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DETAILED SUMMARY OF CHARACTERISTICS AND ATTRIBUTES OF API STEEL INTENDED FOR GASEOUS HYDROGEN PIPELINE SERVICE

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ABSTRACT: A renewed push for controlling greenhouse gases has brought the use of hydrogen as an energy source in industry and transportation to the forefront in many different areas of the world. Part of the infrastructure development for the use of hydrogen is to use pipelines for transportation and potentially even as temporary storage vessels. The pipelines being explored for use are a combination of the existing oil/natural gas pipeline network plus the addition of new pipelines to support the volume of hydrogen required. The pipelines may transport pure gaseous hydrogen or a mix of natural gas and hydrogen gas. As has been well documented over the years, hydrogen will diffuse, with assistance from various mechanisms of corrosion and pressure, into steel and degrade the mechanical properties through embrittlement or hydrogen induced cracking. Of particular concern are critical ductility properties such as fracture toughness and fatigue crack growth. There has been substantial fracture and fatigue evaluation of various industrially produced API pipeline and structural steels grades in a gaseous hydrogen environment up to 21 MPa (3000 psi). Based on the results of the research, testing and experience compiled over the past 15-20 years, this paper will summarize the fracture performance of various API grade steels from X52 to X80 in relationship to microstructural characteristics that affect ductility. The intent of this summary is to give end users guidance on fracture performance in repurposing of existing API grade pipelines and construction of new pipelines for high pressure gaseous hydrogen service.

1. INTRODUCTION

Hydrogen pipelines have been in very limited use since 1938 with a small increase in use since the 1990's by the industrial gas companies serving the petrochemical industry. The negative influence of hydrogen on the performance of structural steels has been well documented over the years (Bernstein, 1970). Metallurgists working for industrial

gas companies and other hydrogen users have long been aware of the potential for hydrogen to degrade the properties of pipeline material, particularly carbon steel. Failures of carbon steel plate and pipe were first observed in the nineteenth century due to release of charged (monatomic) hydrogen into the material in aqueous acidic conditions (Johnson, 1875). Gaseous (diatomic) hydrogen can also result in material failure at unexpectedly low stress levels. With the increase in pipelines for hydrogen transport in the 1990's, many industrial gas companies evolved internal specifications to guide their engineering staff in the design of safe pipeline/piping systems. In 2004, the industrial gas companies created, jointly with Compressed Gas Association (USA) and European Industrial Gas Association, a globally harmonized best practice: IGC Document 121/04, Hydrogen Pipeline Systems (eiga, 2004). This document listed recommended chemistry and metallurgical properties limited to a maximum strength grade of API 5L X52 for pipelines intended for hydrogen service. ASME B31.12 Codes and Standards for Hydrogen Piping and Pipelines was released in 2008 with a design up to 21 MPa (ASME, 2008). This code is a combination of ASME B31.8, primarily oriented toward natural gas pipelines, and many supplementary best practices utilized by the hydrogen gas industry. In looking at the design requirements in ASME B31.12, Option A provides for a basic design factor of 0.5 for API X52 or lower which is essentially a multiplier to reduce design operating pressure based on location. To increase operating design pressure, either thicker pipe is required or ASME B31.12 offers Option B, which contains additional fracture-fatigue assessment testing in gaseous hydrogen to prequalify materials for hydrogen service.

It is well understood and documented that hydrogen can reduce the ductility performance of C/Mn steels (Martin, 2019; Cialone, 1984). Of importance to the operational safety performance of pipelines are two key properties of ductility: fatigue and fracture. Metallurgical attributes that affect C/Mn steel ductility performance have been identified in both the IGC Document 121/04, "homogenous fine-grained microstructures is preferred", and ASME B31.12-2019 Non-mandatory Appendix G, "desired steel microstructure is one of polygonal ferrite and acicular ferrite as uniformly distributed through the steel cross section", Note (f) "ASTM 9 or finer" (ASTM, 2019). In particular, through-thickness (surface to center) grain size and homogeneity, especially high angle grain boundaries (HAGB $D15^\circ$), have been identified as significant metallurgical attributes for overall ductility and corresponding toughness performance (Isasti, 2014, Stalheim, 2018). **The question then remains: what level of fineness or homogeneity of a particular microstructure gives an optimum ductility performance in gaseous hydrogen?**

