

# EVALUATION OF METAL MATERIALS FOR HYDROGEN FUEL STATIONS

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## ABSTRACT

Under government funded project: " Development for Safe Utilization and Infrastructure of Hydrogen" entrusted by New Energy and Industrial Technology Development Organization (NEDO), special material testing equipment with heavy walled pressure vessel under 45MPa gaseous hydrogen is facilitated. Tensile properties, strain controlled, low-cycle and high-cycle fatigue and fatigue crack growth tests on CrMo steel (SCM435 (JIS G 4105)) which will be applied for the storage gas cylinders in Japanese hydrogen fuel stations are investigated.

The results of the tensile tests under 45MPa ultra high purity hydrogen gas ( $O_2 < 1\text{ppm}$ ) at room temperature shows that there are no difference in yield and maximum tensile strength with those tested in air. However, the reduced ductilities with brittle fracture surface were observed which indicates the occurrence of hydrogen environment embrittlement. It was also found by tensile tests that the embrittling origin is not only caused by machined traces on surface but also by the non-metallic inclusions dispersed on surface. Further discussions on surface treatment effects will be presented.

In low cycle fatigue tests, considerable reductions in cycles to failure in 45MPa ultra high purity hydrogen gas were observed. However, there are tendencies that the effect of hydrogen environment embrittlement becomes not so significant as the plastic strain range decreases. It was demonstrated that there was no effect of hydrogen on fatigue limit and this implies that CrMo gas cylinders can be operated in limited fatigue safe condition. Another series of hydrogen test results, temperature effect, fatigue crack growth rate, delayed fracture test using wedge opening loaded specimens, and fatigue test of CrMo gas cylinders under repeated internal pressure with artificial crack will be presented.

## 1. INTRODUCTION

For the safe use of fuel cell cars, the Japanese government and industry are now looking at the regulations and recommended practices for the utilization of hydrogen gas. Since many metal materials will be applied in hydrogen fuel station, it is necessary to establish the appropriate design, manufacturing practice and inspection planning considering material performance under high pressure hydrogen environment. Since hydrogen fuel stations in Japan are now designed to supply 35MPa high pressure hydrogen to fuel cell vehicles, the storage pressure might be higher than 35MPa and thus components must withstand under 45MPa (or more higher) hydrogen gas environment.

Almost no service failures of commercial 15MPa hydrogen pressure cylinders have not been reported to date. This is because steels used for those cylinders are low strength carbon steels which are, fortunately, not susceptible to hydrogen embrittlement. However, in case of high strength, low alloy steel, it had been recognized that external hydrogen gas would cause severe hydrogen embrittlement. Ohnishi [1] surveyed hydrogen embrittlement of AISI 4340 steel in ambient gaseous hydrogen and presented that hydrogen cracking occur with almost "no incubation time". During 1960-1970's, several researchers identified such characteristic behaviors in gaseous hydrogen [2] [3] [4], and this phenomenon is denoted "hydrogen environment embrittlement(H.E.E.)" as distinguished from the embrittlement of hydrogen charged steel(Table1) [5]. A lot of work supports the fact that H.E.E. occurs after the steel (or metal) is subjected to the plastic deformation. This is considered because crack initiation is associated with hydrogen adsorption and absorption process at the fresh metal surface breaking the oxide barrier. It is also well known that the impurity gases such as oxygen significantly interfere hydrogen embrittling process at the crack tip even in ppm level [2] [6]. Knowing that such

Table 1 Hydrogen embrittlement classification by H.R.Gray [6]

Category	Example
I.H.E. Internal Reversible Hydrogen Embrittlement	Cracking by absorbed hydrogen •Delayed fracture of HSLA steel •HIC •Cold cracking etc.
H.R.E Hydrogen Reaction Embrittlement	1.Formation of hydride Ti,Zr,Hf,V,Cb,Ta,Mn,Ni,Pd,U,Pu,Th 2.Hydrogen Attack Methane bubbles formation under high press. High temp. H
©H.E.E Hydrogen Environment Embrittlement	Cracking by gaseous hydrogen environment •Failure incident of hydrogen storage tank of 18Ni-Maraing steel 30years ago.

