HYDROGEN ENVIRONMENT EMBRITTLEMENT OF METALS IN HIGH-PESSURE HYDROGEN STORAGE

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ABSTRACT

A new material testing equipment in 70 MPa hydrogen at room temperature was developed to facilitate the measurement of the actual load on a specimen inside a pressure vessel with an external load cell. The tensile behaviors of different types of austenitic stainless steel (SS), namely, 304, 316, 316L, 316LN and 310S, and aluminum alloy, A6061, for use in high-pressure hydrogen storage in hydrogen fuel-cell vehicles were investigated using this equipment in hydrogen or argon of 70 MPa at an initial strain rate of 4.17 x 10^{-5}/s at room temperature. The effect of strain-induced martensite on hydrogen environment embrittlement (HEE) was examined. Type 304 and 316 SSs showed significant HEE and type 316L and 316LN SSs showed slight HEE, but type 310S SS and A6061 did not show HEE. A brittle transgranular fracture was observed mainly on the surfaces of type 304 and 316 SSs and slightly on the surfaces of type 316L and 316LN SSs in hydrogen. No brittle fracture was observed in type 310S SS and A6061. A ductile dimple rupture was observed on the entire fracture surfaces of all the specimens fractured in argon. It was discussed that strain-induced martensite enhances the HEE of type 304, 316, 316L and 316LN SSs.

1 INTRODUCTION

Hydrogen has been expected as an energy carrier since the 20^{th} century. With the recent invention of fuel cells, polymer electrolyte fuel cells have been applied in automobiles, and many automobile companies have been promoting the development of fuel-cell vehicles in the world. As hydrogen storage tanks are set up in vehicles, their size is limited, thus high-pressure hydrogen storage has been awaited. Although polymers are candidate materials for storage tanks, metallic materials are still expected as a liner of the tank or body of storage vessels of hydrogen station. Many industrial metallic materials show hydrogen embrittlement, particularly hydrogen environment embrittlement (HEE), thus HEE is a key issue in high-pressure hydrogen storage.

Hydrogen storage at 70 MPa is currently expected, thus the HEE of candidate materials, such as austenitic stainless steels (SSs), ferritic steels and aluminum alloys, for use in hydrogen storage should be tested in 70 MPa hydrogen. Chandler and Walter [1], Thompson [2] and Caskey [3] investigated the HEE of many types of steel, nickel-base superalloy and aluminum alloy at 69 MPa at room temperature. They found that some of these candidate materials are sensitive to HEE and some of them do not show HEE, particularly type 316 SS (Chandler [1], Thompson [2] and Caskey [3]). However, we have reported recently that type 316 SS is markedly sensitive to HEE even at room temperature (Fukuyama [4]) and shows a maximum HEE at 200 K (Fukuyama [5]).

In this study, a new material testing equipment in 70 MPa hydrogen was developed and the HEE of austenitic SSs and aluminum alloy was examined in 70 MPa hydrogen. HEE of these materials was discussed.

2 EXPERIMENTAL

A new material testing equipment in 70 MPa hydrogen at room temperature was developed by our laboratory based on our patent. The apparatus consisted of a pressure vessel with a circulating fluid controlled at a given temperature and a hydraulic loading machine. The apparatus was designed to measure the actual load on a specimen with an external load cell irrespective of the axial load caused by high pressure and friction at the sliding seals.

The materials used for the tensile tests were different types of commercially available austenitic SS, namely, 304, 316, 316L, 316LN and 310S, and aluminum alloy, A6061. The chemical compositions of the different types of steel are listed in Table 1. These steels were heat-treated by solution annealing and A6061 was subjected to T6. The materials were machined into cylindrical smooth tensile specimens with a gauge length of 20 mm and a diameter of 4 mm. The tensile direction of the specimen was parallel to the rolling direction of the materials. The surfaces of all the specimens were prepared using sandpaper, polished with paste and finally washed in an ultrasonic cleaner in an acetone bath before performing tensile tests. The tensile tests on the materials were conducted in 70 MPa hydrogen or argon at room temperature. The purities of the testing gases were 99.9999 % for hydrogen and 99.999 % for argon. All the tests were conducted at an initial strain rate of 4.17 x 10^{-5}/s. The fracture surfaces of the specimens were observed using scanning electron microscopy (SEM) after the tensile tests. Strain-induced martensite was detected by magnetic measurement.