Since 2005, DGS Metallurgical Solutions has been working with researchers to characterize a diverse range of API X-grade steels (X52 to X80 plates/pipes) for hydrogen service. These steels represent a range of production eras and microstructures as listed in Figure 1 (Stalheim, 2011, 2012). Both fatigue and fracture properties of these steels have been measured in high pressure gaseous hydrogen, utilizing state-of the art facilities. (San Marchi, 2011, Slifka, 2018, Stalheim, 2012). Several of the previously tested steels have been metallographically characterized to define through-thickness hardness, grain size, and homogeneity with a focus on high angle grain boundaries (HAGB 15°). In addition, transverse Charpy V-notch (TCVN) testing at three different temperatures was performed to determine the average and standard deviation TCVN values. It is the intention of this manuscript to present a framework in which Charpy information along with microstructural characterization can be used to understand fracture/crack arrest performance in high pressure gaseous hydrogen to give guidance in repurposing existing pipelines or building new pipelines for hydrogen or blended gas service.

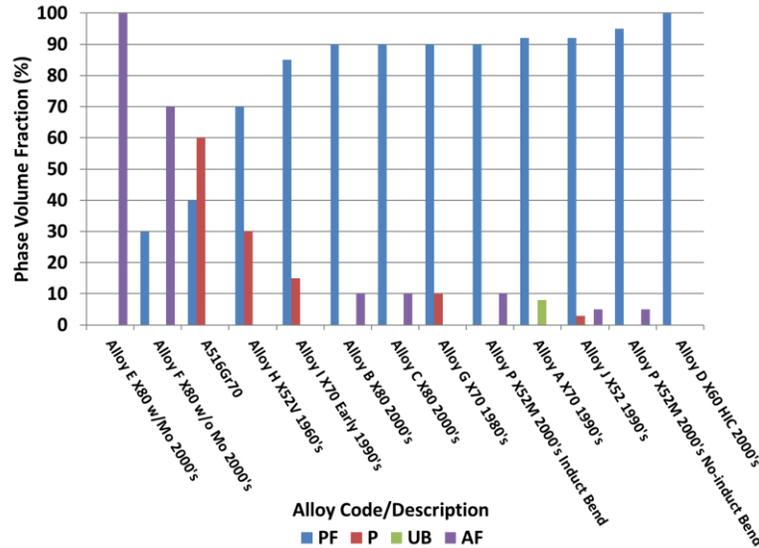


Figure 1. Evaluated API grade X52-X80 and their dominant microstructural phases: PF-Polygonal Ferrite, P-Pearlite, UB-Upper Bainite, AF-Acicular Ferrite

2. PIPELINE STEEL DUCTILITY COMPONENTS AND HYDROGEN PERFORMANCE

Fracture and fatigue performance in any pipeline system regardless of the liquid or gas being transported are always key components that are factored into the safe and economical design of a pipeline. Fracture/crack arrest performance in the form of required Charpy and Drop Weight Tear Test (DWTT) performance, typically at sub-zero temperatures, represents the principal mechanical property requirements for both the pipeline company and the steel producer. Basic development of an economical and safe pipeline design consists of a combination of the strength, pipe wall thickness, and crack arrest characteristics for the desired operating conditions. The ability to balance pipe wall thickness by increasing strength for a maximum pressure is key to the economics of operation. Increasing operating pressure then needs to be balanced with the ductility performance of the steel pipe, which eventually affects its fracture/crack arrest characteristics. For optimum safe operation, fracture/crack arrest characteristics should drive decisions on what grade steel, mechanical properties and the maximum operating pressure. If increased operating pressure is required for economical and operational considerations, then fracture/crack arrest characteristics are paramount. Ductility performance of any pipeline steel includes the fracture/crack arrest characteristics along with fatigue, elongation, reduction of area (%RA) and formability. These characteristics are determined by the through-thickness microstructure of the pipeline steel. The metallurgical attributes that contribute to ductility can be related to the fracture appearance transition temperature (50% FATT) in the following relationship (Isasti, 2014, Stalheim, 2018):

$$50\% FATT (^{\circ}C) = -11Mn + 42Si + 700(Nfree)^{0.5} + 15(\%pearlite + \%M/A)^{1/3} + 0.5\Delta\sigma_y - 14(D_{mean15^{\circ}})^{-0.5} - 39(Dc20\%/D_{mean15^{\circ}})^{0.5} + 23.9(D_{M/A})^{0.5} \quad [1]$$

In particular, two of the key metallurgical attributes are the average high angle grain boundary size ($D_{mean15^{\circ}}$ or $D15^{\circ}$) and a grain-size homogeneity factor as defined by the grain size of the 20% area fraction distribution ($Dc20\%$) divided by the average $D15^{\circ}$ (Figure 2). Larger HAGB grains in the red box are considered a detriment to ductility performance. Smaller HAGB grains to the left of the red arrow/box in Figure 2 are considered beneficial to ductility performance. The average $D15^{\circ}$ and homogeneity factor $Dc20\%/D15^{\circ}$ surface-to-center values can then be averaged to represent the $D15^{\circ}$ grain size and homogeneity of the steel that can be used in the surface-to-center characterization of the toughness performance, 50% FATT in Equation 1. It should be noted that the component $\Delta\sigma_y$ consists of

dislocation density, precipitation strengthening from V and Ti and can encompass overall steel cleanliness and inclusion quality.