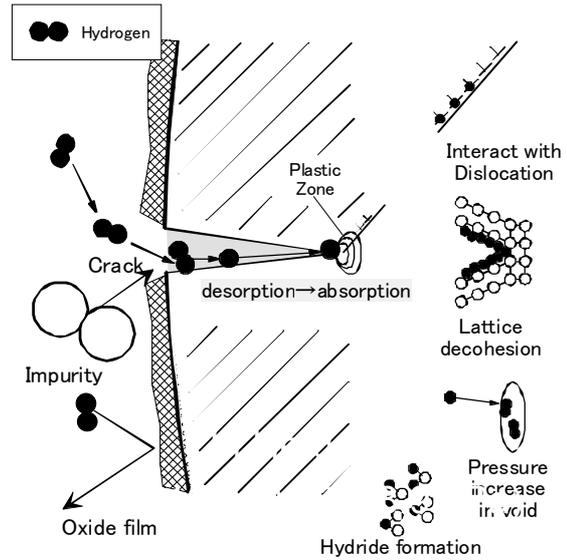


Figure 1 Factors affecting hydrogen environment embrittlement by Nelson .H.G. [3]

characteristic behavior in gaseous hydrogen, to contribute the development of recommended practices for material selection, safety operation and inspection intervals for hydrogen fuel station, the material testing on CrMo steels for gas cylinders under 45MPa gaseous hydrogen was extensively performed.

## 2. EXPERIMENTAL

### 2.1 Test equipments

Table 2 shows test items. In order to perform such tensile test, fatigue test and fracture mechanics testings, hydraulic servo controlled testing machine with pressure vessel (Figure 2) was facilitated. The pressure vessel has an inside diameter of 240mm and the depth of 500mm. The actuator capacity is 240kN in tension and 100kN in compression. Load calculator cancels load component raised from the pressure so that the external load cell can measure the specimen load only. Strain was measured by clip-on type extensometer or measured through the rod mounted to the specimen so that the transducers outside of the top projection of the autoclave detected the rod position.

Figure 3 shows 45MPa H<sub>2</sub> exposure autoclave for the delayed fracture tests. The critical depth of flaw that would not propagate under the static, sustained displacement controlled load, was evaluated by long term hydrogen exposure of wedge opening loading(WOL) specimens. Tests were conducted by exposing stressed WOL specimen to hydrogen gas in temperature-controlled autoclave for up to 1000hrs.

Figure 4 shows pressurization test equipment system on artificially defected cylinder specimen. The cylinder test specimen was pressurized by hydrogen in the water filling outside chamber. Then repeated outside water pressure was applied from 0 to 45MPa in the speed of approximately 4cycles /minute, which condition is almost equivalent internal gas pressurization condition.

Table 2 Test items

Test Items	Environment	Purpose	Method
Tensile test	45MPa H <sub>2</sub> -40~+85°C	Hydrogen gas effect on tensile properties(0.2%Yield strength, Tensile strength, Ductility)	Ultra high purity hydrogen gas(7N) environment, below 1ppm O <sub>2</sub> level(all tests) Evaluate surface finishing effect
Fatigue test	45MPa H <sub>2</sub> RT	Hydrogen gas effect on crack initiation and cycles to failure	Strain controlled low cycle fatigue tests Load controlled high cycles fatigue tests Tension/Compression cycles(R=-1)
Delayed fracture test	45MPa H <sub>2</sub> -40~+85°C	Threshold stress intensity factor K <sub>IH</sub> under static loading conditions	Wedge Opening Loaded specimen in long term H <sub>2</sub> exposure
Fracture toughness test	45MPa H <sub>2</sub> -40~+85°C	Hydrogen gas effect on fracture toughness of the steel	Evaluate fracture toughness using pre-cracked specimen(ASTM E399)
Crack growth test (da/dN)	45MPa H <sub>2</sub> RT	Hydrogen gas effect on fatigue crack growth rate	Evaluate crack growth rate(da/dN) using pre-cracked specimen
Pressurization test on defected cylinders	45MPa H <sub>2</sub> RT	Clarify hydrogen fracture behavior of cylinders	Apply repeated external water pressurization to 45MPa H <sub>2</sub> pressurized cylinder

Table 3 Chemical compositions of the CrMo steel

Chemical composition			Mass %								
			C	Si	Mn	P	S	Cu	Cr	Ni	Mo
Steel	Spec.	Max.	0.32	0.15	0.6	-	-	-	0.9	-	0.15
		Min.	0.39	0.35	0.85	0.030	0.030	-	1.2	-	0.3
	Heat No.	1	0.36	0.23	0.76	0.014	0.010	0.020	1.06	0.03	0.19
SCM435	Spec.	Max.	0.38	0.15	0.60	-	-	-	0.90	-	0.15
		Min.	0.43	0.35	0.85	0.030	0.030	0.030	1.20	-	0.3
	Heat No.	A	0.42	0.22	0.76	0.008	0.003	0.02	1.10	0.02	0.24
		B	0.40	0.24	0.76	0.012	0.004	0.02	1.02	0.01	0.21
C	0.42	0.23	0.77	0.012	0.0016	0.02	1.00	0.02	0.18		

