

Effect of Hydrogen Charging Time and Tensile Loading Speed on Tensile Properties of 304L Stainless Steels

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〈Abstract〉

This study dealt with the tensile strength characteristics of stainless steel 304L steel by hydrogen charging. Especially, the effect of hydrogen charging time on the tensile strength and ductility of 304L stainless steels was evaluated, in conjunction with the observation of their fracture surfaces. The tensile properties of hydrogen-charged 304L stainless steels were also investigated with the variation of tensile loading speeds. The hydrogen amount of 304L stainless steels obviously increased with the increase of hydrogen charging time. The tensile properties of 304L stainless steels were clearly affected by the short term charging of hydrogen. In particular, the elongation of 304L stainless steels decreased with increasing hydrogen charging time, due to the hydrogen embrittlement. It was also found that the tensile properties of hydrogen-charged 304L stainless steels were very sensitive to the crosshead speed for tensile loading.

Keywords : *Hydrogen Embrittlement, Electrochemical Hydrogen Charging, 304L Stainless Steel, Tensile Property, Fractograph*

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1. Introduce

The development of eco-friendly clean energy technology in the energy industry, has been promoted by the rapid acceleration of air pollution and global warming. In recent years, hydrogen-related energy technologies having excellent characteristics in various industrial fields have been actively developed[1-4]. Hydrogen is being considered as a high-efficiency energy source for the next-generation energy industry, such as liquid hydrogen vehicles and fuel for space launch vehicles.

However, since hydrogen is stored and transported in the form of pressurized gas, cryogenic liquid, and solid fuel, the development of hydrogen containers for liquid hydrogen storage and transportation is an important task in the field of hydrogen energy utilization[5-7]. The materials for the storage of liquid hydrogen are required not only to have mechanical properties such as high strength and toughness but also to be stable by chemical or physical interaction with hydrogen. Particularly, the toughness of the materials in the design of hydrogen storage vessel is an important issue to be ensured, because the hydrogen-related phenomena such as hydrogen embrittlement, blistering or hydrogen cracking are accompanied by rapid progress of cracking.

As a candidate material, austenitic stainless steel which is used as a structural material of a cryogenic vessel has been considered[8-11].

In particular, 304L stainless steel is classified as austenite-type Ni-Cr steel with low carbon content. Corrosion resistance is similar to that of 304 stainless steel, but it has excellent resistance to intergranular corrosion after stress-relief heat treatment. 304L stainless steel has good high-temperature strength, corrosion resistance and oxidation resistance, so it is used as a main piping material in petrochemical industry, chemical textile industry and nuclear power plant. Because of these environmental resistance, it is considered as a storage tank or carrying pipe materials for hydrogen energy. In order to expand the utilization of 304L stainless steel as a storage material for hydrogen energy, it is necessary to identify the change in mechanical characteristics due to hydrogen charging. The hydrogen embrittlement of 304L stainless steel are very important considering the material damage and the material deterioration that may occur during use of storage vessel or carrying pipe for liquid hydrogen.

The charging of hydrogen for structural materials has been considered as a method using high pressure hydrogen which requires a large scale safety facility and an simple electrochemical method using electrolyte. In particular, electrochemical method is known to be a very effective method compared to using high-pressure hydrogen gas[12-14]. Electrochemical methods are known to be highly efficient in the laboratory level, which can lead to high levels of hydrogen charging

on the surface of the material using the thrust of hydrogen potential without special high-pressure equipment. In order to apply various kinds of stainless steels to the hydrogen energy industry, it is necessary to identify changes in the characteristics of those materials by direct hydrogen charging, and the physical properties of hydrogen-charged stainless steels are very important for the design of hydrogen storage vessels and parts.

In this study, the mechanical properties of hydrogen-charged 304L stainless steel by electrochemical method were investigated. Especially, the tensile strength and ductility of 304L stainless steel were evaluated according to the changing time of hydrogen. The influence of cross-head speed of tensile test on the tensile strength of hydrogen charged 304L stainless steel was investigated. The fracture profile was observed to characterize the 304L stainless steel due to hydrogen charging.