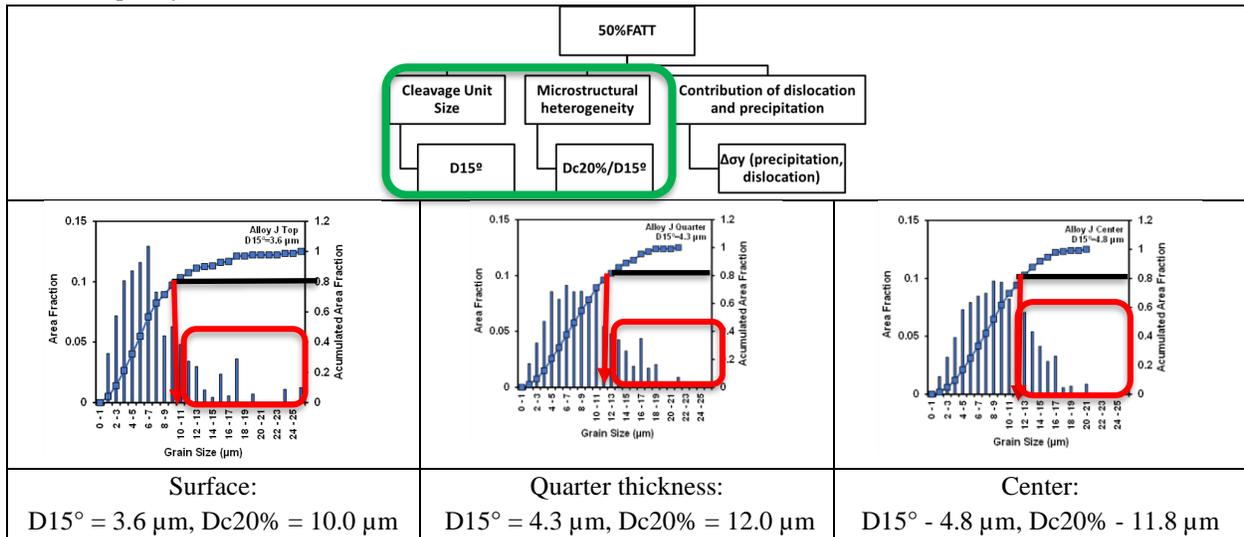


Figure 2. The grain size and homogeneity factor are two key metallurgical attributes that define ductility performance. Histograms of area fracture of HAGBs in API X52 steel at surface, quarter thickness and center of the pipe thickness, noting the D15° and the Dc20% values.

The components that comprise the ductility performance in Equation 1 can be determined by through-thickness metallographic analysis (Uranga, 2017, Stalheim, 2018, Stalheim, 2021). Figure 3 gives an example of the determination of these parameters from Equation 1 for API X52 steel at the quarter thickness. Eight of API X-grade steels from Figure 1 have been characterized, surface to center, in this way. The components used in determining the analytical 50%FATT are shown in Figure 4. The “fineness” (represented by the D15° mean value) and the “homogeneity” (represented by the factor Dc20%/D15°) clearly are the main components in the analytically determined 50%FATT and can be used to assess a steel’s ductility.

