage. At $P_{H_2}$ of less than 0.1 MPa, however, the percent brittle fracture surface lowered with a decrease in $P_{H_2}$. The percent brittle fracture of $c$ was 55%, and the fracture surface of $d$ was entirely a ductile fracture surface. Although no figures are posted, the fracture surfaces of test pieces in each condition with $P_{H_2}$ higher than that of $a$ turned to brittle fracture surface in their entirety. Meanwhile, the whole fracture surface of test piece at $P_{H_2}$ of 5.0 kPa, which was lower than for $d$, became a ductile fracture surface.
3.4. Analyses of Surface Hydrogen

Test pieces were strained up to 20% in hydrogen gas under pressure levels from 0.1 up to 75 MPa and the concentration of surface hydrogen of the test pieces was analyzed using a thermal desorption method. Apparent hydrogen contents obtained through the analyses are shown in Table 3. Nos. 7 through 9 in Table 3 are the results of the tests on Type316LSS test pieces, conducted for the purpose of comparison. Nos. 1 and 7 also show the apparent content of hydrogen which desorbed from Type304SS and Type316LSS test pieces not exposed to hydrogen, and which was measured immediately after pre-treatment under the same test condition with the tests carrying other numbers. Nos. 6 and 9 are the apparent hydrogen content obtained from the test pieces pre-strained up to 20% in air and then exposed to hydrogen gas of 75 MPa. The duration of exposure was 7 hours, which is the same amount of testing time for straining up to 20% in hydrogen gas.

As indicated in Nos. 2 through 5 in Table 3, for the test pieces which were strained in hydrogen gas the amount of occluded hydrogen increased corresponding to $P_{H_2}$. However, the hydrogen content for No. 2, i.e. under 0.1 MPa

![Fig. 5. SEM views of the fracture surfaces of the Type 304 ss specimens after SSRT at RT in several H\textsubscript{2} partial pressures with 5%H\textsubscript{2} - Ar gas and pure-H\textsubscript{2}.](image)
Table 3 as typical examples of hydrogen desorption curves. Every hydrogen desorption curve, excluding that of Nos. 1, 2, 6, 7 and 9 where no significant hydrogen desorption was detected, shows a line having a single peak at around 110°C regardless of hydrogen gas pressure levels or steel types. Strictly speaking, the peak temperature showed a tendency to drop slightly corresponding to the maximum value of hydrogen desorption rate. For example, the peak temperature at 75 MPa hydrogen partial pressure (No. 5 in Table 3) was 106°C, which is lower than in the case of 1.1 MPa (No. 3 in Table 3) by approximately 10°C.

4. Discussion

4.1. Critical Hydrogen Partial Pressure in Hydrogen Embrittlement

In SSRTs in 5%H2-Ar gas, which is the fundamental environment, the relative reduction of area was 1.0 in every case when hydrogen partial pressure $P_{102}$ was 55 kPa or lower (Fig. 4), and fracture surfaces of test pieces were all ductile fracture surface (Fig. 5). In other words, no embrittlement was detected on the test pieces in SSRTs under hydrogen partial pressure of 55 kPa or lower. Meanwhile, even in gas of the same composition, the relative reduction of area dropped to 0.5 or lower under each condition where $P_{102}$ was 0.30 MPa or higher, and fracture surfaces turned to brittle fracture surface in their entirety. While the relative reduction of area in pure H2 gas of 0.1 MPa (c in Fig. 4) was equal to that in 5%H2-Ar gas with $P_{102}$ of 0.30 MPa (b in Fig. 4), the percent brittle fracture in the former was 55% and lower than that in the latter (c and b in Fig. 5). The relative reduction of area and fracture surfaces at $P_{102}$ of 0.1 MPa or higher were, as stated in sections 3.2 and 3.3, not dependent on gas composition but as a function of mean hydrogen content included in the hydrogen gas exclusively. From this it is inferred that the relative reduction of area and fracture surfaces in pure H2 gas of 0.1 MPa are equivalent to the results obtained in inert gasses including any hydrogen gas with $P_{102}$ of 0.1 MPa. From the above results and consideration, the critical $P_{102}$ at which Type304SS embrittlies in a room temperature inert gas environment with mixed hydrogen is inferred to be between 0.05 and 0.1 MPa. Even from a conservative judgment, we can conclude that hydrogen embrittlement fractures are unlikely to occur to members made of Type304SS in an environment of near room temperature and where $P_{102}$ is around one tenth of the atmospheric pressure or lower (i.e. 0.05 MPa).