Table 4 Mechanical properties of steel tested

Steel	Heat	Thickness	Heat treatment		Tensile test				Impact test
			Austenizing	Tempering	T.S. (N/mm <sup>2</sup> )	0.2%Y.S. (N/mm <sup>2</sup> )	Reduction of Area (%)	Elongation (%)	2mmU Notch -RT (J/cm <sup>2</sup> )
SCM435	-	35mm	850°Cx2.0hr/OQ	530°Cx4.0hr/AC	958	781	19	58	80
SCM440	A	16mm	855°Cx0.7hr/AC	580°Cx0.7hr/AC	1060	947	20	58	-
	B	70mm	860°Cx2.0hr/OQ	560°Cx2.5hr/AC	979	773	19	54	58
	C	28mm	855°Cx1.2hr/OQ	580°Cx1.2hr/AC	1018	875	21	59	150

## 2.2 Specimen Preparation

Figure 5 shows the specimens used in hydrogen mechanical testing. Tensile specimen was prepared in order to study the surface finishing condition, i.e. 1) Roughly machined surface, 2) Highly polished surface by abrasive paper (#800), 3) Electro polished surface. Fatigue test specimen was prepared by highly polished surface by abrasive paper (#800). For fracture toughness testing, compact tension specimens of 25.4mm thick (1T-CT) were pre-cracked in air then long term H<sub>2</sub> exposure were conducted.

For delayed fracture test, wedge-opening load specimen of 25.4mm thick (1T-WOL) were pre-cracked in air then stressed by load pin and bolting. The 1T-WOL specimens were stressed in air to predetermined stress intensity factor levels and placed in the autoclave. The specific testing method is according to JSPS [7] method in principle and the test conditions were determined by referring to the work of Loginow and Phelps [8].

The Pressurization test on cylinders with internal surface defects were performed. Cylinder specimen made of CrMo steel, has an inside diameter of 100mm, 7mm in thickness and 500mm in length with artificial defect at inside surface. Initial artificial defect was inserted by electro spark machining then after that, fatigue crack was propagated in air by pressing the cylinder surface using hydraulic test machine. Fatigue crack was propagated until the surface crack reaches 4mm in length, and the 1mm in depth.

## 2.3 Material

Test materials are commercial quenched & tempered SCM(JIS G 4105) low alloy series: SCM435 and SCM440 which are the popular materials for the high-pressure equipment. Chemical compositions and mechanical properties are shown in Table 3 and Table 4. The SCM435 steel was supplied by 35mm thick forged plate. SCM 440 heat A,B and C are 16mm, 70mm and 28mm in each thickness and all are rolled plate.

## 2.4 Environment

It is well known that the hydrogen environment embrittlement is affected by the purity of surrounding hydrogen gas since hydrogen environment embrittlement by gaseous hydrogen occurs by gas phase diffusion of molecular hydrogen to some critical location where metal is stressed and/or stressed crack surface. For such reason, to minimize the experimental uncertainty caused by impurity gases, hydrogen gas used for material testing is 99.99999% purity by volume with the following impurity levels: O<sub>2</sub><0.02ppm, CO<0.01ppm with a dew point of - 80°C. Pressurization and system purging is conducted before testing:through (1) pressurization with dry N<sub>2</sub> gas, (2) evacuation and (3) pressurization/ depressurization with the pure hydrogen gas.

## 3. RESULTS AND DISCUSSION

### 3.1 Tensile Properties

Figure 7 shows stress versus strain curves tested in various crosshead speeds using highly polished specimen by abrasive paper (#600) in 45MPa gaseous hydrogen at room temperature. There were no significant differences in tensile deformation behaviors between air environment and 45MPa hydrogen until the maximum load point. However, hydrogen tested specimen ruptured with less ductilities and examination of fracture surfaces revealed the occurrence of hydrogen embrittlement. The effect of surface finishing conditions on the hydrogen ductility was surveyed. Figure 8 shows the comparison of hydrogen tested specimen surface between as-machined condition and electro polished condition. Many cracks on surface generated along with the machined traces for as-machined specimen. On the other hand, for the electro-polished specimen, almost no surface crack observed. The duplicated

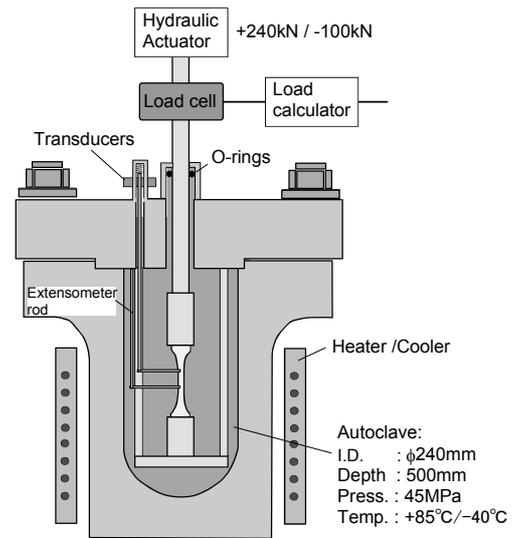
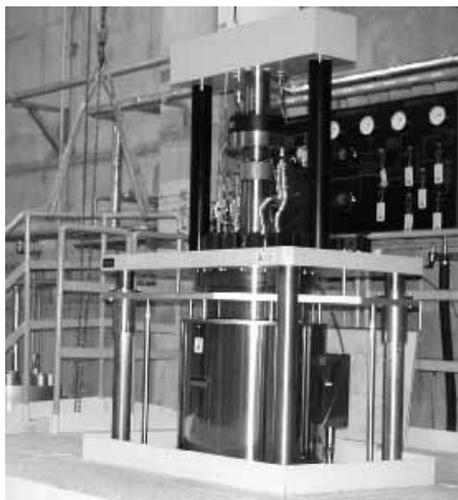