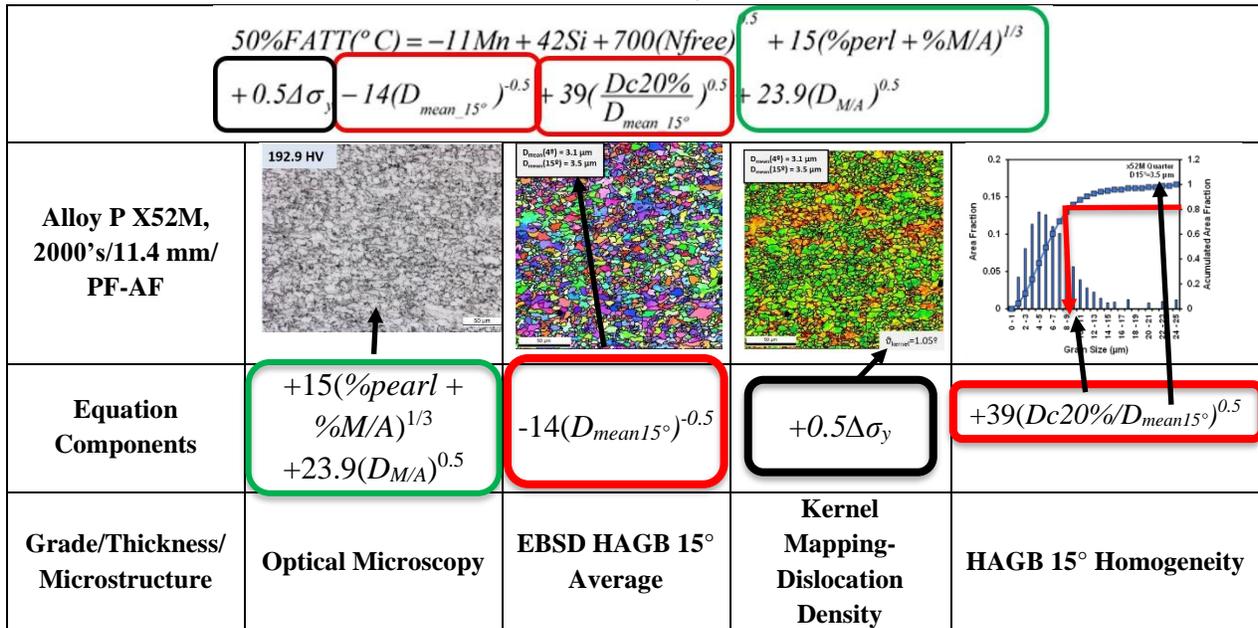


Figure 3. Metallographic analysis of API X52M steel to determine the analytical FATT(50%) ductility parameter.

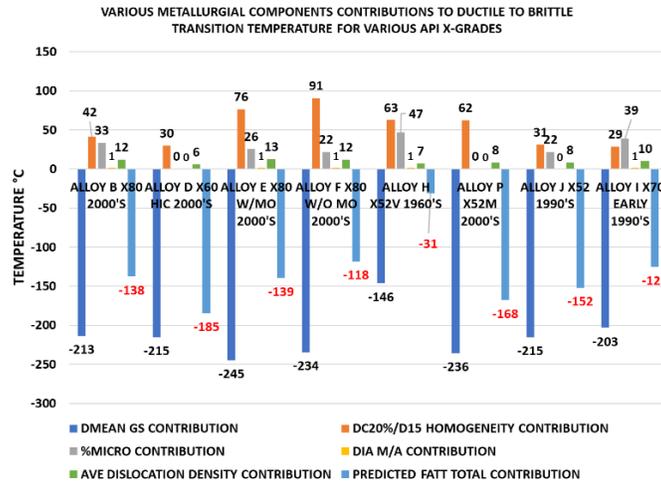


Figure 4. Results of the metallurgical analysis of eight API X-grade steels showing individual contribution of the components in the determination of the analytical 50%FATT value. Note that %MA and MA diameter were estimated based on alloy design and microstructure produced. This example does not include the presence of inclusions or precipitates of V or Ti that may be present that can only further increase the FATT temperature.

The fracture toughness of eight API X-grade steels is shown in Figure 5 for three testing environments: air as well as hydrogen at pressure of 5.5 and 21 MPa respectively, along with average and standard deviation Charpy V-notch (TCVN) results in air @ -40 °C for each shown in Figure 5. These steels represent diverse microstructure and grades from X52 through X80. Two tendencies stand out in the fracture performance of these steels with increasing hydrogen pressure in Figure 6. The first tendency is well documented in the literature and shows a significant initial decrease in fracture toughness from air to 5.5 MPa hydrogen. This decrease can vary from 30-70%, but typically it is in the 40-60% range with the value of K in the range of 100-150 MPa-m^{1/2} (note these measurements represent a mixture of K_{JQ} and K_{EE} (ASTM E992—84 (1989)) values, i.e., different measurements of fracture toughness). However, with increasing hydrogen pressure the second tendency is that three of the API X-grades remain stable to 21 MPa hydrogen pressure (remaining in the 90-150 MPa-m^{1/2} range) and the other five API X-grades further degrade in fracture performance to the 70-120 MPa-m^{1/2} range. Curiously, the steels that show additional degradation at higher pressure (21 MPa) also show higher fracture resistance than the other population at the lower pressure (5.5 MPa). While the fracture resistance at 5.5 MPa is higher, this suggests that there are additional components that are contributing to the degradation as pressure increases.

