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Abstract

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Effect of gaseous hydrogen charging on the tensile properties of standard and medium Mn X70 pipeline steels

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Abstract

The tensile properties of two X70 steels with high (1.14 wt.%) and medium (0.5 wt.%) Mn contents have been investigated by testing at 25 °C of tubular specimens charged with an internal gas pressure of 10 MPa of hydrogen or argon. The hydrogen-charged samples were additionally tested at 50 and 100°C.

Tensile testing showed that the equiaxed ferrite-pearlite microstructure of higher Mn steel was most sensitive to hydrogen embrittlement (HE) and that the banded ferrite-pearlite microstructure of the higher Mn strip was more susceptible to HE than the medium Mn strip. The more highly banded ferrite-pearlite microstructure in the higher Mn steel provided numerous sites for concentration of hydrogen to levels that promoted crack initiation and growth.

Test temperatures up to 100°C reduced the yield and tensile strengths, increased the total elongation and decreased the extent of HE because of enhanced dislocation mobility and less effective hydrogen trapping.

Keywords: pipeline steel; hydrogen gaseous charging; tensile testing; hydrogen embrittlement; microstructure

1 Introduction

Significant cost advantages can be obtained from the use of higher strength steels for the manufacture of pipelines, but increases in strength can be accompanied by a higher susceptibility to hydrogen embrittlement [1]. This kind of embrittlement is normally manifest as a significant loss in ductility without a marked decrease in strength. Pipeline steels can contain small amounts of hydrogen because of absorption during pipe welding or as a result

of environmental exposure. The presence of even small concentrations (ppm) of hydrogen can increase the susceptibility of steel to hydrogen-induced cold cracking (HICC) – a specific type of HE [2]. Once a steel pipeline is exposed to an acidic environment, its surface oxidizes and produces hydrogen. The absorbed hydrogen atoms diffuse into the steel and become trapped at certain microstructural features, such as interfaces between non-metallic inclusions and the steel matrix, at precipitates, dislocations and (sub)grain/phase boundaries [3, 4]. HICC can occur if the trapped hydrogen reaches the critical concentration necessary for crack initiation. The absorbed hydrogen atoms can also recombine and form molecules [5].

Hydrogen-induced degradation has generally been investigated through the ex-situ testing of electrolytically-charged specimens. However, cathodic charging cannot fully replicate the damage caused by gaseous hydrogen in transportation pipelines. Thus, this work addresses the effect of gaseous hydrogen charging as a function of Mn content, as well as microstructure.

It has been reported that the as-quenched martensitic microstructure has the lowest resistance to HE, whereas tempered bainitic or tempered martensite microstructures have the highest resistance [6]. Ferrite-pearlite microstructures sit between these two extremes. The most important factors that control the susceptibility of a microstructure to hydrogen embrittlement are the hydrogen permeability and hydrogen trapping capacity of that microstructure. The grain coarsened heat affected zone (GHAZ) adjacent to the weld zone is also a critical region for HE [6-8]. The susceptibility to hydrogen cracking can also be related to the steel composition and the processing history as these factors affect non-metallic inclusions (size, morphology and type). Large inclusions such as elongated manganese sulfides and stringers of oxide increase the HICC susceptibility [9]. The concentration of impurities has also been found to increase the susceptibility of HICC [10]. Since welded pipelines exhibit different microstructures, it is important to know how hydrogen affects these different microstructural regions.

In recent years, there have been attempts to design steels with lower Mn levels (0.2-0.5%) in order to reduce centreline segregation. Formation of MnS from the liquid in steels having lower Mn concentration and a given S content will take place closer to the solidification temperature resulting in their smaller size [11].

As there is little information available in the literature on the effect of temperature on the mechanical properties of pipeline steels subjected to in-situ gaseous hydrogen charging, the effect of elevated temperature has also been investigated. From a practical viewpoint, exposed pipelines can be subjected to elevated service temperatures.

In summary, this study was conducted with the aim of investigating the effect of Mn content, microstructure and test temperature on HE, as reflected in the tensile properties of X70 steels.

2 Experimental Procedures

Two API X70 grade hot rolled strip samples (10 mm thick) were received from BlueScope Steel Ltd. Table 1 gives the chemical compositions of the steels. The steel with the higher Mn content (1.14%) is typical of the standard alloy design (S-X70), whereas the medium (0.5%) Mn steel (M-X70) is designed to reduce centreline segregation. The M-X70 steel contains higher levels of Cr and C to offset the hardenability loss due to the reduction in Mn. The S-X70 steel was also supplied as a sample taken prior to the finishing stage of hot rolling process, so called transfer bar (TB) with a thickness of 28 mm.

