The 2017 World Congress on
Advances in Structural Engineering and Mechanics (ASEM17)
28 August - 1 September, 2017, Ilsan(Seoul), Korea

Hydrogen Susceptibility of Austenitic Stainless Steel Pipes Brazed with Ni-30Cr-4Si-6P Filler Metal

Susumu Motomura[1)], Hisao Matsunaga[2)], Junichiro Yamabe[2) 3)], Saburo Matsuoka[2)] and Norikazu Osawa[4)]

[1)] Graduate School of Kyushu University, 744 Motooka Nishi-ku, Fukuoka, Japan
[2)] Kyushu University, 744 Motooka Nishi-ku, Fukuoka, Japan
[3)] HydroMate, 744 Motooka Nishi-ku, Fukuoka, Japan
[4)] Tatsuno Corporation, 200 Iijima-Cho Sakae-ku, Yokohama, Japan
** 2TE16712Y@s.kyushu-u.ac.jp*

ABSTRACT

In hydrogen refueling stations, Coriolis flowmeters are used to measure the mass flow rate of hydrogen gas. This type of flowmeter possesses certain brazed parts which are exposed to high-pressure hydrogen gas. However, the hydrogen compatibility of the brazed metals has not been investigated in detail. Consequently, the objective of this study was to clarify the influence of hydrogen on the strength of brazed, stainless steel elements, in order to ensure the safe use of brazed components in high-pressure hydrogen gas. The specimen used for this research was an XM-19 pipe with threaded Type 316 bases which had been brazed with Ni-30Cr-4Si-6P filler metal. Tensile tests were performed in hydrogen gas at both 0.7 MPa and 95 MPa at room temperature. A study was also conducted on a hydrogen-charged specimen which had been exposed to high-pressure hydrogen gas at an elevated temperature. The shear strengths obtained for the brazed sections were calculated from the load at final rupture. Neither the hydrogen gas environment nor the hydrogen-charging led to any notable degradation, as compared to the strength obtained in air. Therefore, it was concluded that the brazed, stainless steel parts had demonstrated sufficient resistance to hydrogen, rendering them eligible for use with a Coriolis flowmeter.

1. INTRODUCTION

The advent of Fuel Cell Vehicles (FCVs) on the market has necessitated the widespread construction of hydrogen refueling stations. In such stations, Coriolis flowmeters are equipped with dispensers so that the mass flow rate of hydrogen can be measured. This type of flowmeter is comprised of certain brazed elements which are exposed to high-pressure hydrogen gas. However, the hydrogen compatibility of these brazed metals has not yet been investigated in detail. In this study, the influence of hydrogen on the strength of brazed, stainless steel components is clarified, with a view to ensuring the safe use of Coriolis flowmeters in high-pressure hydrogen gas.

2. EXPERIMENTAL PROCEDURE

2.1 Measurement of the hydrogen diffusion coefficient in the brazing filler metal

The specimen used for measuring the hydrogen diffusion coefficient in the brazing filler metal is depicted in Fig. 1. It is cylindrical in shape, with both a diameter and a thickness of 5 mm.

The specimen was exposed to high-pressure hydrogen gas at an elevated temperature, so as to obtain a uniform distribution of hydrogen over its cross-section. The particular conditions of exposure to hydrogen were as follows: a gas pressure of 100 MPa, at a temperature of 270°C, for a holding time of 200 hours. After exposure, the specimen was subjected to TDA (Thermal Desorption Analysis) at constant temperatures (i.e., 150°C, 200°C, 270°C and 350°C), with the hydrogen diffusion coefficient obtained from the hydrogen release curves at the respective temperatures.

2.2 Tensile specimens

Tensile specimens were produced in order to simulate the brazed components of a Coriolis flowmeter. Details of their shapes and dimensions are indicated in Fig. 2. The specimens consisted of XM-19 pipes with threaded bases (Type 316 stainless steel) which had been brazed in a vacuum with Ni-30Cr-4Si-6P filler metal at 1070°C.

Figure 2 (a) presents Specimen A, prepared with a view to confirming the greater strength of the brazed elements in relation to the pipe itself. In this specimen, the brazed section was identical to the actual brazed component found in a real flowmeter. Figure 2 (b) displays Specimen B, used for investigating the shear strength of the brazed parts under the influence of hydrogen.

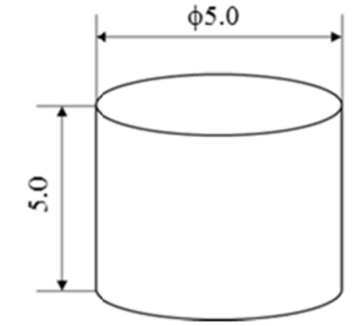
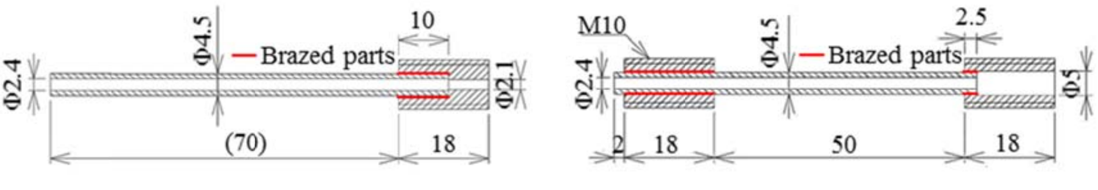


Fig. 1: Dimensions of specimen for thermal desorption analysis, in mm.