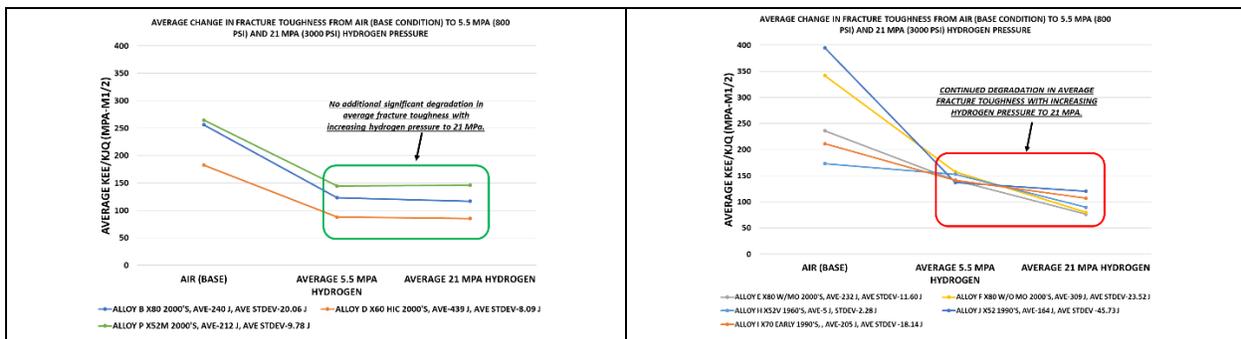


Figure 5. Fracture toughness of eight API X-grades evaluated in gaseous hydrogen at two different pressures. The steels in the panel on the left show little difference in fracture resistance at 5.5 and 21 MPa, whereas the steels in the right panel show additional degradation in fracture resistance at the higher pressure. Note that TCVN @ -40 °C performance for each is shown in the legend.

To better understand the fracture performance in hydrogen and more importantly the influence of hydrogen pressure, one would have to start by understanding the differences in the through-thickness ductility components of these eight API X-grade steels. The transverse Charpy V-notch (TCVN) properties can be used to help define the through-thickness ductility. The two main components of ductility as defined in Equation 1 of D15° and the homogeneity factor (Dc20%/D15°) can be represented by the TCVN values and the standard deviation in these values (between a minimum of 3 TCVN Charpy samples). HAGB (Dmean 15°) has shown a beneficial effect for ductility on fatigue crack growth in hydrogen (Song, 2018). The average TCVN and standard deviation for Charpy testing at -40 °C is provided in Figure 6 for eight API X-grade pipeline steels. A red line has been drawn at 200 J average and 20 J standard deviation which were selected as a benchmark that represents desirable TCVN properties that reflect both good ductility and homogeneity in the microstructure.

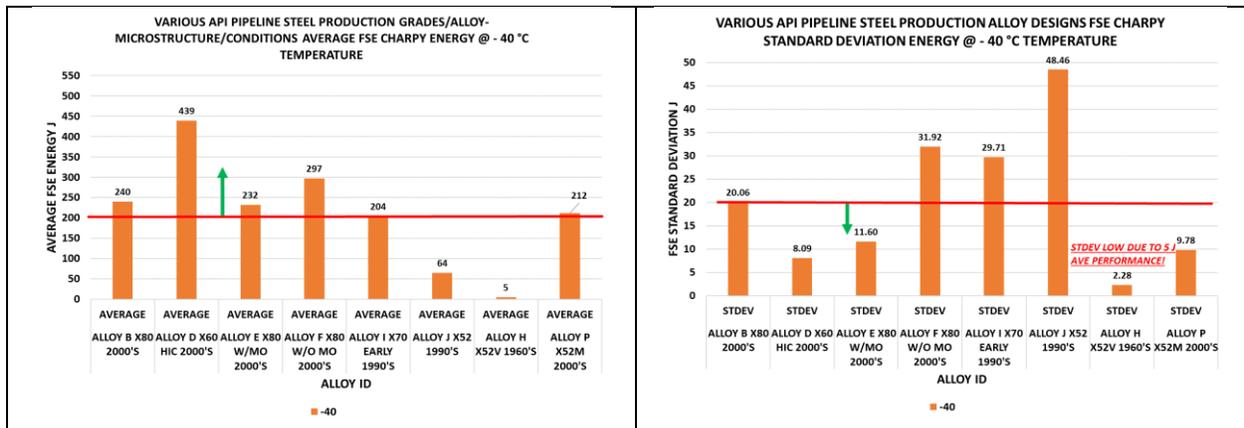


Figure 6. TCVN and standard deviation (3 tests) in air at temperature of -40 °C for eight API X-grade steels. Green arrow points toward the desirable side of the benchmark line (red line).

