

Hydrogen Susceptibility of Pre-strained Type 316L Austenitic Stainless Steels in Aqueous Solutions

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Abstract. This paper presents the observations made as a result of hydrogen effects in austenitic stainless steels which led to reduction of its original mechanical properties. This paper therefore seeks to understand the mechanisms and effects induced by hydrogen leading to embrittlement. The samples of Type 316L austenitic stainless steel with 20% pre-strain were charged with hydrogen through galvanostatic cathodic loading for 12, 24, 36, and 48 hours respectively, with sample as Cathode and the platinum wire as Anode. Afterwards, they were fractured under tensile test at a slow strain rates. The loss of ductility was evident as observed by the brittle nature of fracture. Small pieces were cut-off near the fracture region and examined through XRD and SEM analysis. The peak widening and slight shifting of the peak positions was observed. The surface cracking was also observed, an indication of surface-induced stresses. The severity of the effects increased with the hydrogen loading time, which is predictive of a real service conditions for austenite steels in aqueous environments.

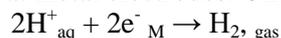
1. Introduction

The hydrogen effects in metals and their alloys are rather complex and takes quite a deal to understand the interaction between hydrogen and constituent metals. Most of other forms of hydrogen degradation involving phase transformations are easily understandable and can therefore be remedied by simply identifying the actual cause of the damage causing process [1-4]. Though a concerted efforts have been dedicated to related research, comprehensive understanding of the damage process involved is much more intricate and overcoming the damage processes has proven quite difficult. This is in relation to its interdisciplinary attribute covering electrochemistry, materials science, and mechanics. Again, hydrogen being the lightest element, it has high mobility and insensitive to external excitations, thus making its detection difficult. Hydrogen and a surrounding stress fields have complex interactions in stainless steel materials [2]. More often, austenitic stainless steels find their various applications in service conditions that are frequently characterized by aqueous environments. The hydrogen source, the temperature and the duration of hydrogen exposure determines the potential severity of hydrogen embrittlement [3]. Consider the power plants for example, which comprises the bulk of austenitic stainless structural materials, and which run for long periods. Absorbed gases, some of which contains hydrogen elements like H₂S in geothermal power plants or hydrogen in water molecule and or the mass evolution of hydrogen gas in nuclear power plants are some of the sources of hydrogen that interact with the structural austenitic stainless steels in service conditions. Hydrogen is absorbed in metals as an atom or screened proton rather than as a hydrogen molecule. So, the absorption of hydrogen requires the presence of atomic (nascent) hydrogen on the metal surface [3-4]. Therefore, aqueous environments are rich source of hydrogen that absorbs into the metallic bulk over time.

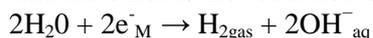


Austenitic stainless steels are less susceptible to hydrogen embrittlement because of low diffusivity and high solubility of hydrogen in the F.C.C. structures, although in severe environmental conditions, the brittle fracture associated with hydrogen embrittlement (HE) is observed [5-6].

The cathodic reaction for usual metallic corrosion is carried by the hydrogen reaction and/or the oxygen reaction. For the hydrogen reaction, there are two cathodic processes that produce hydrogen gas at metal electrodes. One is the reduction of hydrogen ions;



and the other is the reduction of water molecules.



Pure diffusion does not sufficiently provide hydrogen penetration far from the surface of the sample because of the low diffusivity of hydrogen in AISI 316L. Therefore, the objective of this study is to identify and predict the progressive degradation involved in HE by cathodic charging for strained Type 316L stainless steel at 40° C.