Figure 2 Hydraulic fatigue testing machine

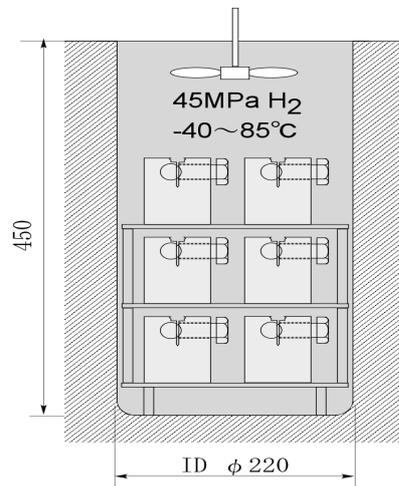


Figure 3 45MPa H<sub>2</sub> exposure autoclave for the delayed fracture tests

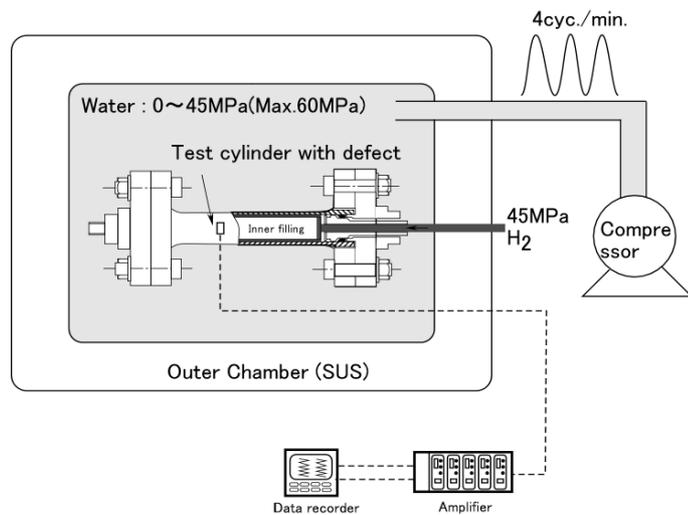
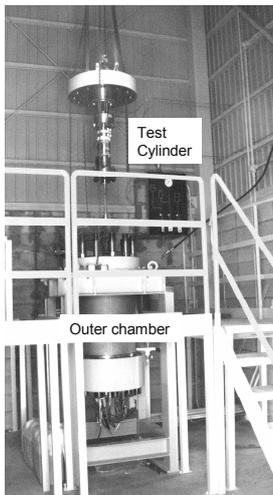


