MICROSTRUCTURE AND MECHANICAL PROPERTY PERFORMANCE EVALUATION OF COMMERCIAL GRADE API PIPELINE STEELS IN HIGH PRESSURE GASEOUS HYDROGEN

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ABSTRACT

Alternative energy sources to the traditional fossil fuels have to be explored and understood. One potential energy source being researched and developed is hydrogen gas which could be economically transported through steel pipelines. The degradation of the mechanical properties of steels in hydrogen service is known to depend on the microstructure of the steel. Understanding the levels of mechanical property degradation of a given microstructure when exposed to hydrogen gas under pressure can be used to evaluate the suitability of the existing pipeline infrastructure for hydrogen service and guide alloy and microstructure design for new hydrogen pipeline infrastructure. Microstructures and fracture toughness performances will be compared along with recommendations for future work related to gaining a better understanding of steel pipeline performance in hydrogen service.

INTRODUCTION

In the last seven years with funding through the US Department of Energy (DOE) Hydrogen Delivery Program there has been on-going research on the effects of high pressure gaseous hydrogen on various/pipeline steels. Prior to that, data on these steels in the presence of high pressure gaseous hydrogen was very much limited. ASME B31.12 code book for Hydrogen Piping and Pipelines released in 2008 has restrictions to operating pressure as there are still many unknowns that need to be explored [1]. Fracture and fatigue testing has been identified by the ASME B31.12 technical committee along with the DOE funded Pipeline Working Group as critical data that is needed to further enhance our understanding of steel performance in high pressure gaseous hydrogen.

Secat, Inc. in collaboration with Oak Ridge National Laboratory and other academic and industry partners with DOE and private sector funding started research of four pipeline steels. The four pipeline steels chosen for research were done so based on their various relevant microstructures used in today's transmission pipeline infrastructure. Microstructure plays a key role in the mechanical property performance of the steel in the presences of high pressure gaseous hydrogen [2, 3]. The focus on the research was on the performance of

the four microstructures in the presence of gaseous hydrogen in pressures of 800 - 3000 psig (5.5-21 Mpa) [4]. These pressures were chosen as they would represent what is believed to be typical operating pressures for a hydrogen transmission pipeline. The interest developed in the original DOE funded testing resulted in a larger matrix to be developed of various microstructures. This paper will only discuss the fracture toughness testing vs. microstructure of various pipeline and one non-pipline steel, secured from a mixture of plate, coil and pipe specimens, in the presence of gaseous hydrogen in the desiginated pressure range done to date, Table 1.

Table 1: Steel and microstructure fracture tougness tested in hydrogen gas

Grade	Description	Code	C (wt. %)	Microstructure/ Comments (%)
API X70	Late 1990's Alloy Design	A	0.08	92 PF/8 UB
API X80	Early 2000's Alloy Design	B	0.05	90 PF/10 AF
API X60 HIC	Current HIC Alloy Design	D	0.03	100 PF
API X80	Current X80 Alloy Design for Spiral Pipe	E	0.05	100 AF
API X80	Current X80 Alloy Design for Long Seam Pipe	F	0.05	30 PF/70 AF
API X70	1980's Alloy Design	G	0.08	90 PF/10 P
API X52	1960" Alloy Design	H	0.26	70 PF/30 P
API X70	Early 1990's Alloy Design	I	0.08	85 PF/15 P/BND
API X52	Current Alloy Design	J	0.06	92 PF/5 AF/3 P
A516 Gr70 Pressure Vessel	Current Alloy Design with Microalloy	L	0.14	40 PF/60 P/BND
X52 Induction Bend	Current Alloy Design	P Ind	0.06	95 PF/5 AF
X52 No Induction Bend	Current Alloy Design	P Nind	0.06	90 PF/10 AF
Microstructure Code: **PF**-Polygonal Ferrite, **P**-Pearlite, **UB**-Upper Bainite, **AF**-Acicular Ferrite, **BND**-Banded. Note volume fractions are reasonable approximations.				