(a) Specimen A

(b) Specimen B

Fig. 2: Dimensions of tensile specimens, in mm.

2.3 Hydrogen-charging conditions

The specimen exhibited in Fig. 2 (b) was exposed to high-pressure hydrogen gas at an elevated temperature, in order to saturate the brazed areas with hydrogen. Hydrogen exposure conditions involved a gas pressure of 115 MPa, at a temperature of 300°C, for a holding time of 200 hours.

2.4 Tensile tests

2.4.1 Tensile test with Specimen A

Using Specimen A, without hydrogen-charging, a tensile test was carried out in air at room temperature, at a crosshead speed of 1 mm/min. This test served to determine whether the brazed components or the pipe segments possessed the greater strength.

2.4.2 Tensile test with Specimen B

Using Specimen B, the following investigations were conducted at room temperature, at a crosshead speed of 0.09 mm/min:

(i) Testing of a non-charged specimen in 0.7-MPa hydrogen gas.
(ii) Testing of a non-charged specimen in 95-MPa hydrogen gas.
(iii) Testing of a hydrogen-charged specimen in air.

The shear strength of the brazed components was evaluated via these tests, whereby the shear strength was defined by the load at final fracture of the specimen, divided by the area of the brazed part.

3. RESULTS AND DISCUSSION

3.1 Hydrogen diffusion coefficient and depth of hydrogen penetration

The equation derived by Demarez (1954) duly describes the change in the distribution of hydrogen concentration, owing to the release of hydrogen from a cylindrical specimen. Equation (1) determines the concentration of hydrogen in the cylinder, R_H, as a function of the holding time, t:

$$\frac{R_H}{R_{Ho}} = \frac{32}{\pi^2}\left[\sum_{n=0}^{\infty}\frac{\exp\left\{-(2n+1)^2\pi^2 Dt/l^2\right\}}{(2n+1)^2}\right]\times\left[\sum_{n=1}^{\infty}\frac{\exp\left\{-D\beta_n^2 t/\rho^2\right\}}{\beta_n^2}\right] \quad (1)$$

where, R_{H0} is the hydrogen concentration at t = 0, l is the height of the cylinder, is the radius of the cylinder and β_n is the nth term of Bessel coefficients of zero order.

Based on the results of TDA, using Eq. (1), the hydrogen diffusion coefficient, D, was calculated at each respective temperature. Upon measurement of the total amount of hydrogen release during TDA, the average hydrogen content in the filler metal at saturated condition was concluded to be 34.7 mass ppm.

Figure 3 illustrates an Arrhenius plot of the hydrogen diffusion coefficient. The vertical axis represents the logarithm for the hydrogen diffusion coefficient, D, with the horizontal axis corresponding to the reciprocal of temperature, T. Equation (2) is Arrhenius's calculation for describing the relationship between the diffusion coefficient, D, and temperature, T:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where, D_0 is the frequency factor, Q is the activation energy and R is the gas constant (= 8.314 J/mol·K). A linear approximation of the diffusion coefficient obtained by the least square method is provided in Fig. 3, shown together with the measured values. The temperature dependencies of the hydrogen diffusion coefficient of 300-series stainless steels and XM-19 (YAMABE 2015) are also documented in Fig. 3. The diffusion coefficient of the brazing filler metal was approximately three times as small as that of the austenitic stainless steels.

During the hydrogen penetration process into a semi-infinite body, the penetration depth from the surface, $x_{1/2}$, at which hydrogen concentration becomes half of the saturated hydrogen level, is given by Eq. (3):

$$x_{1/2} = \sqrt{Dt} \quad (3)$$

Based on the results shown in Fig. 3, the hydrogen diffusion coefficient in the brazing filler metal, D = 4.19×10^{-12} (m^2/s), is obtained at 300°C. Assuming that the brazed component is a semi-infinite body, $x_{1/2}$ = 1.7 mm is obtained, deeper than half the length of the brazed part (=1.25 mm) in Specimen B. Since hydrogen can penetrate into the filler metal from both ends of the brazed section, it can be assumed that the entire brazed area was saturated with hydrogen.

3.2 Shear strength of brazed parts

During the tensile testing of Specimen A in air at room temperature, fracture occurred in the region of the pipe. This result confirmed that the brazed section was indeed stronger than the pipe. The shear stress acting on the brazed part was = 68 MPa.