Normalising of TB was carried out before machining the tensile samples. A transfer bar sample was heat treated at 950°C for 20 minutes and then air-cooled to room temperature. Surfaces of the NTB sample were machined to a depth of 2 mm of metal in order to remove the oxide layer.

Hollow cylindrical samples (Fig. 1) were machined along the rolling direction from S-X70, M-X70 and the NTB sample of the S-X70 steel. The test pieces were tested in uniaxial tension at 25, 50 and 100 °C under 10 MPa internal pressure of gaseous hydrogen. The tests were performed on an Instron 1341 tester using Syntest software (Syntest Version 1, developed by Arthur Carlton Synapse Technology Pty Ltd) (Fig. 2). For comparison, samples were also charged to 10 MPa with 99% high purity argon before tensile testing at 25°C. The tests were carried out at the slowest possible cross-head speed (0.003 mm/s) to allow time for hydrogen diffusion. At least 3 samples were tested per condition.

Samples for metallographic analyses were hot mounted in Bakelite, ground and polished according to standard metallographic methods for C-Mn steels [12]. The Struers TegraPol-21 machine was used for automatic grinding and polishing. The polished samples were etched using 2 % Nital solution. Optical microscopy was performed on a Leica DMR optical microscope fitted with a DFC295 digital camera using Video Pro 32 version 6.003 software. Measurements of pearlite area fraction and ferrite grain size were performed using the standard point count method according to ASTM E 562 [13], whereas the grain sizes were measured by the linear intercept technique according to ASTM E112-10 [14].

Scanning electron microscopy of the fracture surfaces was performed on a JEOL LV6490 SEM operating at 20kV. Prior to observation, specimens were subjected to an ultrasonic cleaning.

Measurement of the hydrogen content was performed on a ELTRA ONH-2000 machine located in the Central laboratory at BlueScope Steel, Port Kembla, approximately 12 km away from the mechanical testing lab at the University of Wollongong. The delay time between the end of the test and measurement was between 30 to 60 minutes, which was long enough for hydrogen to escape. In order to prevent loss of hydrogen before testing, the samples were kept in liquid nitrogen [15]. However, loss of hydrogen was possible by effusion from the test piece walls and the fracture surface before test piece retrieval and, subsequently, during manual cutting of a small piece of fractured pipe before it was immersed in liquid nitrogen. The hydrogen was measured by a fusion process with sensitivity of 0.01 ppm and an indication range of 0-100%.

3 Results

3.1 Microstructure Characterisation

The microstructure of NTB is an equiaxed ferrite-pearlite microstructure with an average grain size of $14 \pm 0.5 \mu\text{m}$ (Fig. 3a). The area percentage of pearlite was determined to be $12 \pm 1\%$.

The edge microstructures of the two 10 mm thick strip samples (Figs. 3b and 3c) correspond to that of the pipe sample wall. In both cases the microstructure was a mixture of ferrite and pearlite grains. For S-X70, ferrite-pearlite grains were present in bands parallel to the rolling direction (Fig. 3b). The edge region consisted of a bimodal distribution of fine ferrite grains with an average size of $5.1 \pm 1.3 \mu\text{m}$ and coarse ferrite grains with an average size of $12.7 \pm 3.5 \mu\text{m}$. The overall average ferrite grain size was $8.1 \pm 4.8 \mu\text{m}$. The area fraction of pearlite was determined to be $9 \pm 0.8\%$. These results are consistent with data in the literature [2, 16].

Bimodal grain size distributions were not found for M-X70 (Fig. 3c), which had an average ferrite grain size of $8.5 \pm 1.8 \mu\text{m}$. The area fraction of pearlite was determined to be $11 \pm 1\%$, higher than for S-X70 due to the higher C content.

3.2 Gaseous Charging Results

3.2.1 Tensile test results

The tensile tests revealed the behavioural differences between the steels tested under pressurised hydrogen and under pressurised argon gas at the selected test temperatures of 25, 50 and 100°C. The total amount of hydrogen measured by the hot extraction method after tensile testing was negligible, indicating that either a small amount of hydrogen was absorbed or, as is more likely, hydrogen was rapidly lost, before immersion in liquid nitrogen, by effusion from the surfaces of the fractured test piece and during the process of manual cutting of a small sample for hydrogen testing.

Macrographs of representative fractured samples are shown in Fig. 4 for room temperature testing. It can be seen that the samples fractured near the centre of the gauge section and that the hydrogen-charged sample (Fig. 4b) showed a substantially less elongation and necking. Necking is clearly significant in the argon-charged sample.

The engineering stress-engineering strain curves are shown in Fig. 5 for hydrogen- and argon-charged test pieces of the S-X70, M-X70 and NTB samples. For the argon-charged tests, the normalised microstructure exhibited the highest total strain and the lowest YS and UTS. Hydrogen charging had a profound effect, reducing the total strain for all three samples. Further, all of the stress-strain curves showed a typical for this class of steels [17] discontinuous yielding.