TEST METHOD

Powertech Labs in Surrey, BC Canada was chosen to do the fracture toughness testing for this study. Powertech Labs is one of the laboratories in North America with equipment and capabilities to do fracture toughness testing in a high pressure hydrogen environment.

As there are many different ways to test the fracture toughness of a material, a testing procedure was adapted with guidance from the following ASTM standards:

- E399 – 08 "Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness K_{IC} of Metallic Materials"
- E992 – 84 (1989) "Standard Practice for Determination of Fracture Toughness of Steels Using Equivalent Energy Methodology"
- E1820 – 08 "Standard Test Method for Measurement of Fracture Toughness"

Specimens were oriented with the notch transverse to the rolling direction (LT) orientation and machined into standard compact tension (CT) specimens.

Fracture toughness tests were conducted in accordance with ASTM standard E992. This method was chosen as a relevant method to compare microstructure performance when anomalous separations were seen in the fracture surfaces. This will be discussed in detail in following sections. Tests were conducted inside a gaseous hydrogen environment using an Instron servo-hydraulic test frame coupled with a pressure vessel designed and built by Powertech Labs.

To calculate K_{EE}, a load value P_E is determined by extending the linear portion of the load-displacement curve until the area under the linear portion equals the area to the maximum load. The procedure is graphically represented in Fig. 2. The equivalent energy fracture toughness is then calculated as per Equation 1. Here, a was obtained from physical measurements of distance from the load line to the tip of the fatigue precrack following the tests.

$$K_{EE} = \frac{P_E}{\sqrt{B_N BW}} f\left(a/W\right) \qquad [1]$$

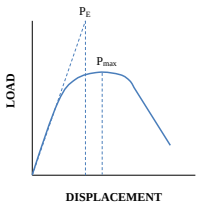
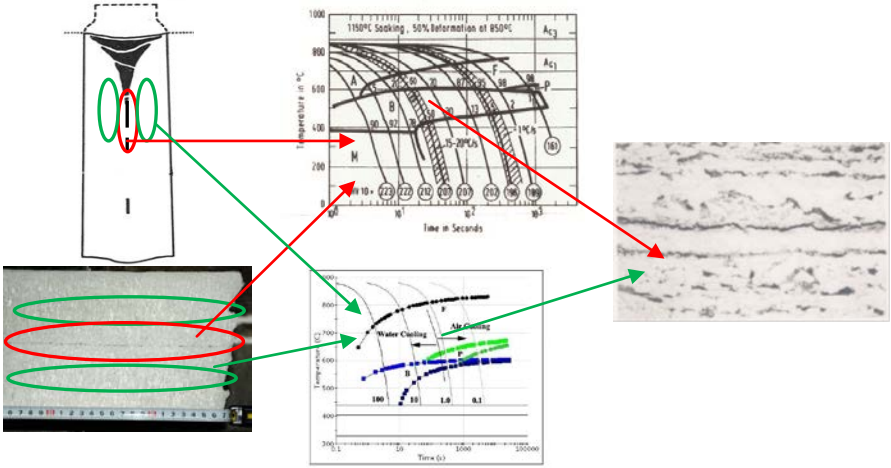


Figure 2: Graphic representation of equivalent energy methodology

MICROSTRUCTURAL ANALYSIS

Microstructures of the various steels were characterized by optical microscopy, scanning electron microscopy (SEM), and transmision electron microscopy (TEM) to identify the various phases, estimate volume fractions of the phases and document any visible microstructural banding. The presence of microstructural banding is important as it can have an influence on the separations seen in the fracture surfaces of the specimens after exposure to hydrogen that can effect the actual calculation of the fracture toughness energy. Microstructural banding can be both on a “macro” scale as seen optically or on a “micro” scale which is more difficult to determine. This microstructural banding is the result of alloy segregation tendencies during steel casting solidification and final cooling after rolling of the plate or coil. The alloy content determines the continuous cooling transformation kinetics for the various microstructural phases that might form for a given cooling rate. How the microstructural banding is created is illustrated in Fig. 3.The importance of this microstructural banding wheter it is in a “macro” or “micro” scale in regard to the fracture toughness testing in hydrogen is in that it becomes a trapping site for hydrogen, cracks/separations can form giving the hydrogen an easy location to accumulate during the testing and not further crack the overall test speciman. Then when calculating the fracture toughness as dicussed above, a “false” high value can be generated.