The Charpy results (including two additional API X-grade steels) are plotted with the metallographic through-thickness D15° and homogeneity factor in Figure 7. The average TCVN and standard deviation appear to trend with the metallographic analysis and can be used to estimate the level of “fineness” and “homogeneity”. Since “fineness” and “homogeneity” are key attributes in ductility performance, the TCVN values and the associated standard deviation can also be used to assess the ductility and we hypothesize that these values can be used to assess fracture performance in hydrogen environments.

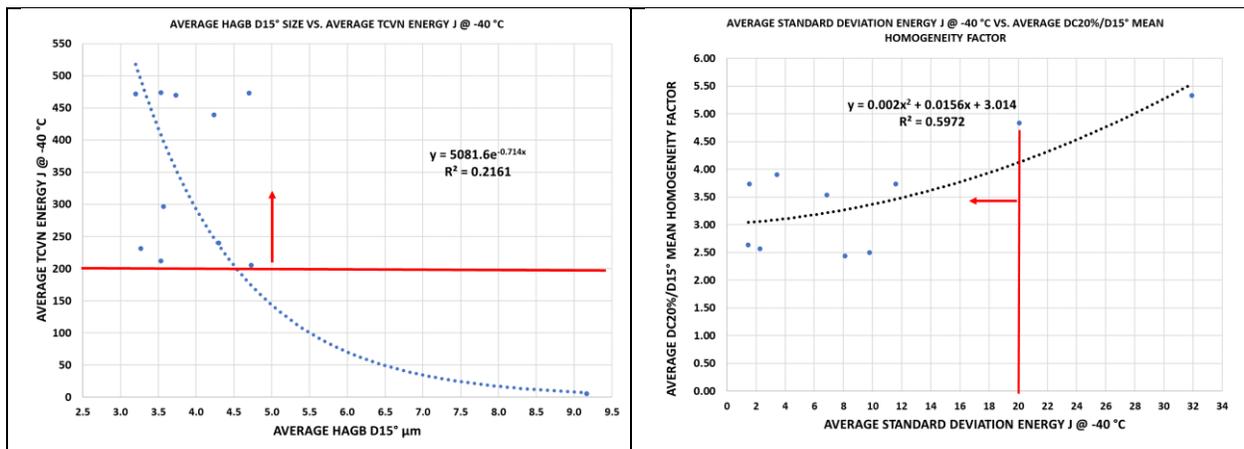


Figure 7. Trend of air TCVN average and standard deviation to average HAGB and average Dc20%/D15° homogeneity factor

However, fracture/crack arrest performance can be affected by microstructural banding from the as-cast alloy, usually manifesting as centerline segregation during solidification in steel production. This microstructural banding reduces the fracture toughness by creating separations, as shown in Figure 8. This results in relatively low TCVN values corresponding with fracture separations, whereas high TCVN values usually do not show separations except in cases of higher-strength bainitic steels with higher carbon equivalents. This is also an area of high stress intensity due to differences in volume expansion of the various microstructural phases during post rolling transformation. Consequently, this area provides strong hydrogen trapping sites and a corresponding tendency for hydrogen-induced cracking (HIC), Figure 8 (Stalheim, 2010, 2016, 2018). These microstructural bands and corresponding separations also appear in fracture tests in air TCVN and fracture toughness tests in hydrogen, and increase in severity and frequency with decreasing TCVN test temperature and increasing hydrogen pressure, Figure 9 (Stalheim, 2012). It can be seen in Figure 9 that the separations follow the same tendencies in both air and hydrogen.