2. Experiment

The apparatus used in this experiment included the galvanostatic cell for hydrogenation, Ringaku Ultima-IV X-ray diffractometer for XRD analysis, Kyowa ME-LUXZ optical microscope for surface observation, JSM- 7610 JOEL Field Emission scanning microscope and AG50KNX (Shimadzu) tensile testing machine. The investigations were performed on commercial type 316L austenitic stainless steel. The as- received sample was annealed at 1000 °C for 1 hour. The test specimens were supplied in the form of 1mm thick plate. The hydrogen cathodic loading was carried out at 40° C by a chemical cell hydrolysis using 0.5M H₂SO₄ for 12, 24, 36, and 48 hours respectively, at current density of 4.5 mA/cm², with sample as Cathode and the platinum wire as Anode. The slow tensile deformation rates (0.02 mm/s) were employed for optimal results. The chemical composition of the 316L stainless steel used in this study is given in Table 1.

Table 1. Chemical composition of the test sample

C	Cr	Ni	Mo	Mn	Si	P	S	Co	N
0.017	18.0	14.0	3.0	2.0	0.75	0.007	0.03	0.15	0.1

3. Results and discussion

The resultant mechanical properties of the samples is given in figure 1 in the form of stress-strain curves and tabulated results as shown in table 2. The hydrogen uncharged and charged specimens including the un-strained/non pre-charged sample. This specimen which in this case is referenced, had zero strain and zero charge. It can therefore be clearly seen that hydrogen charging deteriorated the ductility property with increasing time of charge. The hydrogen charging decreased the elongation from 40.7% to 35% after 48 hours of charge. The hydrogen effect on tensile strength showed distinct decline with increased charging time though the results fluctuates between 24 hours and 36 hours of charge time.

Table 2. Mechanical properties before and after charging.

Specimen	UTS MPa	Yield Strength Mpa	Elastic Modulus GPa	Ductility %
0% S 0 hour charged	524.7	203	193	40.7
20% S 12 hour charge	506.1	197	218	39.3
20% S 24 hour charge	504.9	420	201	35.7
20 % S 36 hour charge	510.0	423	187	37.1

20% S 48 hour charge	488.7	405	170	35.0

On the other hand, hydrogen charging effects on the yield strength drastically increased with time, and the mixed results on Modulus of elasticity was observed. The results of the charged specimens fluctuated above and below that of the As-received annealed sample. The general tendency on the mechanical property deterioration increased with increasing hydrogen charging time. In many studies of the hydrogen embrittlement, the elongation and reduction of area loss (RA) are often used as the evaluation criteria, due to the well-established knowledge of hydrogen effect on the material ductility[7], though in this paper, the RA is not utilised owing to the geometry of the test samples used. The changes in tensile strength can be attributed to densities of dislocations and mechanical twins induced by pre-strain, different absorption rates of hydrogen into the material's voids partly occasioned by the pre-strain [6-7].

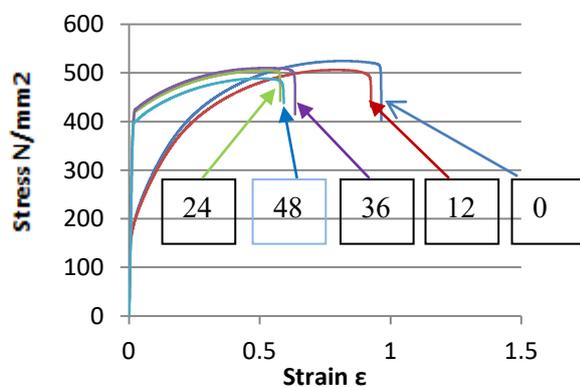


Figure 1. Stress-strain tensile curves of the tested Samples.

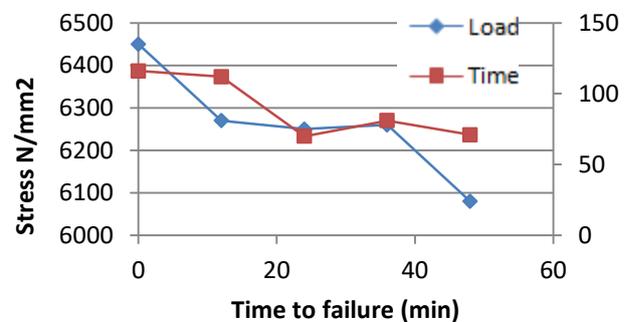


Figure 2. Stress to failure time.