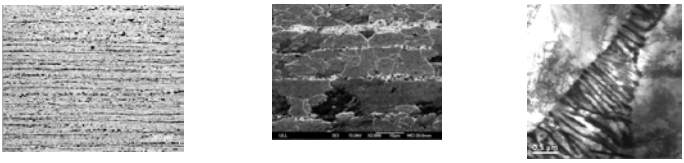
Steel ingot and continuous cast slab alloy segregation. Red circle represents area with highest concentation of alloy segregation (macro). Green circle represents area of lower alloy segregation (micro).

Continuous Cooling Transformation (CCT) diagrams for 2 different alloy contents. Green arrows from ingot/slab show what the CCT diagram might look like. Red arrows show an entirely different CCT diagram for the red circled alloy segregated regions of the ingot/slab.

Upon the same cooling rate of 1 °C/s the CCT diagram shows that for the alloy segregated region the microstructure would be approximately 95% polygonal ferrite and 5% bainite. However for the same 1 °C/s cooling rate the alloy segregated region the microstructure would be approximately 90% polygonal ferrite and 10% pearlite.

Figure 3: Illustration of various microstructure formation based on alloy segregation tendencies created during the steelmaking casting process

An example of one the microstructures in the study can be seein Fig. 4.



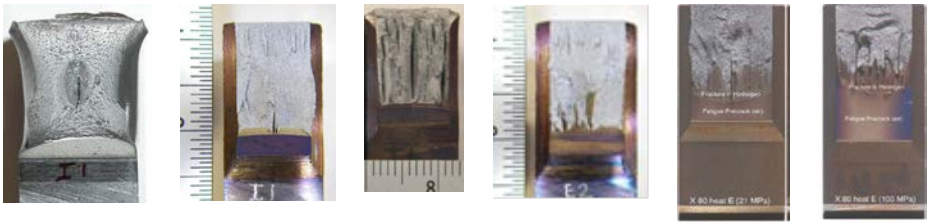
Alloy I – 85% Polygonal Ferrite, 15% Pearlite, Banded

Figure 4: Examples of optical, SEM and TEM microstructural characetization

FRACTURE TOUGHNESS RESULTS

Fracture toughness testing was conducted on the alloys at 800 psig (5.5 Mpa) and 3,000 psig (21 Mpa). During the analysis of this fracture testing it was observed that the presence of abnormal crack propagation (separations) during the test. The presence of these separations made calculations of fracture toughness as per ASTM E1820/E992 somewhat challenging. As the severity of the separations increased, the calculated fracture toughness also increases. This of course gives one a false sense that the steel has excellent fracture toughness characteristics in hydrogen but in fact the steel fracture toughness is most likely much lower if the crack propagation in hydrogen would have been normal and as expected. This is something that has been seen by others in conducting

ASTM E1820 fracture toughness testing [5,6]. These separations can be seen in fracture toughness testing in air and in hydrogen and appear to increase in severity with increasing pressure, Fig. 5.