In order to measure the strength of the brazed elements, subsequent tensile tests were performed on Specimen B in air, as well as in hydrogen gas at pressures of either 0.7 MPa or 95 MPa. A hydrogen-charged specimen was also tested in air. The various shear strengths that were obtained are indicated in Fig. 4. The shear strength of the non-charged specimen in air was discovered to be = 224 MPa, nearly identical to the result for similar brazed parts as reported by Miyazawa (2002). On the other hand, the corresponding strengths of the non-charged specimen were found to be 202 MPa and 210 MPa, in 0.7-MPa and 95-MPa hydrogen, respectively. The strength of the hydrogen-charged specimen tested in air was 225 MPa. The afore-mentioned results confirm that neither hydrogen-charging nor hydrogen gas environments can degrade shear strength, as compared to the impact on strength observed in air.

During the testing of Specimen A, when the final fracture of the pipe segment occurred, the shear stress acting on the brazed part was = 68 MPa, much smaller than the actual strength of the brazed portion. Hence, it can be concluded that the brazed components in the Coriolis flowmeter are sufficiently strong and demonstrate adequate resistance to hydrogen.

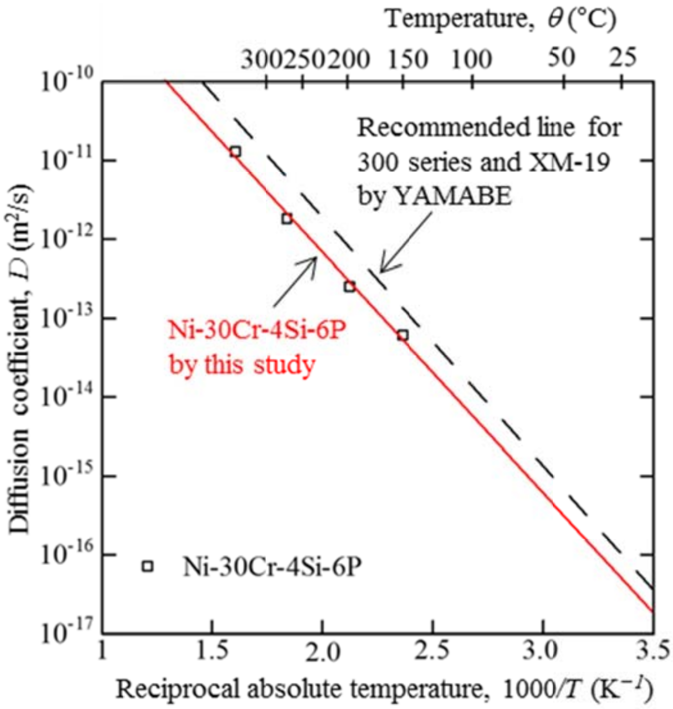


Fig. 3: Arrhenius plot of the diffusion coefficient.

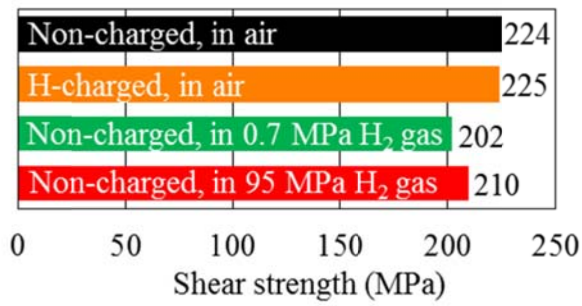


Fig. 4: Nominal shear stress at final fracture.

4. CONCLUSIONS

An investigation was conducted into the hydrogen diffusion properties of the brazing filler metal, Ni-30Cr-4Si-6P. In addition, the effect of hydrogen on the strength of the brazed components was studied. The following conclusions were derived:

1. The hydrogen diffusion coefficient of the brazing filler metal, Ni-30Cr-4Si-6P, was approximately three times as small as that of austenitic stainless steels.
2. The shear strength of the brazed parts did not degrade during the test in 95-MPa hydrogen gas, nor during the test of the hydrogen-charged specimen.

Therefore, it can be established that the brazed elements demonstrated sufficient resistance to hydrogen, thereby confirming their eligibility for use with Coriolis flowmeters, such as are currently used in hydrogen refueling stations.

REFERENCES

A.L. Demarez, A.G. Hock and F.A. Meunier (1954), "Diffusion of hydrogen in mild steel", *Acta metallurgica*, Vol.2, 214-223.

Junichiro YAMABE, Tohru AWANE, Hisatake ITOGA, Hisao MATSUNAGA, Saburo MATSUOKA (2015), "Hydrogen Diffusion Behavior of Various Austenitic Stainless Steels", *Proceedings of the Japan Conference on Structural Safety and Reliability.*

Yasuyuki Miyazawa, Kenji Denda, Yasuhito Totsuka, Yasuo Miyamoto, Tadashi Ariga, Pornsak Attavanich (2002), "Strength of Stainless Steel Joint Brazed by Various Nickel-based Brazing Filler Metals", *JSME/ASME International Conference on Materials and Processing*, Honolulu.