The Modulus of elasticity and ductility tends to gradual decrease with time and agrees well with many research findings [7-9]. This is expected because of hydrogen accumulation at pores and microspores associated with the grain boundaries and micro structural defects caused by the pre-strain, leading to the hardening of the material. These results indicate that the overall resistance to HE deteriorated with the charging time. Hydrogen diffusion is well known to be activated by plastic deformation and that the activation is time dependent [8]. The time-to failure results supports that theory as is evidently shown in figure 2. This result is consistent with transport of hydrogen by dislocations occasioned by pre-strain [6, 9]. The presence of hydrogen in steel reduces tensile ductility and causes premature failure under static load that depends on the stress and time [10, 14].

To investigate the effects relating to ductility loss with hydrogen charging time and the pre-strained condition of the specimens, small pieces were cut off near the fractured region and the XRD and SEM tests conducted on them. All the xrd fractographs showed an austenite single phase without the reflections of ϵ -martensite peak. The diffraction patterns were analysed and plotted as shown in figure 3. Although the hydrogenation of 316L stainless steel seems to have caused the expansion of the austenite lattice, there were no significant reflections other than FCC that appeared in the diffraction patterns.

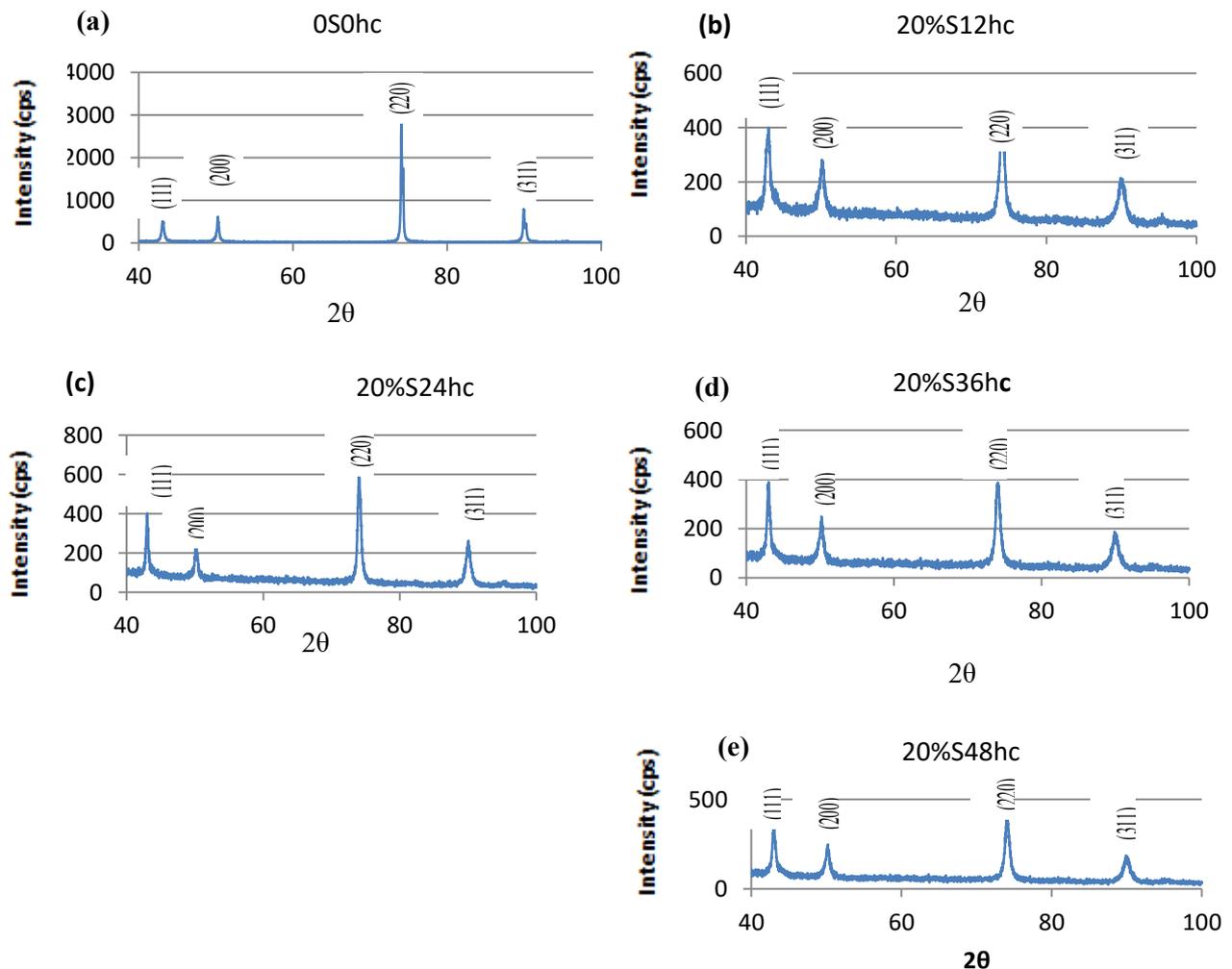


Figure 3. XRD diffraction patterns, (a) Unstrained and uncharged, (b) 20% strain with 12 h charge, (c) 20% strain with 24 h charge, (d) 20% strain with 36h charge and (e) 20% strain with 48h charge.

Based on investigations carried out on austenitic stainless steels type 304 and 310 [11], it was observed that there was continuous expansion of the austenite lattice due to hydrogen charging of 304 and 310 stainless steels. Slight shift of diffraction peaks and lines broadening were observed after hydrogen charging. Hydrogen penetration considerably expands the lattice and causes the significant shift of diffraction peaks toward the lower 2θ angles. After 48 hours of hydrogen charging, the 1 1 1 peak centroid was displaced by 0.153 of 2θ .