Alloy I air fracture | **Alloy I 800 psig H2 fracture** | **Alloy I 3,000 psig H2 fracture** | **Alloy E 800 psig H2 fracture** | **Alloy E 3,000 psig H2 fracture** | **Alloy E 15,000 psig H2 fracture**

Figure 5: Examples of seperations in air and various hydrogen pressures

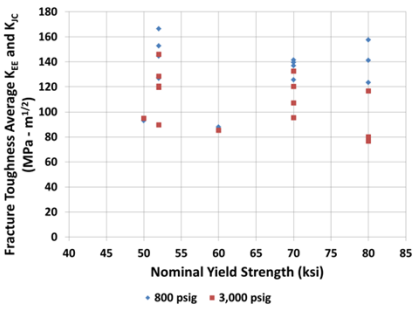
It would appear from the fractures that the severity of the separations increases with increasing pressure which may be due to a high potential of hydrogen collection aggravating microstructural inconsistencies. It is known from the microstructural characterizations some obvious macro banding could be seen optically. Not all of the steels exhibited separations in the fractures in air or hydrogen under pressure. A summary of the fracture toughness and noted separation severity is seen in Table 2.

Table 2: Summary of fracture toughness results

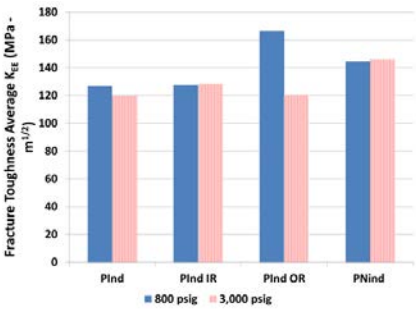
Project Code	**Fracture Toughness in Air Single Specimen (Mpa-m$^{1/2}$) and Separation Severity Rating**		**800 psig Fracture Toughness K_{EE}/K_{JQ} (Mpa-m$^{1/2}$) and Separation Severity Rating**				**3,000 psig Fracture Toughness K_{EE}/K_{JQ} (Mpa-m$^{1/2}$) and Separation Severity Rating**			
A	327.8[3]	1	140.7	0	138.5[1]	2	94.5[1]	2	96[1]	2
B	NA	NA	117.9[1]	1	128.8	0	114.8	0	118.7[1]	1
D	NA	NA	86.6	0	89.2	0	85.3	0	85.3	0
E	236.1	2	129.2[1]	2	153.4[1]	2	71[1]	3	82[1]	3
F	341.7	2	155.6	0	159.6	0	75	0	85	0
G	192.8	2	128.6[1]	2	122.8[1]	2	127.6[1]	3	-	2
H	173.3	0	150.2	0	155.4	0	91.6[1]	1	87.6	0
I	394.7[3]	1	133.4[1]	1	140.3	0	81.8[1]	2	159[1]	3
J	211.3	0	141.2	0	141.8	0	107	0		
L	265.0	0	85.6	0	100.3	0	94.8	0	95.1	0
P Ind	325.2	0	133.3	0	120.4	0	123.7	0	115.7	0
P Ind IR[2]	342.3	0	113	0	142.2	0	139.4	0	117.7	0
P Ind OR[2]	312.4	0	136.3	0	196.5	0	113.5	0	127.4	0
P Nind	264.8	0	145.9	0	143.3	0	147.4	0	144.5[1]	1
Separations Rating Code: 0-None, 1-Slight, 2-Moderate, 3-Severe										

1 - Calculated K_{EE} and K_{JQ} values may be falsely high due to the presence of various severity levels of separations. Only calculated K_{EE} and K_{JQ} values with a "0" separations rating should be considered reasonable.
2 - OR and IR are outside and inside radius of the induction bend
3 – Air testing done without side grooves machined on specimen which may yield higher values. All others specimens machined with side grooves.

There are several observations that can be made of the data. Fracture toughness measured in air ranged between 173-395 Mpa-m$^{1/2}$. It was expected and in general and on average the fracture toughness in air was approximately two times higher than those achieved in hydrogen at 800 psig (5.5 Mpa). The separations generated in the air fracture toughness testing tended to be less in frequency and also severity than those observed at either 800 (5.5 Mpa) or 3000 psig (21 Mpa) hydrogen testing. There were a variety of different yield strength levels in this study from a nominal 52 ksi (360 Mpa) to 80 ksi (550 Mpa). As has been observed in prior work and contrary to previously published data, at the tested pressures, there is not any significant difference in fracture toughness. Induction bending only reduced the fracture toughness slightly regardless of test pressure. In addition, there was no appreciable difference in the outside or inside radius of the induction bend, Fig. 8.