In calculating the UTS for the tensile tests, the 10 MPa gas pressure was considered to be a pre-stress. The internal pressure within a thin-walled cylinder produces an axial tensile stress of $Pr/2t$ [18], where P , r and t are the charging pressure, the internal radius of the specimen and the wall thickness, respectively. The UTS of specimens was calculated by adding the charging pressure to the tensile strength value estimated from the peak load and final wall thickness.

As shown in Fig. 5 and Table 2, the UTS of S-X70 samples charged with 10 MPa of hydrogen gas at 25°C was reduced by 4.5 % compared to argon-charged samples. The error limits shown in Table 2 are conservative and the trend of decrease in UTS for all three hydrogen-charged samples compared to their argon-charged reference samples is clearly established by the data. These results are consistent with those of previous reports [19, 20] on hydrogen embrittlement. Since the M-X70 and NTB samples showed lower reductions in UTS of 3.6% and 3.7%, the sensitivity of tensile strength to hydrogen clearly depends on the chemical composition and the microstructure of the steel.

The total strain at fracture (Table 2) was used to calculate an embrittlement index (E_i):

$$E_i = 100 \times (\varepsilon_A - \varepsilon_H) / \varepsilon_A \quad (1)$$

where ε_A is the total strain for argon-charged sample and ε_H is the total strain for the hydrogen charged sample. An index of zero indicates no HE.

The indexes for samples tested at 25°C were 35%, 25% and 22% for the NTB, S-X70 and M-X70 samples, respectively. These results indicate that the microstructure of NTB is more susceptible to hydrogen embrittlement than the strip samples. Further, the S-X70 samples were more embrittled by gaseous hydrogen than M-X70.

One important difference in the stress-strain curves after the peak load is the post-necking strain. The specimens charged with hydrogen gas showed less post-necking strain, while the reference sample charged with argon gas showed extensive post-necking strain and the maximum strain at fracture. Even though the nominal wall thickness of the specimen was 1.0 mm, the real thickness varied by about 100 μm due to the machining followed by polishing of the walls. Thus, a conversion of the load information to the stress value in the Instron software is based on the nominal wall thickness and the accuracy is limited to $\pm 10\%$.

Table 2 shows that the yield strengths of S-X70 and M-X70 are higher than that of NTB. As the ferrite grain sizes of the S-X70 and M-X70 are finer compared to NTB, there is a Hall-Petch effect [18] that leads to an increase in the yield strength, in agreement with the literature [21]. In addition, the higher density of dislocations in S-X70 and M-X70 strips due to controlled thermo-mechanical processing contributes to a rise in the yield strength [22].

It should be noted that for the samples tested at room temperature, hydrogen charging had no apparent effect on the yield stress. However, the ultimate tensile strength was lowered slightly by hydrogen charging. As a result, the yield to tensile ratio is higher for hydrogen-charged samples compared to the argon-charged samples.

3.2.2 *Effect of Temperature*

Although the shapes of the stress-strain curves for hydrogen-charged S-X70, M-X70 and NTB samples were similar for all test temperatures (Fig. 5), the strength decreased and the ductility increased with increasing temperature. Moreover, both the uniform and total strains under hydrogen gas showed slightly higher values with increasing temperature (Table 2). Correspondingly, the embrittlement indexes were also lowered. However, these are likely to be slightly underestimated because the reference total strain was taken as that for Ar at

25°C, as due to limitation in the number of samples, elevated temperature tensile testing was not conducted on argon-charged samples. The increase in total elongation with test temperature increase is in agreement with the literature [23, 24]. Similarly, the decrease in yield and tensile strengths with increasing temperature is in agreement with the results of Michler's [25] which covered a lower temperature range (-80°C to 20°C). Hofmann and Rauls [23] showed that, for air charged normalised plain carbon steel tensile samples, an increase in the temperature from 25°C to 100 °C decreased the reduction in area and total elongation in fractured samples because of ageing effect. In contrast, Table 2 indicates that a temperature increase from 25°C to 100°C increased the total elongation of tested samples in the presence of hydrogen in the steels investigated. This observation is consistent with the hypothesis that hydrogen embrittlement would be reduced at higher temperatures because the diffusion and desorption rates of hydrogen are increased, inhibiting hydrogen build-up at potential crack sites such as particle interfaces and other slip barriers [26].

3.2.3 *Fractography*

The effects of the hydrogen exposure on the fracture behaviour were analysed using fracture surface observations of S-X70 samples. The comparison of the fracture surface of an S-X70 sample tested under 10 MPa hydrogen gas with its counterpart tested under argon gas is shown in Fig. 6.