Figure 4 Pressurization test equipment system on defected cylinder specimen

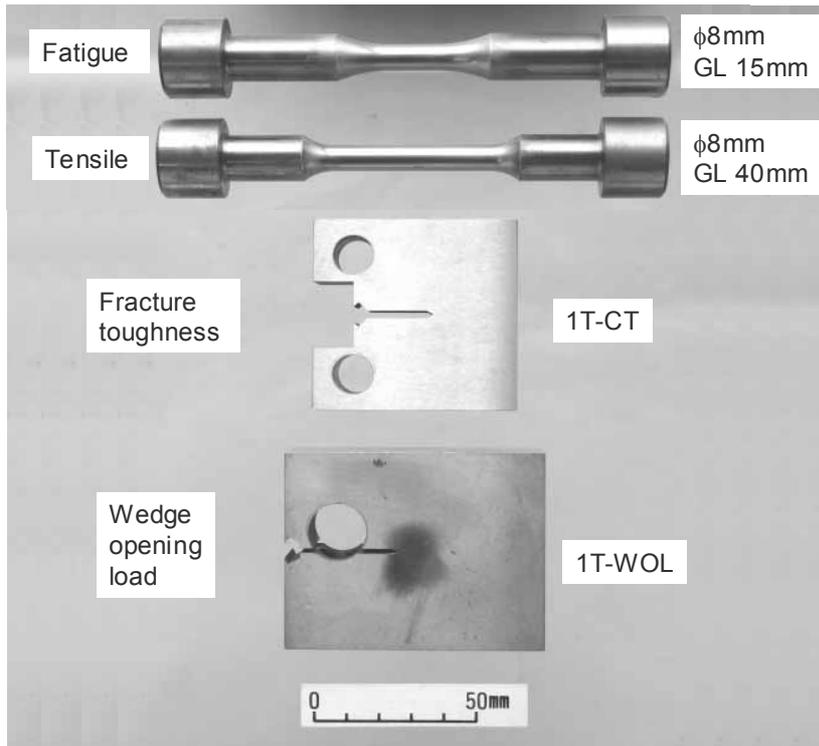


Figure 5 Specimens used in 45MPa hydrogen mechanical tests

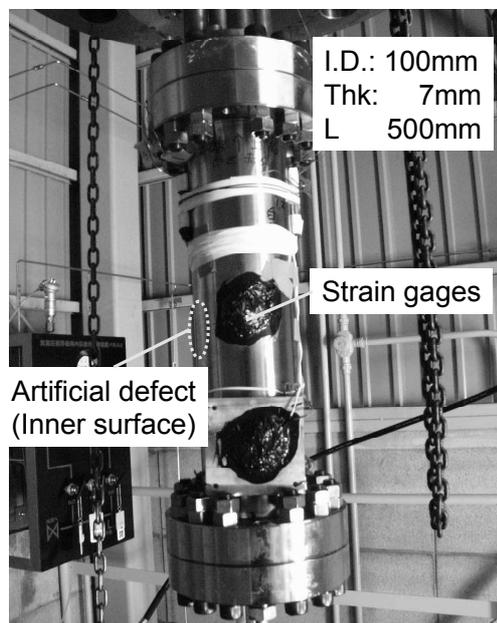


Figure 6 Cylinder specimen with artificial defect

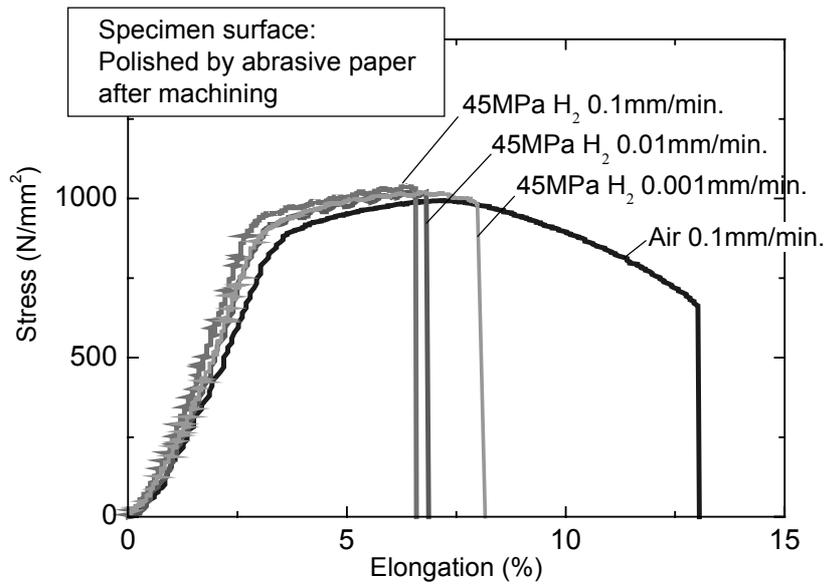


Figure 7 Tensile curves of SCM440-heat A under 45MPa gaseous hydrogen and 0.1MPa air(tested by another facility)

hydrogen tension tests on those two different kinds of specimen surface conditions were conducted at a strain rate of approximately  $10^{-5}/s$ . The scatters in ductilities are shown in the form of Weibull diagram in Figure 9. The apparent tendency except one data point for the electro-polished specimen can be recognized that as -machined condition is lower and more scattered in ductilities than the electro polished ones. The cause of the one exception of electro-polished specimen, which resulted in poor ductility is in question however, the fracture is possibly due to the non metallic inclusion which was observed at the very center of the fracture origin in Figure 8(b). The important findings are, that surface roughness, dispersed non metallic inclusions acts as embrittling origin and such surface characters drastically affects the tensile ductilities in hydrogen gas.