In the uniform solid solution, the intensity of the diffraction peaks decreases due to local lattice distortion. The reason for peak broadening is the formation of non-uniform solid solution of hydrogen in austenite [12].

SEM micrographs of the fracture surface after charging for 12h, 24h, 36h and 48h are given in Figure 4. Transition between brittle and intergranular ductile fracture was observed in all the hydrogen charged samples, with the outermost edges bearing the brittle fracture, but the fracture mode changes to ductile in the inner depths from the surface. Near the brittle zone, small micro voids of low spatial density are observed (Figures 4c-d). This particular pattern corresponds to a decrease in ductility caused by hydrogen which is present in lower concentrations than near the surface of the

specimen where brittle fracture is prominent [12]. In the case of non-charged sample, the ductile failure is evident where the morphology of micro voids (decrease of density and size) is observed [13].

The presence of hydrogen atoms in a solid metal dissolve in the metal grid and accumulate in disturbed lattice regions resulting in the reduction of its ductility by decreasing the energy of cohesion and thus increasing its probability of brittle failure [14]. In Figure 4c, 4d and 4e, the ductile fracture surface is characterised by the presence of increasingly denser, shallower and smaller equi-axed micro voids, but in figure 4a and 4b, the dimples are larger and deeper. In all the charged samples, quasi-cleavage tear ridges were also observed in different regions of the fracture profile, a confirmation of a significant degree of brittle fracture. These results agree well with the tensile test results in table 2. The decrease of the amount of hydrogen varied inversely with the depth from the surface of the samples to the center because of the lower diffusivity of hydrogen in the austenitic phase [1]. The presence of quasi-cleavage morphology from the brittle areas is a significant effect of the hydrogen transport by dislocations [15]. Shallow brittle multiple cracking were observed on all the sample surfaces. The inhomogeneous hydrogen distribution results in high multiaxial compressive stresses at the surface [16]. Although in this research hydrogen uptake has not been quantitatively analyzed, the results thus obtained cumulatively affirm that the 316L austenitic stainless steels stability to hydrogen embrittlement is significantly affected.