Fracture toughness vs. strength at 800 psig (5.5 Mpa) and 3,000 psig (21 Mpa)



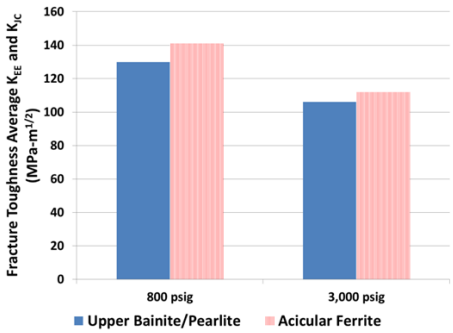
Comparison of induction bend vs. non-induction bend fracture toughness at 800 psig (5.5 Mpa) and 3,000 psig (21 Mpa)

Figure. 8: Fracture toughness results vs. nominal yield strength and induction bending

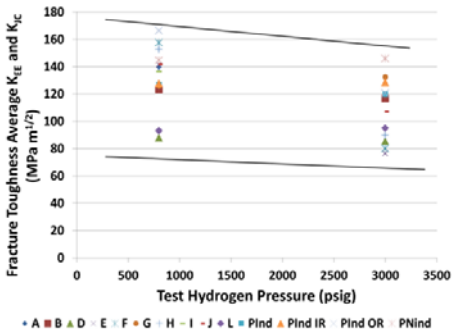
Overall on average, a polygonal ferrite/acicular ferrite microstructure performed slightly better than a polygonal ferrite/upper bainite-pearlite microstructure at each pressure. It should be noted that Alloy L with the highest volume fraction of pearlite did have significantly lower overall fracture toughness values at each pressure. The differences in microstructures fracture toughness performance in hydrogen depends on what role separations play in masking the actual performance. Regardless of microstructure, increasing hydrogen pressure does lower overall fracture toughness. However, in several alloy/microstructure designs tested it is not significant, Fig. 9.

Since chemistry plays a major role in the macro and micro chemical segregation tendencies resulting in potential for macro/micro banded microstructures, a comparison of carbon equivalent as measured by the Ito-Bessyo Pcm formula might give some direction. Carbon equivalent as measured by Pcm seems to play a role in the average measured fracture toughness, especially with the higher 3,000 psig (21 Mpa) pressure. Lower Pcm results in a

trend of higher average measured fracture toughness. However, at 800 psig (5.5 Mpa) hydrogen pressure the trend is less significant, Fig. 10.

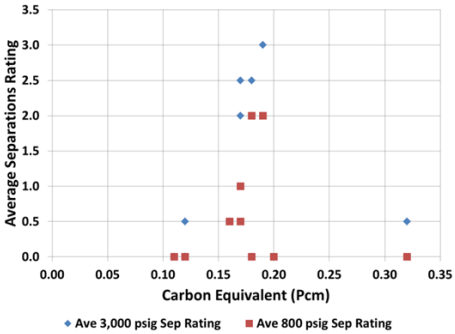


Average fracture toughness vs. microstructure

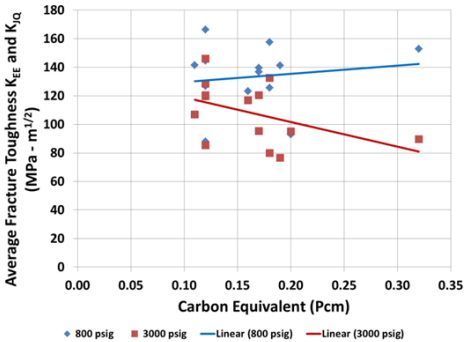


Fracture toughness vs. hydrogen pressure

Figure 9: Fracture toughness vs. microstructure and hydrogen pressure



Carbon equivalent vs. average separations rating at different hydrogen pressure. Pcm - C+Si/30+(Mn+Cu+Cr)/20+Ni/60+Mo/15+V/10+B