2. Procedure of Experiments

The material used in this study is 304L stainless steel with chemical composition 0.024% C - 0.4% Si - 0.03% P - 0.005% S - 1.46% Mn - 8.04% Ni - 18.47Cr - Bal. Fe and has a lower carbon content than 304 stainless steel. Charging of hydrogen for 304L stainless steel was carried out by electrolysis. Galvano / Potentiostat (Model: HA 151-A),

which can utilize a potential difference, was used for hydrogen charging. A test specimen of 304L stainless steel which is to be charged by hydrogen was attached to a cathode, and platinum was attached to an anode part. 1N H_2SO_4 and As_2O_3 were used as the electrolytic solution for the generation of hydrogen. During the hydrogen charging, the current density was kept constant at 100 mA/cm^2 at the cathode. High purity hydrogen atoms released from H_2SO_4 are charged to the surface of the test specimen by the driving force of the potential in the cathode reaction through the chemical reaction of the electrolyte. The charging time of hydrogen for 304L stainless steel was 12, 24 and 48 hours. The amount of charged hydrogen into 304L stainless steel according to the charging time was measured by hydrogen degassing test using OH-900 system (Eltra GmbH, Germany). The amount of hydrogen charged was measured by supplying a nitrogen gas to the test specimen, and detecting the hydrogen generated in the process of dissolving the test specimen by using a heat conduction detector. Cylindrical test specimens with a diameter of 3.0 mm and a height of 6.0 mm were used to measure hydrogen charging.

The tensile tests of 304L stainless steel according to the charging time of hydrogen were evaluated at room temperature. The tensile tests were carried out immediately after hydrogen charging and rinsing to minimize the release of hydrogen charged

into the tensile specimen. Tensile test specimens of 304L stainless steel were machined in parallel to the rolling direction of the rolled-steel having a thickness of 12 mm. Tensile test specimens were produced in the form of round bars based on the ASTM G142 standard. The total length of the specimen was 76.2 mm and the diameter and length of the center of the parallel part were 6.0 mm and 28.6 mm, respectively. In order to evaluate the sensitivity of the 304L stainless steel to hydrogen charging, the cross-head speed of tensile load was changed from 0.12 to 5.0 mm/min. In order to investigate the change of tensile strength of 304L stainless steel according to charging amount and time of hydrogen, fracture shape and surface of specimen were observed by scanning electron microscope (SEM).

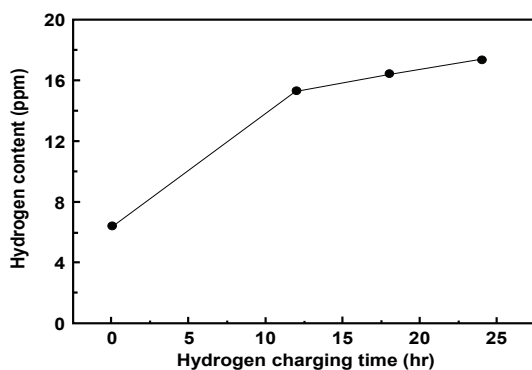


Fig. 1 Effect of hydrogen charging time on the hydrogen content of 304L stainless steels.

3. Results and Discussion

Fig. 1 shows the effect of hydrogen charging time on the hydrogen content of 304L stainless steel which was charged with hydrogen by an electrochemical method. 304L stainless steel has a hydrogen content of about 6.0 ppm when no hydrogen is charged. It can be seen that the hydrogen content increases greatly with the increase of the hydrogen charging time. This means that the electrochemical method is efficient for hydrogen charging on 304L stainless steel. In particular, when hydrogen was charged for 24 hours, the 304L stainless steel showed hydrogen content of about 18.0 ppm, which is about three times that of 304L stainless steel without hydrogen.

Fig. 2 shows the tensile load-displacement curves of 304L stainless steel with variation in hydrogen charging time. The cross-head speed used in the tensile test of 304L

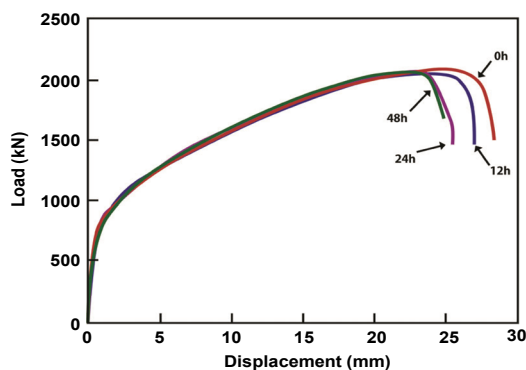


Fig. 2 Load-displacement curves of 304L stainless steels depending on the variation of hydrogen charging times.

stainless steel was 0.12 mm/min. The tensile test was carried out immediately after hydrogen charging and washing to suppress the release of hydrogen from the surface of the sample. 304L stainless steel showed similar behavior regardless of hydrogen charging time and showed typical ductile fracture behavior. However, as the hydrogen charging time increases, it shows different fracture behavior after the proportional limit. It can be seen that the fracture displacement decreases greatly decrease with increasing charging time.