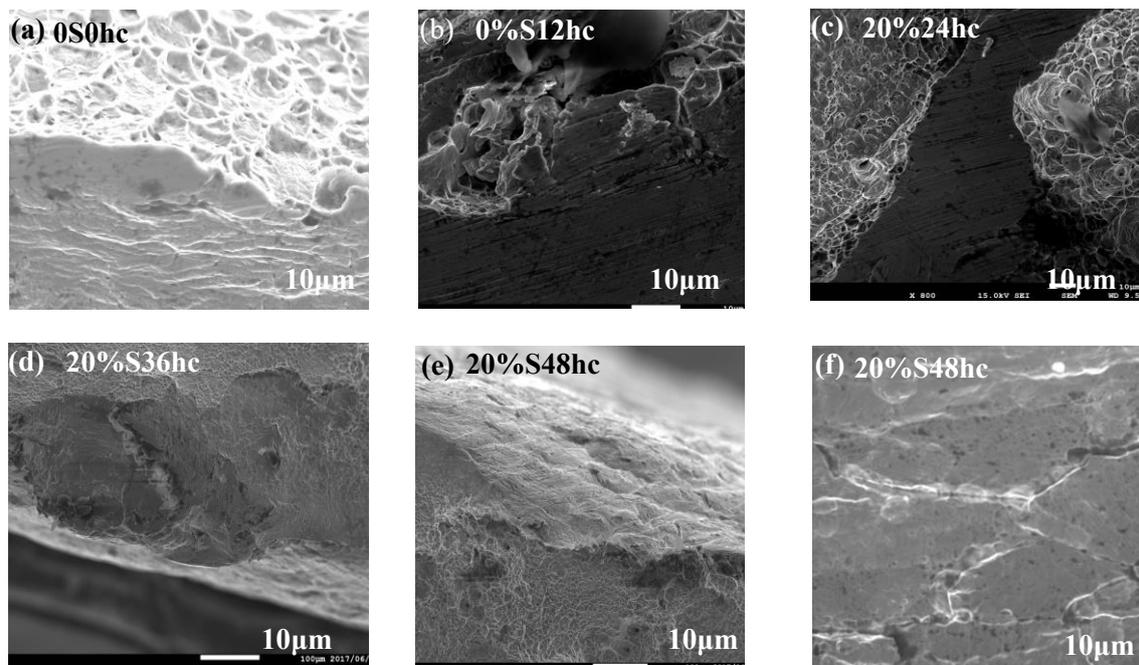


Figure 4. SEM images of the fracture morphologies: (a) non-charged, (b) 12h charge, (c) 24h charge, (d) 36h charge, (e) 48h charge and (f) the surface cracks developed at fracture.

4. Conclusion

The 316L austenitic stainless steels is mildly susceptible to hydrogen embrittlement and the effects increases with time of exposure. Warm temperatures coupled with pre-strain increases the hydrogen uptake and enhanced embrittlement as evidenced by reduction in ductility and brittle fracture morphologies. The 316L stability to HE may not be fully guaranteed especially if the material undergoes long periods of exposure to similar hydrogen environmental service conditions. The density, nature and size of micro voids present on dimpled fracture surfaces is a result of hydrogen effects on the material.