The fracture surfaces after argon charging are characterised by dimples, as shown in Fig. 7b. The mean diameter of the dimples is $2.5 \pm 0.3 \mu\text{m}$. However, predominantly brittle fracture was observed in the hydrogen-charged specimen at 25°C (Fig. 8b). In all cases of hydrogen atmosphere testing, partial or complete brittle fracture by quasi-cleavage was observed. HICC associated with inclusions and other stress-concentrating defects would be required to initiate and extend cracking by quasi-cleavage, which dominated the fracture mode of the hydrogen-charged samples that were tensile tested at 25°C. Electrolytic charging of the same steels [27] clearly established the presence of hydrogen cracking throughout the strip cross-sections and it is therefore reasonable to expect the presence of cracking in regions surrounding the final crack surface in the present case. However, the presence of sub-critical cracks was not confirmed because it was not considered to have a significant bearing on the main findings of the work.

The area of cleavage surface decreased as the temperature was raised to 100°C with a corresponding increase in the area of dimpled fracture (Fig. 9). The size of the dimples was smaller for the S-X70 sample charged in hydrogen at 100°C (Fig. 9b) compared to that charged with argon at room temperature (Fig. 7b). This observation is in agreement with the measured tensile strength and elongation (Table 2). The mean diameter of dimples for hydrogen-charged S-X70 tested at 100°C is $2.1 \pm 0.2 \mu\text{m}$.

One of the most significant differences shown in Figs. 7 and 8 is the wall thickness: dynamic shear deformation in the neck of the argon-charged specimen (Fig. 7) substantially reduced the cross-sectional area, with the wall thickness being less than 40 % of the initial wall thickness. In contrast, there was much less necking under hydrogen gas (Fig. 9) with the wall thickness being about 85 % of the initial thickness. Further, dynamic shear deformation did not occur at the hydrogen-exposed inner wall of the specimen, contrary to the surfaces exposed to argon gas. The ductile fracture surface in Fig. 7 has a slope in the loading direction, but the fracture formed in the sample exposed to hydrogen gas (Fig. 8) shows predominantly brittle, outward crack growth perpendicular to the loading direction.

The S-X70 specimen that fractured in hydrogen gas at 100°C (Fig. 9) also displayed a fracture morphology partially similar to that fractured at 25 °C, but the extent of brittle fracture was reduced to about 18 % due to the contribution of ductile fracture. Fig. 9 shows brittle fracture around the edges of the fracture surface where the material was exposed to hydrogen. Beyond the brittle area the fracture surface of this specimen shows evidence of ductile fracture. The presence of mixed fracture modes (cleavage facets together with dimples), indicates higher plastic deformation levels during the fracture process compared to S-X70 sample charged with hydrogen at room temperature.

The widths of the brittle fracture surfaces in Fig. 9 can be related to the critical concentration of hydrogen: at 100°C, the mobility of hydrogen atoms is higher, with a reduction in the probability of localised accumulation of hydrogen at traps to the critical concentration required to induce hydrogen cracking. Hence, less brittle fracture is to be expected.

The micro-voids in the argon-charged samples are elongated in the tensile loading direction (Fig. 7b), whereas the voids in the hydrogen-charged at 100°C sample appear to be nearly spherical (Fig. 9b). These observations indicate that the hydrogen-charged specimen tested at 100°C undergoes lower elongation before fracture than the argon-charged specimen at 25°C.

These are consistent with results of Lee et al. [28], who conducted the same tensile test on X65 hollow cylindrical samples with hydrogen or nitrogen inside. They also found brittle fracture surface with almost no necking under hydrogen charging.

A series of low resolution SEM images were taken from the fracture surface of all samples. The percentages of ductile and predominantly brittle fracture were then calculated for two samples per condition and the results are summarised in Fig.10.

4 Discussion

As reported by Haq et al. [29] for permeability studies of the same steels, the average diffusivity (D) of hydrogen was $\sim 2 \times 10^{-10} \text{ m}^2/\text{s}$ for M-X70 strip; $\sim 2.53 \times 10^{-10} \text{ m}^2/\text{s}$ for S-X70 strip; and $\sim 5.24 \times 10^{-10} \text{ m}^2/\text{s}$ for the NTB sample. For the constant tensile extension rate of 0.003 mm/s , the duration (t) of the tensile tests at room temperature varied from 1512 s to 1860 s . The corresponding maximum diffusion distances, x , for hydrogen were calculated by the relation $x = \sqrt{(6Dt)}$, to be 5.5 to 6.1 mm , well in excess the 1.0 mm wall thickness of the tensile test piece. Therefore, the hydrogen gradient would be expected to extend fully across the wall thickness from the early stages of testing, and provide the reservoir of mobile hydrogen atoms to interact with, and modify, the mechanisms of deformation, crack initiation and extension.