Fig. 3 shows the effect of hydrogen charging time on the maximum tensile strength and yield strength of 304L stainless steel. The 304L showed tensile strength of about 750 MPa and yield strength of about 280 MPa before hydrogen charging. It can be seen that the maximum tensile strength of 304L stainless steel is somewhat affected by hydrogen charging compared to yield strength. As the hydrogen charging time

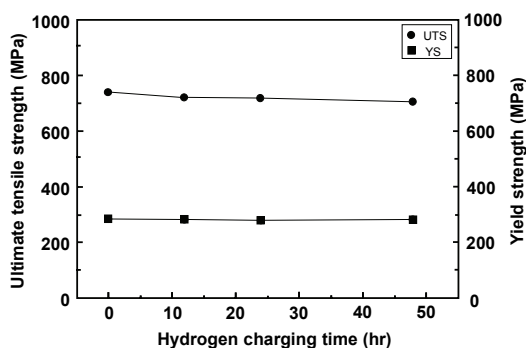


Fig. 3 Effect of hydrogen charging times on the ultimate tensile strength of 304 stainless steels.

increases, the yield strength of 304L stainless steel is about 280 MPa, which is almost constant, while the maximum tensile strength tends to decrease. This is due to the surface embrittlement associated with the increase in hydrogen content by charging time and is similar to that of the previously reported 304 stainless steel[15].

Fig. 4 shows the effect of hydrogen charging time on the elongation of 304L stainless steel. The elongation of 304L stainless steel without hydrogen charging was also shown. It can be seen that the elongation of 304L stainless steels decreases linearly with increasing hydrogen charging time. 304L stainless steel without hydrogen charging exhibited an excellent elongation of about 69%, but after 48 hours of hydrogen charging, the elongation decreased to about 62%. As shown in Fig. 5, the ductility of 304L stainless steel is clearly related to the charging of hydrogen. In addition, charging of hydrogen for 304L stainless steel is more

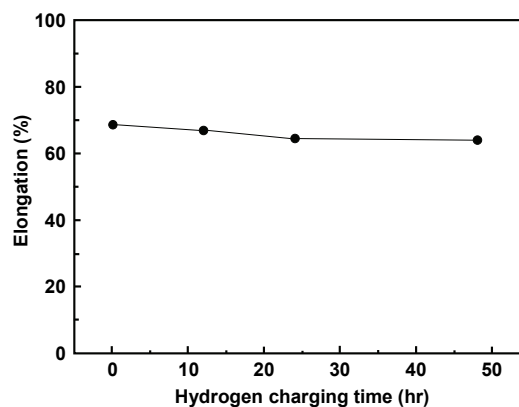


Fig. 4 Effect of hydrogen charging times on the elongation of 304L stainless steels.

relative to ductility than strength in Fig. 3.

Fig. 5 shows the relation between the fracture elongation and the hydrogen charging amount of the 304L stainless steel. It can be seen that the elongation at break of 304L stainless steel is very sensitive to the amount of hydrogen charged. In other words, as the amount of hydrogen charged increases, the fracture elongation of 304L stainless steel generally shows linear decrease. The elongation was about 68% at the hydrogen charging of about 6 ppm, but the fracture elongation decreased to about 62% as the hydrogen charging increased to about 18 ppm. From these results, it can be seen that charging of hydrogen causes embrittlement of the material and acts as a cause of reducing ductility.

Fig. 6 shows the effect of cross-head speed on the maximum tensile strength of hydrogen-charged 304L stainless steel. The hydrogen charging time for the tensile test

specimens of 304L stainless steel was constant at 12 hours. The maximum tensile strength of hydrogen-charged 304L stainless steel shows a tendency to decrease as the cross-head speed increases. When tensile test was carried out at a cross-head speed of 0.12 mm/min, the 304L stainless steel exhibited a maximum tensile strength of about 740 MPa. On the other hand, the maximum tensile strength with the cross-head speed of 5.0 mm/min is about 650 MPa. Thus, it can be seen that the speed reduction of the cross-head in the tensile test causes an increase in the strength.