Table 1 Chemical compositions of different types of steel used (wt%).

Type	C	Si	Mn	P	S	Cr	Ni	Mo	N	Fe
304	0.060	0.59	1.01	0.018	0.009	18.33	8.35	**	**	Bal.
316	0.040	0.48	0.66	0.010	0.021	17.10	10.05	2.02	**	Bal.
316L	0.022	0.77	1.39	0.032	0.011	17.04	12.16	2.04	**	Bal.
316LN	0.013	0.46	1.25	0.024	0.010	17.46	10.50	2.82	0.138	Bal.
310S	0.060	1.24	1.53	0.002	0.009	24.63	20.21	**	**	Bal.

3 RESULTS AND DISCUSSION

3.1 Material testing equipment

A new material testing equipment is shown in Figure 1. The pressure vessel, 8, in which a specimen is installed, on the right side of the figure is set in the frame, 1, of the hydraulic loading machine. The test gas is compressed by a compressor in the pipeline on the left side of the figure and is transported to the pressure vessel. As the O-rings are used as a sliding seal for the high-pressure gas inside the pressure vessel, friction is enhanced by the high pressure inside the pressure vessel at the rings when the pull rod, 5, is moved by the actuator rod, 2, of the hydraulic loading machine. The load acting on the specimen in the pressure vessel is measured using the external load cell, 3, and the actual tensile load on the specimen can be obtained graphically by subtracting the frictional force, a constant value, from the measured load.

As axial load is affected by the high pressure inside the pressure vessel, the axial load due to the high pressure acting on the pull rod is eliminated by the method that we previously developed. The pressure balance cylinder with the piston is mounted onto the vessel lid to compensate for the axial load due to the high pressure acting on the pull rod and the specimen. The pull rod and piston are processed into one piece, and the effective area of the piston in the pressure balance cylinder is designed to be equal to the cross-sectional area of the pull rod in the pressure vessel. By introducing a high-pressure gas from the upper pressure vessel into the pressure balance cylinder through a connecting pipe, the axial load due to the high pressure in the pressure vessel is balanced by the compressive load caused by the same pressure in the pressure balance cylinder; thus no resultant force appears on the load cell before the tensile test. Details are cited from (Fukuyama [4]). The following tensile tests were conducted using this equipment.

3.2 HEE of materials evaluated

Hydrogen showed a considerable effect on the tensile property of type 304 and 316 SSs, a slight effect on that of type 316L and 316LN SSs and a negligible effect on that of type 310S SS and A6061 at this strain rate. The HEE of a material is quantitatively represented as the relative reduction of area, namely, the ratio of the reduction of area in hydrogen to that in helium (hydrogen/helium). A relative reduction of area of 1.0 indicates no hydrogen influence. The more this parameter decreases, the more the hydrogen influence increases. The HEE of type 304, 316, 316L and 316LN SSs are shown in Figure 2. The HEE of type 304 and 316 SSs decreases with increasing hydrogen pressure and that of type 304 SS is more severe than that of type 316 SS. Slight HEE of type 316L and 316LN SSs is observed.