The significant effect of hydrogen on the tensile behaviour of the steel specimens is clearly demonstrated by total elongations at fracture that are substantially lower than those of the corresponding Ar-charged specimens. The reduction in total elongation for S-X70 corresponds to an embrittlement index of 25% compared with 22% for M-X70 tested at 25°C . This difference is probably due a higher tendency for crack progress by quasi-cleavage in S-X70 compared to the slightly lower strength microstructure of M-X70. This trend is consistent with Fig. 10 which shows that the % brittle failure was higher for S-X70 strip for testing with Ar compared to that for two other samples. No externally applied stress-concentrating notch was present and, applying the Beachem model [30], the two strip structures responded to the hydrogen gradient by fracturing in the mode that was most characteristic of the microstructures. The balance between void formation and cleavage fracture was slightly shifted towards void coalescence (micro-plastic failure) in the lower strength structure on M-X70. The presence of a higher concentration of hydrogen trapping particles in this steel over S-X70 did not appear to increase the HE effect in M-X70.

While ductile fracture surfaces were observed under an argon atmosphere, quasi-cleavage fractures were identified under hydrogen gas conditions regardless of the test temperature. However, the fraction of predominantly brittle fracture decreased with an increase in test temperature. Hydrogen-charged samples at room temperature were characterised by the effective absence of necking and a fully quasi-cleavage fracture surface. Gaseous hydrogen did not have a significant effect on the yield strength of both steels, but slightly lowered the tensile strength. This observation is consistent with the contribution of hydrogen cracking to fracture at a lower stress compared to testing in the absence of hydrogen. The NTB sample showed the maximum embrittlement index, consistent with the results of three point bend (TPB) testing reported in [27].

Although there are reports of tensile testing in the presence of gaseous hydrogen of X65 steel at room temperature [28], stainless steel at -20 to -250°C [31] and medium carbon steel at room temperature [32], tensile testing of X70 steel under hydrogen at elevated temperatures (50 and 100°C) has not previously been reported. Since pipelines located in desert environment are subject to deformation at low strain rates and can reach 50°C and over, the current work constitutes an attempt to simulate this service condition.

Elevated temperatures (up to 100°C) increased the uniform elongation and decreased the yield and tensile strengths of hydrogen-charged specimens compared to room temperature specimens, due to both the attenuation of the embrittling effect of hydrogen and the increased mobility of dislocations. All tested samples responded similarly to the effect of temperature.

It is well known, particularly in steel welding (e.g. see Ref. [33]), that HICC is essentially a "cold" phenomenon which diminishes with increasing temperature above ambient and does not occur at all above about 200 °C. Preheating is routinely practised in welding to facilitate reduction in hydrogen content and to decrease the capacity of residual hydrogen to induce cracking. Raising the temperature increases hydrogen atoms mobility and reduces the probability of accumulation of hydrogen at stress-concentrating structural sites – a pre-requisite for crack initiation. Hydrogen-induced cracks can propagate by cleavage or enhanced slip with the localised formation of voids and their coalescence. As the temperature is raised the effectiveness of hydrogen in modifying the deformation and fracture mechanisms is attenuated and the "normal" deformation and fracture modes start to dominate. In particular, increased dislocation mobility leads to more generally distributed plastic behaviour rather than *localised* (hydrogen-induced) plastic behaviour, thereby leading to a marked increase in the total elongation at fracture.

Although the S-X70 steel was found to be more susceptible to HE than M-X70 for tensile testing under 10 MPa hydrogen pressure, it was found to be less susceptible to HE when electrolytically hydrogen-charged samples were subjected to TPB tests [27]. In the TPB tests the surface subjected to bending was parallel to the rolling plane, so that the microstructure ahead of the advancing notch-induced crack was banded, particularly for the S-X70 steel. Even though the S-X70 and M-X70 samples were electrolytically pre-charged to the same hydrogen concentration, the banded microstructure could provide serious interfacial obstacles to crack propagation normal to the bands, thus accounting for the higher observed HICC resistance compared to the M-X70 steel. For the present case of tensile testing, the axis of the test piece was parallel to RD, and hydrogen diffused inwards while the sample was being strained. Since hydrogen charging was carried out in the presence of an external stress, hydrogen transport in the specimen would be expected to occur by means of a combination of diffusion and dislocation transport mechanisms. The hollow cylindrical test pieces were cut along the rolling direction within the thickness of the strip, and therefore hydrogen will diffuse inwards in both the transverse and normal directions. It is expected that inward diffusion of hydrogen would be easier in the transverse direction along the ferrite-pearlite bands. The hydrogen gradient extending from the internal surface would be expected to pre-dispose crack initiation at stress concentration sites in near-surface regions. Crack propagation would be promoted by hydrogen trap sites, particularly at ferrite-pearlite interfaces of the more highly banded S-X70, in the stress concentrated zone ahead of the inwardly advancing crack [34-36]. In M-X70 samples, hydrogen would be expected to diffuse faster in both the transverse and normal directions, flattening the hydrogen gradient and attenuating hydrogen build-up at deep traps. This hypothesis offers an explanation for the reduced HE of M-X70 compared to S-X70. However, there is another possible reason for the difference in HE indicated by the tensile and TPB tests results. Due to the sample geometry of the tensile test pieces, the volume containing centreline segregation was removed, whereas it was present in the TPB samples. Unlike S-X70, the centreline region of M-X70 strip contained elongated MnS stringers with some blocky inclusions among these stringers, as well as a higher number density of oxides [27]. These microstructural features have been reported by Domizzi *et al.* [37] to promote HICC and they could, therefore, have contributed to the higher incidence of HICC in the TPB tests of M-X70.