Fig. 7 shows the effect of cross-head speed on yield strength of 304L stainless steel charged with hydrogen for 12 hours. The yield strength of 304L stainless steel shows a tendency to decrease as the cross-head speed increases. However, even if the cross-head speed increases, unlike the variation in the

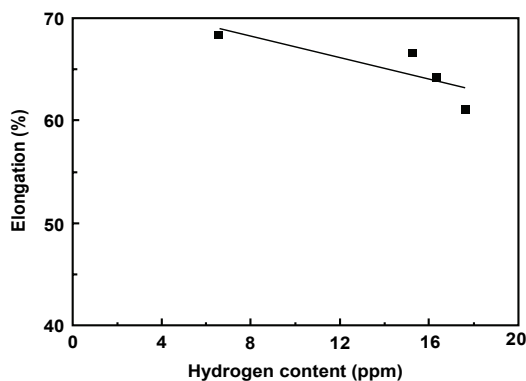


Fig. 5 Relationship between hydrogen content and fractured elongation for hydrogen-charged 304L stainless steels.

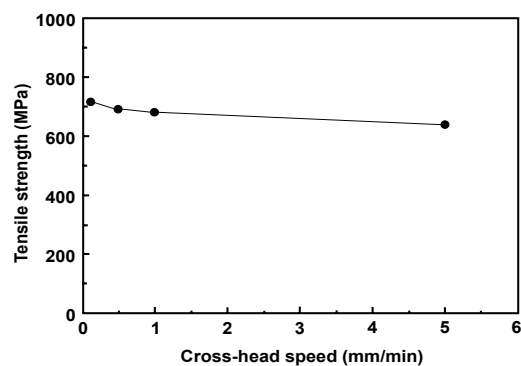


Fig. 6 Effect of cross-head speeds on the ultimate tensile strength of hydrogen-charged 304L stainless steels.

maximum tensile strength shown in Fig. 6, the yield strength may not be significantly affected. 304L stainless steel charged with hydrogen exhibited a yield strength of about 370 MPa at a cross-head speed of 0.12 mm/min. This corresponds to 50% of the maximum tensile strength. On the other hand, the 304L stainless steel showed a yield strength of about 340 MPa at a cross-head speed of 5.0 mm/min.

Fig. 8 shows the influence of the cross-head speed on the elongation of 304L stainless steel charged with hydrogen for 12 hours. It can be seen that the fracture elongation of 304L stainless steel is greatly affected by the change in cross-head speed. As the cross-head speed increases, the fracture elongation of 304L stainless steel is clearly decreasing. In particular, the elongation of 304L stainless steel is drastically reduced at cross-head speeds ranging from 0.12 to 1.0 mm/min. However, 304L stainless

steel showed similar elongation at 1.0 and 5.0 mm/min. In other words, 304L stainless steel exhibited an average elongation of about 76% at a 0.12 mm/min, while the elongation was about 62% at 5.0 mm/min, which is equivalent to about 81% of the elongation at 0.12 mm/min. Thus, it can be seen that the fracture elongation of the 304L stainless steel is very sensitive to changes in the cross-head speed.

Fig. 9 shows the observation of the fracture surface of tensile specimen of 304L stainless steel without hydrogen charging. 304L stainless steel typically exhibits ductile fracture with necking and shear-lip at the ends of tensile fractures. In addition, in the tensile fracture surface, there are some pores at the grain boundaries and the inclusions are observed, but the dimples are generally observed. Especially, it can be seen that a ductile-fracture mechanism in which a large amount of dimples are present in the necking

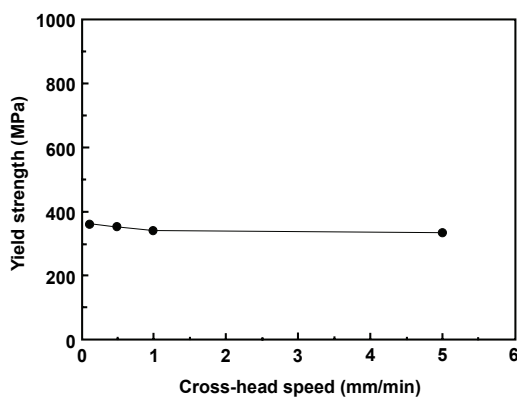


Fig. 7 Effect of cross-head speeds on the yield strength of hydrogen-charged 304L stainless steels.

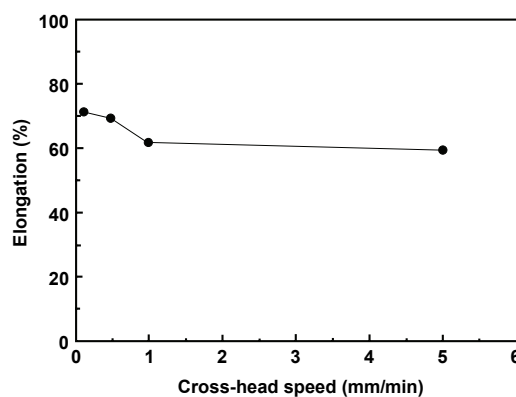


Fig. 8 Effect of cross-head speeds on the fractured elongation of hydrogen-charged 304L stainless steels.