The fracture surfaces of type 304, 316, 316L and 316LN SSs fractured in argon and hydrogen are shown in Figure 3. A ductile dimple rupture is observed on the fracture surfaces of all the specimens in argon. Crack initiation occurs at the specimen surface and the crack propagates inside type 304 and 316 SSs in hydrogen. Cracking is limited near the specimen

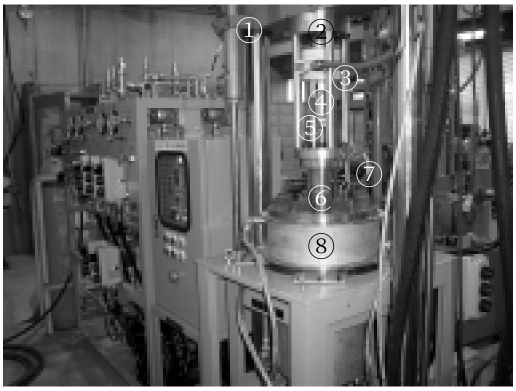

Figure 1. Material testing equipment in high-pressure hydrogen at room temperature.
(1: frame, 2: actuator rod, 3: load cell, 4: universal joint, 5: pull rod, 6: pressure compensation device, 7: connecting pipe, 8: pressure vessel)

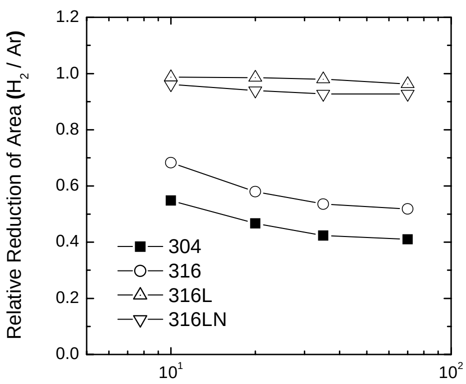

Figure 2. Effect of hydrogen pressure on relative reduction of area of type 304, 316, 316L and 316LN stainless steels at room temperature.

surface and the crack does not propagate inside type 316L and 316LN SSs in hydrogen. A brittle transgranular fracture along martensite laths are observed on the hydrogen-induced fracture surface.

Chandler and Walter [1], Thompson [2] and Caskey [3] reported that type 316 SS does not