In the case of NTB, the density of reversible traps such as dislocations and grain boundaries, is much lower than for S-X70 and M-X70. Therefore, grain boundaries will quickly become hydrogen-saturated, allowing HICC to be initiated at grain boundary nodes

and promoting easy crack propagation by quasi-cleavage, consistent with the relatively high proportion of brittle fracture evident in Figure 10. As a consequence, the HE index was found to be highest for the NTB sample.

5 Conclusions

- Tensile testing of the gas-charged tubular specimens resulted in approximately similar stress-strain curves regardless of the charging gas or temperature. However, the uniform elongations and the total elongations at fracture were significantly lower in the hydrogen-charged specimens than for the argon-charged specimens.
- Predominantly quasi-cleavage fractures were observed in all samples charged with hydrogen gas, whereas ductile fracture surfaces were evident in those tested with argon. The fraction of ductile fracture in hydrogen charged samples increased with increasing in temperature.
- The most significant impact of hydrogen-charged specimens on the tensile behaviour was reduction in the elongation at fracture. The embrittlement indexes estimated from these data were 36%, 25% and 22% for the normalised transfer bar with equiaxed ferrite-pearlite microstructure, high Mn strip and medium Mn strip specimens with banded ferrite-pearlite microstructure, respectively.
- Elevated temperatures (up to 100°C) increased the uniform elongation and decreased the yield and tensile strengths of hydrogen-charged specimens compared to room temperature specimens, due to both the attenuation of the embrittling effect of hydrogen and the increased mobility of dislocations.
- Increase in ferrite grain size in the normalised transfer bar sample (14 μm) compared to high Mn strip (about 8-9 μm), together with a decrease in dislocation density, increased the susceptibility to gaseous hydrogen embrittlement. The presence of a much lower density of reversible trap sites is considered to lead to faster accumulation of hydrogen in deep grain boundary traps, thereby promoting crack propagation.

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References

1. Williams, J.G.: 'Advances in steels for high strength ERW linepipe application in Australia', *Materials Forum*, 2007, **31**, 1-10.
2. Dong, C.F., Li, X.G., Liu, Z.Y., and Zhang, Y.R.: 'Hydrogen-induced cracking and healing behaviour of X70 steel'. *Journal of Alloys and Compounds*, 2009, **484**, 966-972.
3. Huang, F., Liu, J., Deng, Z.J., Cheng, J.H., Lu, Z.H., and Li, X.G.: 'Effect of microstructure and inclusions on hydrogen induced cracking susceptibility and hydrogen trapping efficiency of X120 pipeline steel', *Materials Science and Engineering: A*, 2010, **527**, 6997-7001.
4. Dong, C.F., Liu, Z.Y., Li, X.G., and Cheng, Y.F.: 'Effects of hydrogen-charging on the susceptibility of X100 pipeline steel to hydrogen-induced cracking', *International Journal of Hydrogen Energy*, 2009, **34**, 9879-9884.
5. Yen, S.K. and Huang, I.B.: 'Critical hydrogen concentration for hydrogen-induced blistering on AISI 430 stainless steel', *Materials Chemistry and Physics*, 2003, **80**, 662-666.
6. Carneiro, R.A., Ratnapuli, R.C., and de Freitas Cunha Lins, V.: 'The influence of chemical composition and microstructure of API linepipe steels on hydrogen induced cracking and sulfide stress corrosion cracking', *Materials Science&Engineering: A*, 2003, **357**, 104-110.
7. Thompson, A.W. and Bernstein, I.M.: The role of metallurgical variables in hydrogen-assisted environmental fracture, in *Advances in corrosion science and technology*. M.G. Fontana, R.W. Staettle, R.W. (Eds.) 1980, Springer. 53-175.
8. Chatzidouros, E.V., Papazoglou, V.J., Tsiourva, T.E., and Pantelis, D.I.: 'Hydrogen effect on fracture toughness of pipeline steel welds, with in situ hydrogen charging', *International Journal of Hydrogen Energy*, 2011, **36**, 12626-12643.
9. Nakai, Y., Kurahashi, H., Emi, T., and Haida, O.: 'Development of steels resistant to hydrogen induced cracking in wet hydrogen sulfide environment', *Transactions of the Iron and Steel Institute of Japan*, 1979, **19**, 401-410.
10. Ren, X., Chu, W.Y., Li, J., Su, Y.J., and Qiao, L.: 'The effects of inclusions and second phase particles on hydrogen-induced blistering in iron', *Materials Chemistry and Physics*, 2008, **107**, 231-235.
11. Williams, J.G.: 'New alloy design perspectives for high strength steels' in *Proceedings of International Conference on Thermomechanical Proceeding of Steel on CD*, Padua Italy, 2008.
12. Williams, R.S. and Homerberg, V.O.: 'Principles of metallography'. *Metallurgy and metallurgical engineering series*, 1948, New York, 319.
13. ASTM E562-11 'Standard Test Method for Determining Volume Fraction by Systematic Manual Point Count' in *Book of Standards*, 03.01, 2011, West Conshohocken, PA, ASTM International.
14. ASTM E112-10 'Standard Test Methods for Determining Average Grain Size', 2010, West Conshohocken, PA, ASTM International.
15. Olden, V., Alvaro, A., and Akselsen, O.M.: 'Hydrogen diffusion and hydrogen influenced critical stress intensity in an API X70 pipeline steel welded joint – Experiments and FE simulations', *International Journal of Hydrogen Energy*, 2012, **37**, 11474-11486.