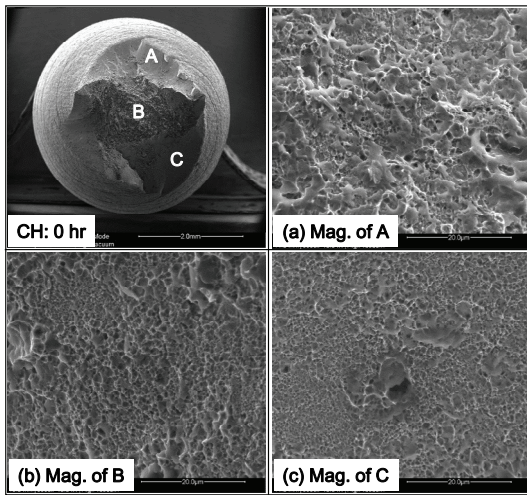


Fig. 9 Fractured surface of 304L stainless steels without the hydrogen charging.

portion and the shear-lip portion in which the plastic deformation is remarkable.

Fig. 10 shows the tensile test specimen fracture of 304L stainless steel with increasing hydrogen charging time. As shown in Fig. 9 and Fig. 10, it can be seen that 304L stainless steel is accompanied by plastic deformation such as shear-lip even when hydrogen is charged, and the tensile fracture pattern does not show a large difference. However, at the edge of the tensile test specimen, the occurrence of dimples is greatly reduced and is turned to a cleavage wavefront as the hydrogen charging time increases. In particular, specimens charged with hydrogen for 48 hours exhibit fracture patterns accompanied by roughly torn fractured surfaces. It can be seen that the tensile failure mode of the 304L stainless steel is greatly affected by the edge portion

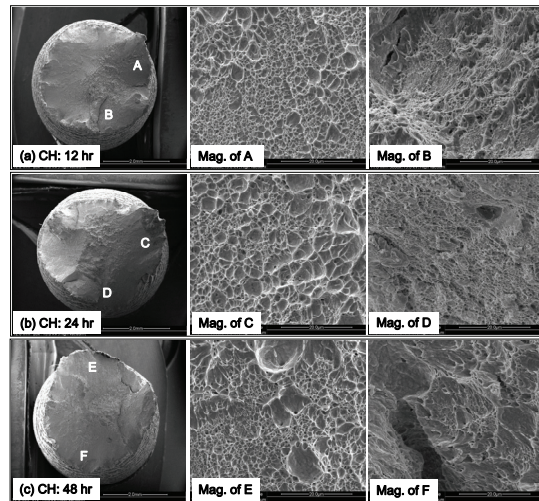


Fig. 10 Fractured surface of 304L stainless steels by the variation of hydrogen charging times.

of the material to which hydrogen is charged. It is believed that the charging of hydrogen to 304L stainless steel causes a decrease in ductility due to surface embrittlement accompanied by a change in the fracture form of the material.

4. Conclusions

- 1) The amount of hydrogen charged into 304L stainless steel increased significantly with increasing hydrogen charging time by electrochemical method. In particular, when hydrogen was charged for 24 hours, the 304L stainless steel showed a hydrogen content of about 18.0 ppm, which is about three times that of a sample not

charged with hydrogen.

- 2) 304L stainless steel without hydrogen charging showed typical ductile fracture behavior with necking and shear-lips during tensile rupture. It also showed tensile strength of about 750 MPa and yield strength of about 280 MPa with fracture elongation of about 69%.
- 3) The yield strength of 304L stainless steel was maintained at a constant level as the hydrogen charging time increased, but the maximum tensile strength tended to decrease. In particular, the fracture elongation of 304L stainless steel was very sensitive to the charging of hydrogen compared to the maximum tensile strength. The increase of the hydrogen content by increasing charging time greatly reduced the fracture elongation accompanied by the embrittlement of the material surface.
- 4) The maximum tensile strength, yield strength and fracture elongation of 304L stainless steel charged with hydrogen showed a tendency to decrease as the cross-head speed increased. In particular, the fracture elongation of 304L stainless steel steeply decreased in cross-head speed range from 0.12 to 1.0 mm/min.
- 5) 304L stainless steel showed similar tensile fracture profile with plastic deformation even when hydrogen was charged. However, as the hydrogen charging time increases, the dimple is

greatly decreased and is changed to cleavage wavefront which means a decrease in ductility on the surface of the material.

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