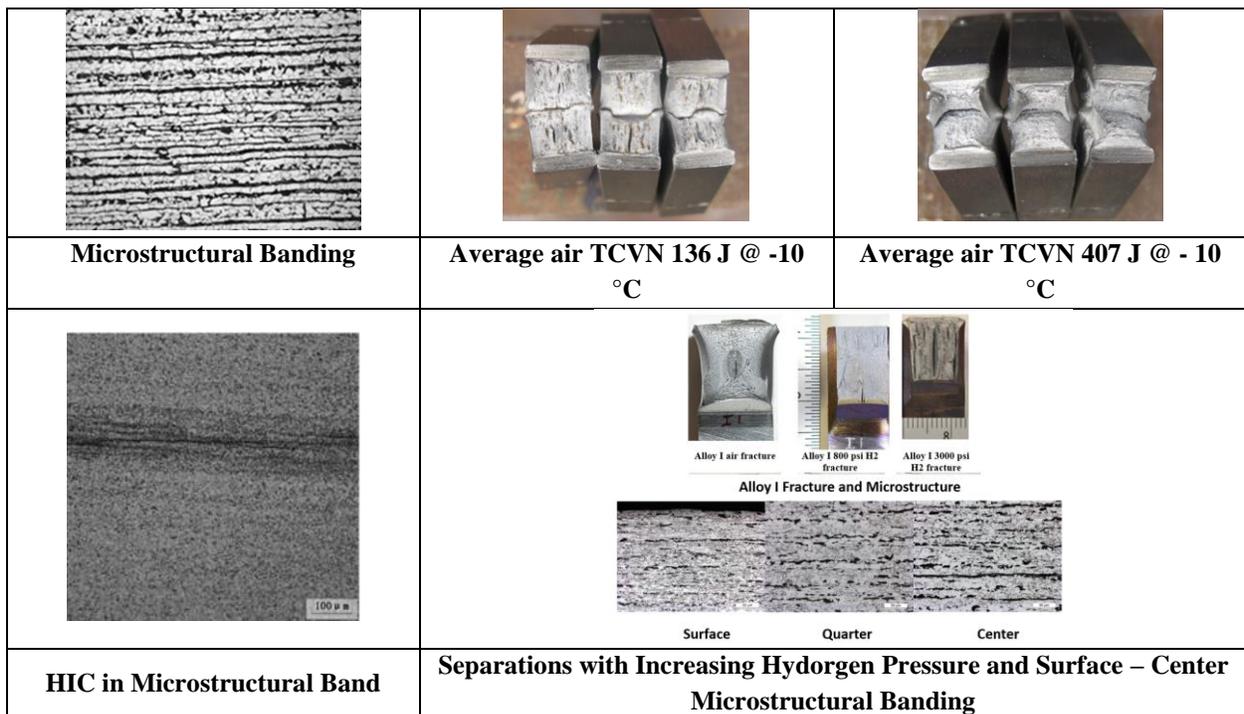


Figure 8. Example of microstructural banding and corresponding effects on separations and fracture toughness performance.

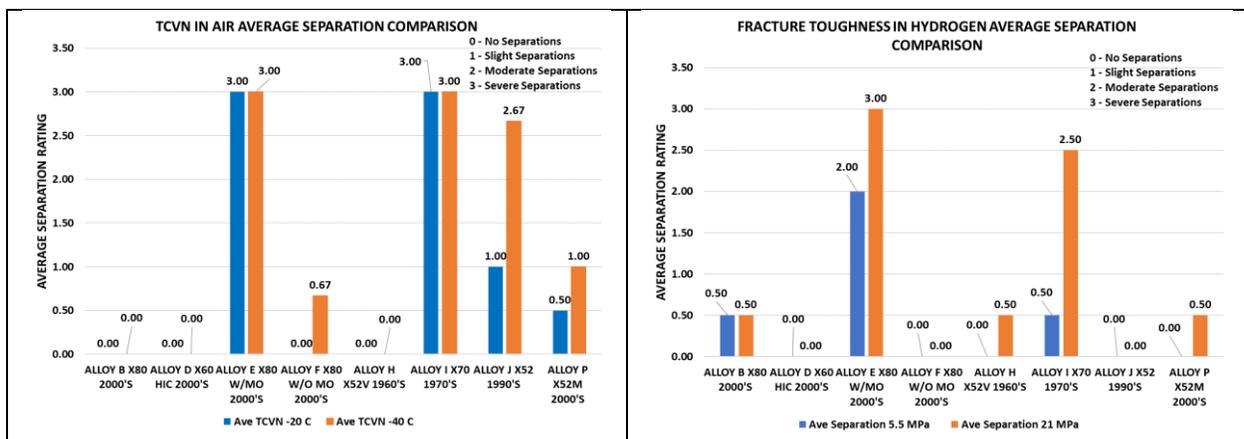


Figure 9. Average visual separations rating for API X-grade steels charpy fracture, TCVN, tested in air and tested for fracture toughness, K, in hydrogen.