In this study we evaluated the environmental embrittlement in materials through SSRTs where plastic strain is continuously applied to test pieces. Piping in actual use, however, is generally used under constant load. As shown in the results of Nos. 5 and 6 or Nos. 8 and 9 in Table 3, the hydrogen concentration on or near the surface of the specimen deformed with being deformed in the hydrogen gas was estimated more than ten times higher than that exposed to the hydrogen gas without being strained; the hydrogen released in thermal desorption tests would be exclusively from on or near the surface of the specimen because the diffusion coefficient of hydrogen in austenitic stainless steel is low enough. These results suggest that the hydrogen concentration on or near surfaces of the piping, when it is used under constant load is actually smaller than...
in test pieces in SSRTs under the same \( P_{H2} \). Based on the above, it is considered sufficiently conservative to estimate the critical \( P_{H2} \) at which hydrogen embrittlement fractures occur to be 0.05 MPa.

Some piping in actual, however, are used under cyclic loading. It would not be applied the critical \( P_{H2} \) obtained by the SSRT to the materials under such a condition, so it would be necessary to carry out fatigue tests under the conditions similar to those in this study, in order to determine the level of \( P_{H2} \) where the embrittlement susceptibility of such material changes greatly.

It is confirmed that the hydrogen embrittlement susceptibility of Type304SS generally decreases with an increase in temperature.\(^9\)\(^\text{5}\) Accordingly, the critical hydrogen partial pressure is inferred to be at a level of 50 kPa or higher when the temperature of use environment is higher than room temperature. Meanwhile, a separate study is deemed necessary for such piping that is used at below room temperature.

### 4.2. Embrittlement Mechanism of Type304SS in Hydrogen Gas

The penetration depth of hydrogen into Type304SS, during the period of around 40 hours between the introduction of high pressure hydrogen gas and the occurrence of fractures in tests conducted in 5%H\(_2\)-Ar gas of 0.1 MPa, is calculated to be as small as 7 \( \mu \)m when calculated using a diffusion equation with a hydrogen diffusion coefficient at room temperature of 3.40\( \times 10^{-12} \) cm\(^2\)/s.\(^10\) Accordingly, the penetrated diffusible hydrogen is considered to be influencing the shallow surface of materials only. From these it is inferred that the hydrogen crack susceptibility is dominated not by hydrogen which has penetrated base materials but by hydrogen which has been absorbed on or occluded immediately underneath the newly formed surfaces at the tip of fractures.

Some believe that the influence of hydrogen on the tip (newly generated surfaces) of an advancing fracture is defined as the lowering of surface energy due to adsorption rather than embrittlement caused by penetration.\(^\text{11}\) Based on the similarity between fracture surfaces of liquid metals where reaction fields are restricted to their surfaces and those of hydrogen embrittlement, Lynch suggests an embrittlement model where hydrogen adsorbed at the tip of a fracture induces local plastic transformation, which then accelerates cracking.\(^\text{11}\) Cracks in Type304SS in high pressure hydrogen gas of room temperature may be explained as a series of phenomena that occur following a similar mechanism, i.e. plastic transformation is induced by the hydrogen adsorbed on crack tip surfaces, by which localized strain-induced martensitic phase formation and related structural changes are accelerated, and such localized transformation is furthered by interactions between hydrogen and these phases and structures.

### 5. Conclusions

(1) At a hydrogen partial pressure level of 0.3 MPa or more in 5%H\(_2\)-Ar gas, elongation as well as relative reduction of area of Type304SS decreased, and brittle fracture surfaces appeared with accompanying quasi-cleavage. Additionally, the values of relative reduction of area both in pure H\(_2\) gas and 50%H\(_2\)-N\(_2\) gas were generally plotted on the test curve of results obtained in 5%H\(_2\)-Ar gas. This means the relative reduction of area under the condition where hydrogen embrittlement is observed on the test pieces has become a function of \( P_{H2} \) regardless of gas composition.

(2) In those test pieces which were strained in hydrogen gas, the amounts of occluded hydrogen increased corresponding to \( P_{H2} \), and their desorption curves show a line having a single peak at around 110°C regardless of hydrogen gas pressure levels or steel types. Meanwhile, no significant occlusion of hydrogen was formed in a pre-strained test piece where it was not strained in hydrogen gas.

(3) The critical \( P_{H2} \) at which Type304SS embrittles in a room temperature inert gas environment with mixed hydrogen is inferred to be between 0.05 and 0.1 MPa. From a conservative judgment, we conclude that hydrogen embrittlement fractures are unlikely to occur to members made of Type304SS when \( P_{H2} \) is around one tenth of the atmospheric pressure or lower (i.e. 0.05 MPa).

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