16. Al Shahrani, A., Schambron, T., Dehghan-Manshadi, A., Williams, J.G., and Pereloma, E.V.: 'Effects of processing parameters on microstructure development in X70 pipeline steel'. Materials Science Forum, 2010, **654**, 98-301.
17. Hwang, B., Kim, Y.G., Lee, S.G., Kim, Y.M., Kim, N.J., and Yoo, J.Y.: 'Effective grain size and Charpy impact properties of high-toughness X70 pipeline steels', Metallurgical and Materials Transactions A, 2005, **36**, 2107-2114.
18. Dieter, G.E. and Bacon, D.: 'Mechanical metallurgy', 1986, McGraw-Hill, New York.
19. Chang, T.L., Tsay, L.W., and Chen, C., 'Influence of gaseous hydrogen on the notched tensile strength of D6ac steel.', Materials Science and Engineering A, 2001. **316**, 153-160.
20. Michler, T. and Naumann, J.: 'Hydrogen embrittlement of Cr-Mn-N-austenitic stainless steels', International Journal of Hydrogen Energy, 2010, **35**, 1485-1492.
21. Afrin, N., Chen, D.L., Cao, X., and Jahazi, M.: 'Strain hardening behavior of a friction stir welded magnesium alloy', Scripta Materialia, 2007, **57**, 1004-1007.
22. Luo, J., Mei, Z., Tian, W., and Wang, Z.: 'Diminishing of work hardening in electroformed polycrystalline copper with nano-sized and ufg-sized twins', Materials Science and Engineering A, 2006, **441**, 282-290.
23. Hofmann, W. and Rauls, W.: 'Ductility of steel under the influence of external high pressure hydrogen (Hydrogen embrittlement of plain steel and Armco iron)', Welding journal, Research supplement, 1965, **44**, 225-S-230-S.
24. Wu, X., Katada, Y., Kim, I.S., and Lee, S.G.: 'Hydrogen-involved tensile and cyclic deformation behavior of low-alloy pressure vessel steel', Metallurgical and Materials Transactions A, 2004, **35**, 1477-1486.
25. Michler, T., Yukhimchuk, A.A., and Naumann, J.: 'Hydrogen environment embrittlement testing at low temperatures and high pressures', Corrosion Science, 2008, **50**, 3519-3526.
26. Senkov, O.N. and Jonas, J.J.: 'Dynamic strain aging and hydrogen-induced softening in alpha titanium', Metallurgical and Materials Transactions A, 1996, **27**, 1877-1887.
27. Hejazi, D., Haq, A.J., Yazdipour, N., Dunne, D.P., Calka, A., Barbaro, F., Pereloma, E.V., *Effect of manganese content and microstructure on the susceptibility of X70 pipeline steel to hydrogen cracking*. Materials Science and Engineering: A, 2012. **551**: 40-49.
28. Lee, Y.H., Lee, H.M., Kim, Y., and Nahm, S.H.: 'Mechanical degradation of API X65 pipeline steel by exposure to hydrogen gas', Metals and Materials International, 2011, **17**, 389-395.
29. Haq, A.J., Muzaka, K., Dunne, D.P., Calka, A., Pereloma, E.V., *Effect of microstructure and composition on hydrogen permeation in X70 pipeline steels*. International Journal of Hydrogen Energy, 2013. **38**(5): p. 2544-2556.
30. Beachem, C.D.: 'A new model for hydrogen-assisted cracking (Hydrogen embrittlement)', Metallurgical Transactions A, 1972, **3**, 437-451.
31. Deimel, P. and Sattler, E.: 'Austenitic steels of different composition in liquid and gaseous hydrogen', Corrosion Science, 2008, **50**, 1598-1607.
31. Fricke, E., Stüwe, H.P., and Vibrans, G.: 'Dissolution of hydrogen from the gas in steel at room temperature', Metallurgical Transactions, 1971, **2**, 2697-2700.
33. Grong, O., *Metallurgical Modelling of Welding*. Materials Modelling Series. 1994, London: The Institute of Materials, 509-512.
34. Hardie, D., Charles, E.A., and Lopez, A.H.: 'Hydrogen embrittlement of high strength pipeline steel', Corrosion Science, 2006, **48**, 4378-4385.