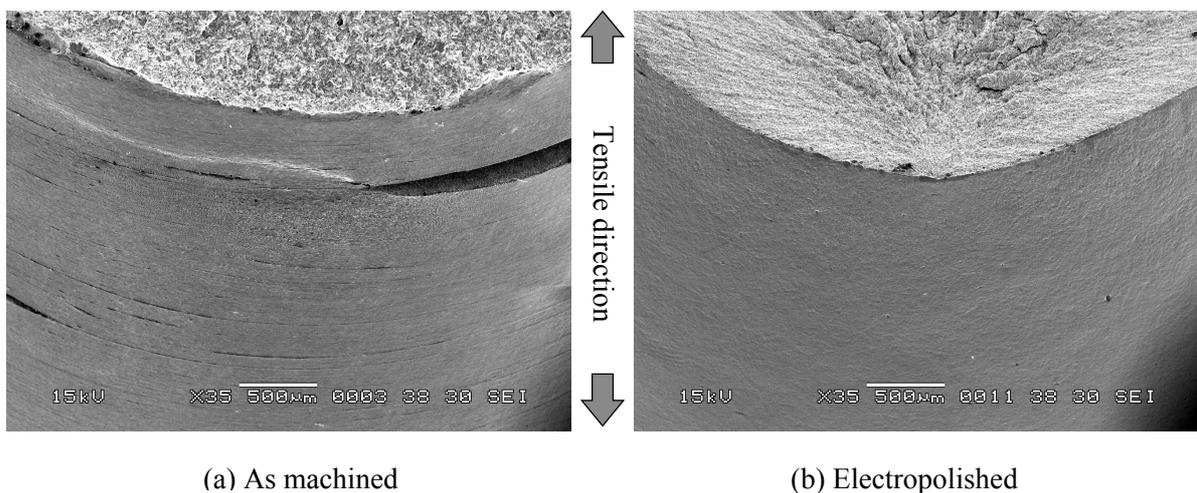


Figure 8 Comparison of fracture surfaces of hydrogen tested specimens

### 3.2 Fatigue effect

Figure 10 summarizes the fatigue test results for both SCM435 and SCM440 heatC steels. In low cycle fatigue tests, considerable reductions in cycles to failure in hydrogen gas were observed while

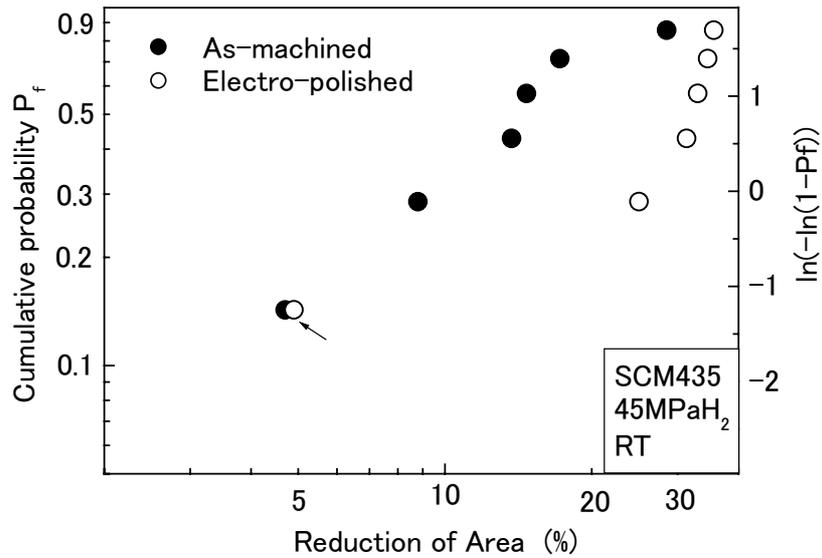


Figure 9 Scatters in ductility in hydrogen tension tests for different surface finishing conditions

there are tendencies that the effect of hydrogen environment embrittlement becomes not so significant as the plastic strain range decreases. High cycle fatigue test demonstrated that there was no effect of hydrogen on fatigue limit. Those tendencies imply that CrMo steel gas cylinders can be operated in such a limited fatigue safe condition that the material is sound without no critical defects as well as the extent of maximum stress amplitude at the critical stressed location not exceed the fatigue limit in air at least. However, surface effects such as roughness, dispersed impurities and residual stress raised from cold working etc. may possibly affect the fatigue properties in hydrogen as implied by hydrogen tension test results, which has to be clarified in the future study.