Carbon equivalent vs. average toughness at different hydrogen pressures

Fig. 10: Carbon equivalent (Pcm) vs. average separations and fracture toughness

FUTURE WORK

From this study the presence of separations and the corresponding potential to falsely indicate higher fracture toughness than may be reasonable based on existing testing methods needs to be understood. What is the mechanism that causes the separations in these fractures when exposed to hydrogen? Is it a macro/micro difference in microstructure? Does increasing hydrogen pressure further aggravate the separations? What fracture toughness is truly needed for safe operation of a hydrogen pipeline at various pressures? What will be the effect on girth/seam welds? Correlation of the fracture data generated to a more traditional fracture testing standard such as a Charpy V-notch test is needed. In addition, seam and girth welds need to be part of any future work. The ultimate goal of the research will be to offer guidance, information and potential specifications to projects that will be built for gaseous hydrogen transmission.

CONCLUSIONS

In conclusion:

1. Commercially available pipeline and pressure vessel steels of various vintages perform differently in gaseous hydrogen at relevant transmission pipeline pressures.
2. Presence of separations makes the standard calculation of fracture toughness per ASTM E1820/E992 difficult and "falsely" high.
3. Separations may be due to the macro/micro differences in microstructures that act as potential hydrogen trapping sites thus creating the separations. Controlling alloy design (lower carbon equivalent Pcm) and pertinent casting parameters can minimize their formation. The whole subject of separations needs to be investigated further to achieve a better understanding.
4. Yield strength does not appear to have a dominant effect on performance in gaseous hydrogen, emphasizing the importance of the microstructure.
5. Overall, a polygonal ferrite microstructure coupled with a volume fraction of up to 70% acicular ferrite appears to perform the best especially at the higher pressures.
6. Induction bending of an API X52 pipe did appear to alter the microstructure slightly which resulted in slightly lower fracture toughness K_{EE} values. However, the decrease was not overly significant which suggests; at least for API X52 of this alloy/microstructure design does not adversely affect fracture toughness in the presence of gaseous hydrogen in pressure up to 3,000 psig (21 Mpa).

ACKNOWLEDGEMENTS

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REFERENCES

[1] Hayden, L, Stalheim, D., "ASME B31.12 Piping and Pipeline Code Design Rules and their Interaction with Pipeline Concerns, Issues and Research", *ASME PVP 2009*, Prague, Czechoslovakia, 2009.

[2] Stalheim, D., Hayden, L., "Metallurgical Considerations for Commercial Steels used for Hydrogen Service", *Hydrogen 08 Conference*, Jackson Hole, WY, USA, 2008.

[3] Secat, Inc., "Materials Solutions for Hydrogen Delivery in Pipelines-Peer Review" – *Department of Energy Peer Review Meeting for Hydrogen Delivery*, Arlington, VA USA, May 2011.

[4] Stalheim, D., et.al, "Microstructure and Mechanical Property Performance of Commercial Grade API Pipeline Steels in High Pressure Gaseous Hydrogen", *Proceedings and Presentation at the 8th ASME International Pipeline Conference*, Calgary, Canada, September 2010.

[5] Stalheim, D., Boggess, T., Ningileri, S., "Summary Report of Fracture Toughness Testing of Three Pipeline Steels in High Pressure Gaseous Hydrogen – Phase 1", *Report to ASME ST-LLC and B31.12 Codes and Standards Committee*, June 2011.

[6] San Marchi, C., et.al, "Fracture Toughness and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen", *Proceedings of the ASME 2011 Pressure Vessels & Piping Division / K-PVP Conference*, Baltimore, MD, USA, July 2011.