35. Lee, H.L. and Lap-Ip Chan, S.: 'Hydrogen embrittlement of AISI 4130 steel with an alternate ferrite/pearlite banded structure', *Materials Science and Engineering A*, 1991, **142**, 193-201.
36. Tau, L. and Chan, S.L.I.: 'Effects of ferrite/pearlite alignment on the hydrogen permeation in a AISI 4130 steel', *Materials Letters*, 1996, **29**, 143-147.
37. Domizzi, G., Anteri, G., and Ovejero-Garcia, J.: 'Influence of sulphur content and inclusion distribution on the hydrogen induced blister cracking in pressure vessel and pipeline steels', *Corrosion Science*, 2001, **43**, 325-339.

Figures and tables captions.

Fig. 1 Schematic of hollow cylindrical sample dimensions.

Fig. 2 Tensile test on the sample with 10 MPa hydrogen inside at 100°C.

Fig. 3 Microstructures of (a) NTB and (b) strip edge of S-X70 steel, and (c) strip edge of M-X70 steel.

Fig. 4 Comparison of fractured tensile test samples for room temperature testing of an argon-charged test piece (a) and a hydrogen-charged test piece (b).

Fig. 5 Stress-strain curves for NTB (a), S-X70 (b) and M-X70 (c) hollow cylindrical samples with 10 MPa of argon at 25°C and 10 MPa of hydrogen at 25, 50 and 100°C

Fig. 6 SEM images of S-X70 samples showing a predominantly brittle fracture after tensile testing with hydrogen at 25°C (a); and mostly ductile fracture after tensile testing with argon at 25°C (b).

Fig. 7 SEM images from the fracture surface of an S-X70 specimen tested with 10 MPa argon at 25°C.

Fig. 8 SEM images from the fracture surface of an S-X70 specimen tested with 10 MPa hydrogen at 25°C.

Fig. 9 SEM images from the fracture surface of an S-X70 specimen tested with 10 MPa hydrogen at 100°C, the red line indicates the transition line between ductile and brittle fracture.

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Table 1 Compositions of the studied steels, wt.%

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Table 1 Compositions of the studied steels, wt.%

Grade	C	P	Mn	Si	Ni	Cr	Mo	Cu	Al	Nb	Ti	V	S	N
S-X70	0.074	0.012	1.14	0.22	0.024	0.029	0.1	0.023	0.019	0.06	0.02	0.002	0.002	0.004
M-X70	0.085	0.01	0.5	0.19	0.018	0.26	0.11	0.011	0.04	0.059	0.035	0.003	0.002	0.005

Table 2 Mechanical properties of tested specimens.

Steel/Gas/Temperature	YS (MPa)	TS (MPa)	Total strain (%)	Embrittlement Index
NTB Argon 25°C	386±8	536±9	23.7±2	-
NTB Hydrogen 25°C	384±7	516±10	15.5 ±1	0.35
NTB Hydrogen 50°C	383±8	494±9	16±1	0.33
NTB Hydrogen 100°C	378±9	493±9	17.4±1	0.27
S-X70 Argon 25°C	518±10	606±10	16.8±1	-
S-X70 Hydrogen 25°C	517±9	579±8	12.6±1	0.25
S-X70 Hydrogen 50°C	511±8	562±7	13.8±1	0.18
S-X70 Hydrogen 100°C	503±7	548±7	14.5±1	0.14
M-X70 Argon 25°C	475±6	588±9	19.8±1	-
M-X70 Hydrogen 25°C	475±7	567±8	15.4 ±1	0.22
M-X70 Hydrogen 50°C	467±9	558±9	16.4±1	0.17
M-X70 Hydrogen 100°C	460±8	550±7	17.5±1	0.12