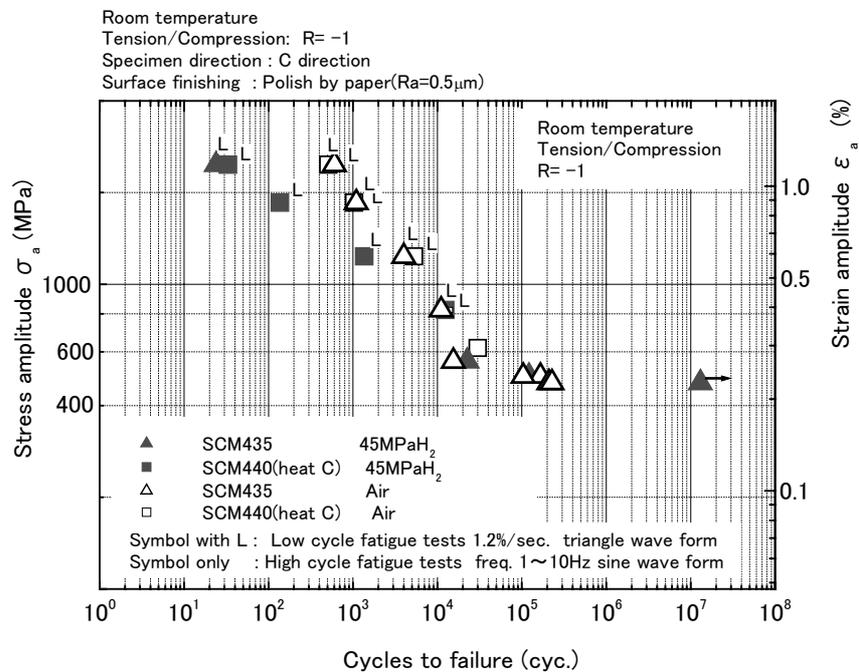


Figure 10 Fatigue test results

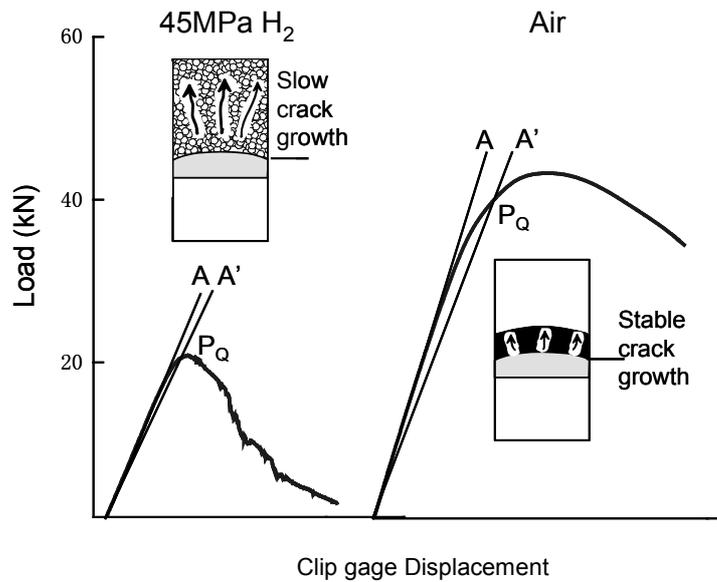


Figure 11 Fracture toughness test results and schematic illustration of fractured specimen

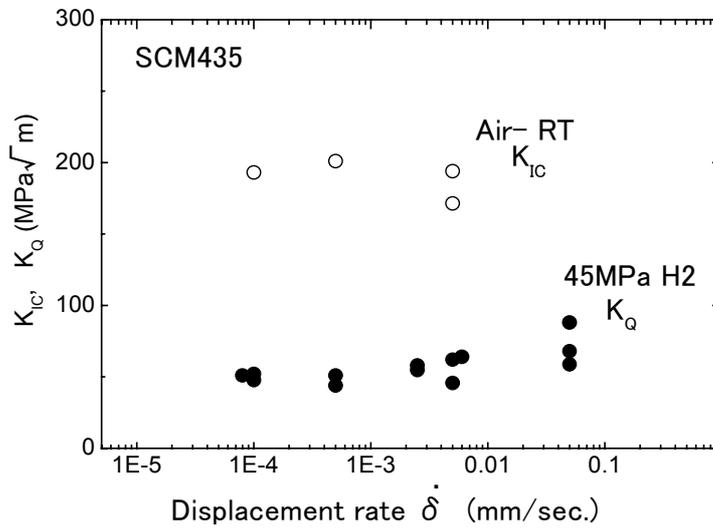


Figure 12  $K_{IC}$  in air and apparent  $K_Q$  in hydrogen evaluated by E399 offset method