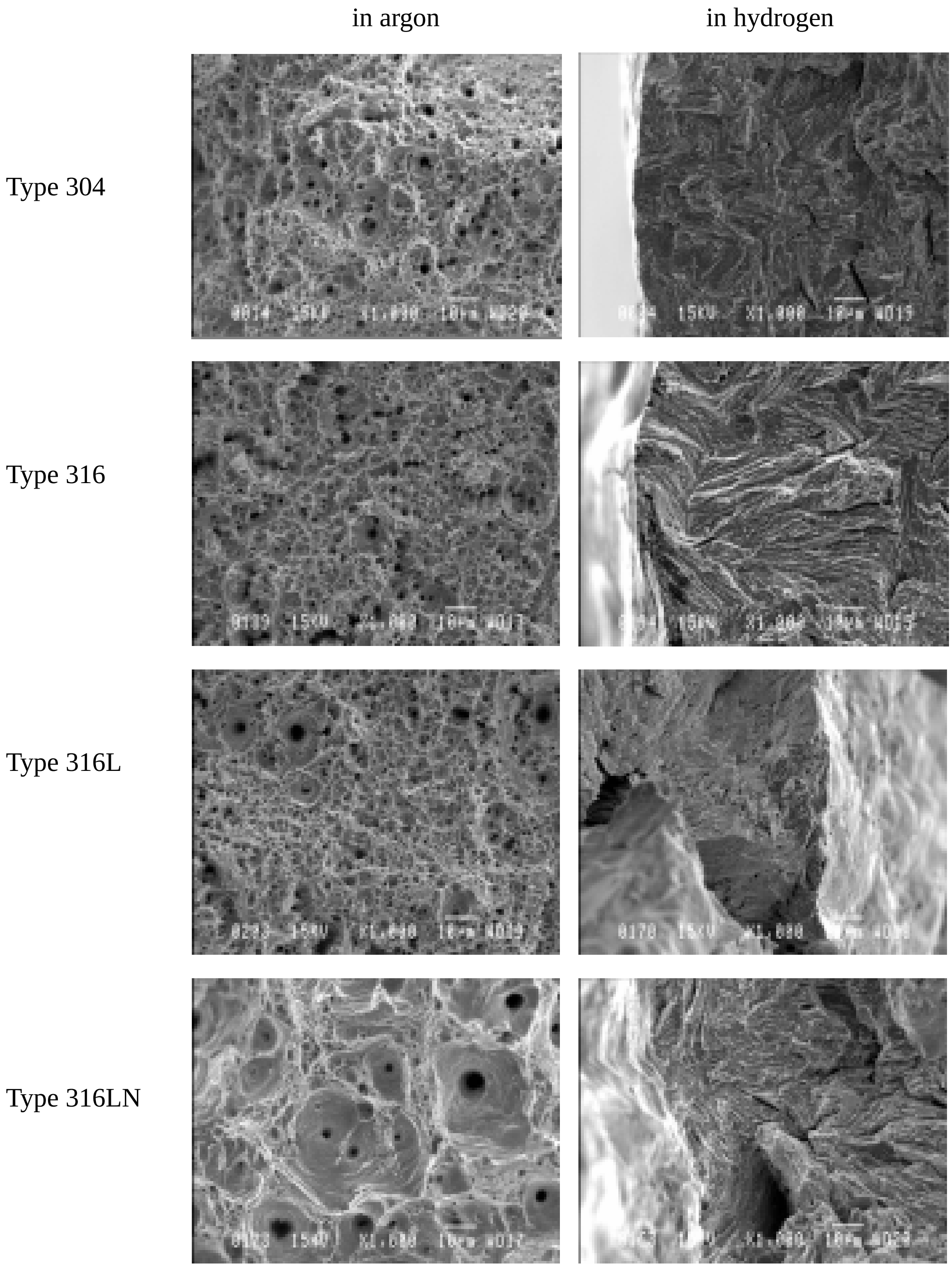

Figure 3 Fracture surfaces of type 304, 316, 316L and 316LN stainless steels in 70 MPa hydrogen and in argon at room temperature.

show HEE at 69 MPa at room temperature, but our result shows significant HEE of 316 SS. We found that the HEE of type 316 SS depends on temperature, and the maximum HEE of this steel is attained at 200 K (Han [6]) similar to type 304, 316L and 316LN SSs (Fukuyama [5]). We also found that the HEE of austenitic SSs depends on strain-induced martensite. Following the magnetic measurement, strain-induced martensite is detected clearly in type 304 and 316 SSs, and slightly in type 316L and 316LN SSs, but not in type 310S SS at room temperature, thus the HEE of type 316 SS can be observed at room temperature under these experimental conditions. Further examinations will be required to clarify the factors affecting HEE.

4 CONCLUSIONS

A new material testing equipment in 70 MPa hydrogen at room temperature was developed to facilitate the measurement of the actual load on a specimen inside a pressure vessel with an external load cell. The tensile behaviors of different types of austenitic SS, namely, 304, 316, 316L, 316LN and 310S, and aluminum alloy, A6061, were investigated using this equipment in hydrogen or argon of 70 MPa at room temperature. The effect of strain-induced martensite on HEE was examined. The results were as follows.

1. Type 304 and 316 SSs showed significant HEE and type 316L and 316LN SSs showed slight HEE, but type 310S SS and A6061 did not show HEE.
2. A brittle transgranular fracture was observed mainly on the surfaces of type 304 and 316 SSs and slightly on the surfaces of type 316L and 316LN SSs in hydrogen. No brittle fracture was observed in type 310S SS and A6061. A ductile dimple rupture was observed on the entire fracture surfaces of all the specimens fractured in argon.
3. It was discussed that strain-induced martensite enhances the HEE of type 304, 316, 316L and 316LN SSs.

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