References

- [1] Cayard, R K(1998) Roles of H₂S the behavior of eng. alloys: InterCorr - CL1 International, Inc. Hassani A et al, Effect of Strain Rate on Stress Corrosion Cracking of 316L Austenitic Stainless Steel *J. of Mat. Eng. and Performance*: 2013, June 2013, Vol 22, Issue 6, pp 1783–1789, Lo K H et al , Recent developments in stainless steels, *Mat. Scie. and Eng. R Reports*, 2009 65(4-6):39-104, Fujita F, Sohmura T (1976) Hydrogen in stainless steel and Fe-Ni alloys, *J. de Physique, Colloques, C6, Déc. 1976, Vol. 37, Numéro pp.C6-379-C6-383*, Herms E et al Hydrogen embrittlement of 316L type stainless steel, *Mat. Sci and Eng. Vol 272 issue 2, (1999)*
- [2] Song, Bonnie R Antoun and Bo (2009) Interaction of Hydrogen and Deformation in 316L Stainless Steel, Sandia National Laboratories, Livermore, CA, 94551-0969, USA.
- [3] Louthan M R Jr.(2008) Hydrogen Embrittlement of Metals A Primer for the Failure Analyst *J. of Failure Analysis and Prevention*, Vol 8, Issue 3, pp 289–307
- [4] Djukic M B et al, Hydrogen damage of steels. Article in *Eng. Failure Analysis*, 2015, Vol.58, pp 485-498
- [5] Che`ne J et al, Solutions to Hydrogen Problems in Steels, American Society for Metals, 1981, pp. 263–271
- [6] Che`ne J et al, Hydrogen transport by dislocations and hydrogen embrittlement in stainless steels, Bernstein I M, Thompson A W(Eds.): Effect of hydrogen on behavior of materials, publication of the Metallurgical Society of AIME, New York, 1976, pp. 455-466
- [7] Xu H et al, Evaluation of hydrogen embrittlement susceptibility of temper embrittled 2.25Cr 1Mo steel by SSRT method, *Eng Fail Anal* 19(2012) 43–50 Ian M R et al Hydrogen Embrittlement Understood, The Minerals, Metals Materials Society and ASM International. 2015, Vol. 46B, June 2015—1085
- [8] Herms E et al, Hydrogen embrittlement of 316L type stainless steel, *Mat sci. and Eng. A272 (1999) 279–28*
- [9] ANTON J. et al: Dislocation Transport and Hydrogen Embrittlement, November 1979, Vol. 10, Issue 11, pp 1675–1682
- [10] DAYAL R K and Parvathavarthini N, Hydrogen embrittlement in power plant steels, Springer link, Aqueous Corrosion and Surface Studies Section, June 2003, Volume 28, Issue 3, pp 431–451
- [11] Mathias H, Y Katz and S Nadviv, *Met. Sci.* 12 (1978) 129 & Gavriljuk et al, *J. of Physics. Condensed Matter*, Vol 10, no. 31, Gavriljuk V G, Hanninen H, Tereshchenko A S, Ullakko K, *Scripta " Metall. et Mater.* 28 (1993) pp 247-252
- [12] Rozenak P et al Hydrogen effects on phase transform. *J. of Mat. Sci.* Feb. 1984, Vol 19, Issue 2, pp 567–573, Beer S, Israel, Narita N et al, *Met Trans.* Hydrogen-related phase transformations in austenitic stainless steels, 1982, Vol 13, issue 8, pp 1355-1365
- [13] Caskey G R Jr., *Microstruct. Sci.* 9 (1981) 413–419, V.H. Desai, K. Scammon, Nace Annual International Conference Corrosion, 1995, paper 161, C.E. Price, L.B. Traylor, *Scr. Metall.* (1983) 901–904
- [14] Fischer F D, Svoboda J and Kozeschnik E (fracture Interstitial diffusion in systems with multiple sorts of traps) Institute of Mechanics, Montanuniversität Leoben, 8700 Leoben, Austria.
- [15] Hazarabedian A, Ovejero-Garcia J, *Rev. Metall.* CIT, septembre 1993. Steel in hydrogen sulphide (H₂S) environment in SSRT conditions
- [16] Narita N, Altstetter C J, Birnbaum H K *Met. Trans.* A 13A (1982) 1355. Vol. 13, Issue 8, pp 1355–136