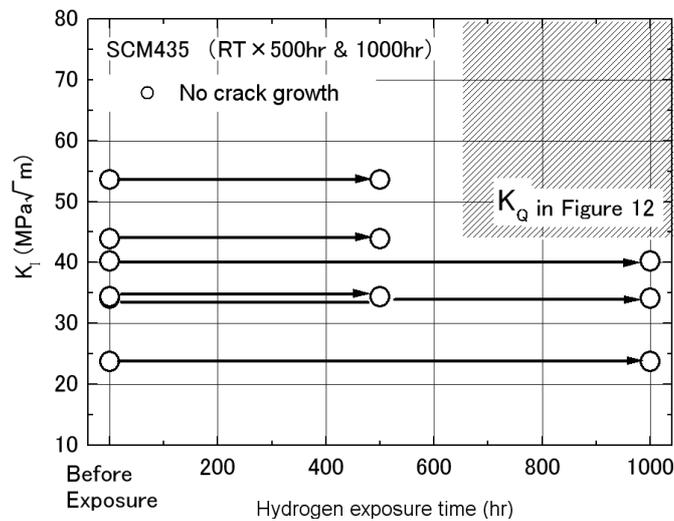


Figure 13 Delayed fracture test result of SCM435 at room temperature

### 3.3 Fracture toughness

Fracture toughness was attempted to be evaluated by the ASTM E399 method (except loading rate is not according to this method here) for SCM435 steel. Figure 11 shows the stress / displacement curves for both in hydrogen and in air with the schematic illustration of fractured specimen surface of the compact tension specimen. In hydrogen tested curve, the non linearity begins at lower load compared to the curve tested in air. This is correspond to the occurrence of slow crack growth as is evidenced by the examination of fracture surface. Therefore, the evaluated load  $P_Q$  by 95% scant line, is the stress intensity factor  $K_Q$  at the onset of crack growth due to the hydrogen environment embrittlement. Rising load tests under various displacement rates ranging from  $1 \times 10^{-4}$  mm/sec to  $5 \times 10^{-2}$  mm/sec (approx.  $\dot{K}=0.01$  to  $0.6 \text{ MPam}^{1/2}/\text{s}$ ) were performed. Those  $K_Q$  in hydrogen and  $K_{IC}$  in air were plotted in Figure 11. In hydrogen, no cleavage fracture occurred in all the specimens tested. The specimen were all fractured in consecutive slow crack growth manner with hydrogen embrittled fracture surface as same as illustration in Figure 11. This means the fracture toughness of the steel itself does not degrade in gaseous hydrogen. Thus, the countermeasure to prevent unstable fracture of hydrogen gas containing component might be at least the steel's toughness in air is sufficient enough to yield 100% shear fracture surface without no cleavage fracture surface at the minimum servicing temperature. The reminded question is that the effect of dissolved hydrogen on the fracture toughness apart from this gaseous hydrogen effect. The susceptibility to the dissolved hydrogen effect on internal hydrogen embrittlement (I.H.E.) might increase with increased exposing pressure and environmental temperature because of the solubility increase. Whether the fracture toughness affected by those dissolved hydrogen remains unresolved so far and should be undertaken for future study especially when pressure becomes higher condition (say for 105MPa).

### 3.4 Delayed fracture test on wedge opening load

In order to evaluate the critical depth of flaw that would not propagate under the static, sustained displacement controlled load, long-term hydrogen exposure of wedge opening loaded specimens was conducted to measure critical stress intensity factor  $K_H$ . Figure 13 represents the test results of SCM435 steel exposed to room temperature 45MPa hydrogen gas for 500hr and 1000hr exposure. No measurable crack extension were observed for all specimens and  $K_H$  was not determined. It is considered that the critical stress intensity factor is at least below the stress intensity factor of  $40 \text{ MPam}^{1/2}$ , however, the stress intensity factor at the onset of crack growth  $K_Q$  measured under rising load condition is  $44 \text{ MPam}^{1/2}$  in Figure 12 while no crack extension in 500hr exposure at applied stress intensity factor level of  $55 \text{ MPam}^{1/2}$ . Such tendency is also reported by several papers [9] [10] that the susceptibility to hydrogen embrittlement cracking is attenuated under sustained load condition while crack growth rate increases under the fluctuating load condition. Thus,  $K_H$  value obtained from this study is interpreted as a threshold stress intensity factor under the limited service condition that the loading condition is controlled displacement type loading and crack has already existed before hydrogen exposure.

### 3.5 Pressurization tests on defected cylinder

To date, we have completed two tests on hydrogen internal pressurizing condition and nitrogen internal pressurizing condition. As a result of those, it was observed that the cycles to failure is shorter in hydrogen-pressurized cylinder than nitrogen pressurized one. Also, hydrogen tested fracture surface was entirely dominated by quasi-cleavage with some intergranular fracture surface. The fracture behavior was a leak before break manner for the hydrogen-tested cylinder as well as the nitrogen - tested cylinder. This result is consistent with the fracture behavior of fracture toughness test specimen where hydrogen gas generates slow crack growth, not result in cleavage, brittle fracture manner, as long as the stress intensity factor at the crack tip does not exceed fracture toughness in air and fracture toughness is sufficient enough to yield ductile 100% shear fracture surface in air.

#### 4. SUMMARY

A series of material testing under 45MPa ultra high purity hydrogen gas for CrMo steels for hydrogen gas cylinders was performed and hydrogen gas effect on steel degradation was evaluated. We have clarified factors affecting external hydrogen gas at 45MPa pressure environment.

1. Strain effect            Hydrogen tension test and fatigue tests evidenced that hydrogen environment embrittlement become significant as the magnitude of plastic strain increases.
2. Surface effect            Surface roughness, dispersed non metallic inclusions act as embrittling origin and such surface characters drastically affects the tensile ductilities in hydrogen gas.
3. Fracture behavior        Hydrogen gas generates slow crack growth, not resulting in cleavage, brittle fracture manner, as long as the stress intensity factor at the preceding crack tip does not exceed the fracture toughness in air and sufficient enough to yield 100% shear fracture surface.

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