5. RANKING OF API STEELS FRACTURE TESTED IN HYDROGEN

Utilizing the framework and data described above related to ductility attributes and corresponding fracture/crack arrest characteristics of a diverse set of API X-grade steels, a composite ranking system has been developed. This system assigns a ranking to average TCVN values and the associated standard deviation along with an assessment of fracture separations in air to rank the influence of pressure on fracture resistance in hydrogen, Figure 5. The scoring system is summarized in Table 1. Increasing values are assigned to attributes that improve ductility performance and negative values were assigned to attributes that degrade ductility performance.

Table 1. Ranking criteria used for development of suitability of API X-grade steels for hydrogen service

Average TCVN Egy J @ -40 °C	Ranking Value	Average TCVN Stdev J @ -40 °C	Ranking Value	Average Visual TCVN Separations in Air	Ranking Value
≥0	-4	≥40	-3	0.00	1
≥25	-3	≥30	-2	0.50	0
≥50	-2	>20	-1	1.00	-1
≥100	-1	≤20	1	1.50	-2
≥150	0	≤10	2	2.00	-3
≥200	1	≤5	3	2.50	-4
≥250	2			3.00	-5
≥300	3				
≥350	4				
≥400	5				

Figure 10 shows the composite ranking of the eight API X-grade steels comparing the differences based on the three TCVN components in Table 1. Note that the three API X-grades that showed the stability in fracture toughness beyond 5.5 MPa are also the three that have the highest overall composite ranking. The other 5 steels that showed the degradation in fracture toughness up to 21 MPa have lower or negative composite rankings (but necessarily the highest fracture resistance when tested in hydrogen at pressure of 21 MPa). Based on this ranking system, steels in the green box should have better overall fracture performance. Lower ranking steels may show similar fracture resistance in hydrogen at high pressure, but the general fracture performance of these steels is more variable and should be considered in the context of the operating environment (especially stress in the pipe wall) and fitness-for-service assessments. It does not mean steels with lower rankings should not be used, but these steels may be more susceptible to other factors such as external damage and corrosion. This type of analysis can be further expanded to give additional guidance for Pcm, hardness, TCVN benchmarks and corresponding microstructures to assess the performance of materials for hydrogen service.

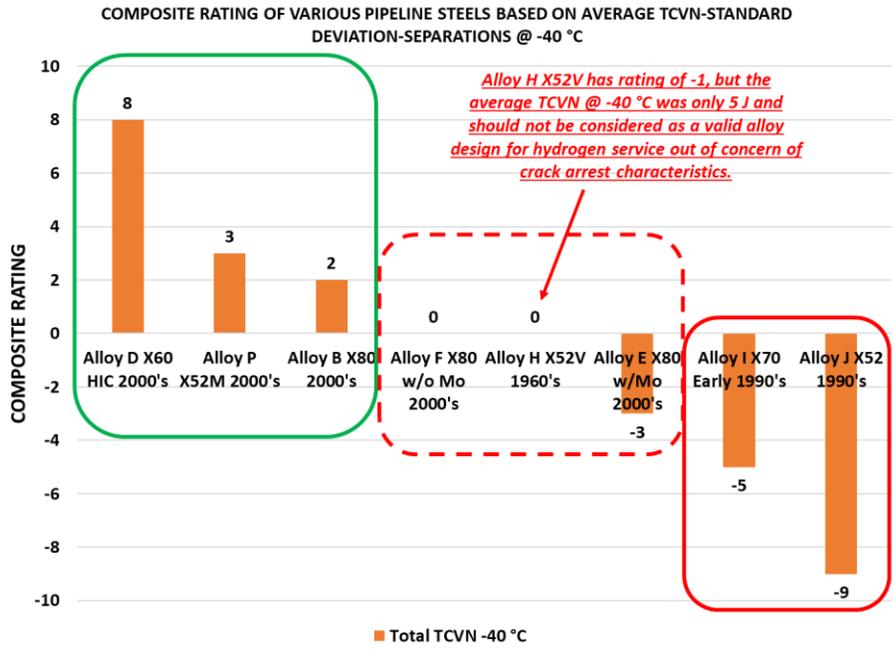


Figure 10. Composite ranking utilizing TCVN -40 °C performance and separation assessment from TCVN testing.

6. CONCLUSIONS

Fracture/crack arrest performance is a critical component to the decision process in operating a hydrogen pipeline in an economical but safe manner. Utilizing the existing hydrogen testing, data, API alloy designs, ductility attributes including Charpy and through-thickness microstructural characterization, a simple ranking system has been developed to provide recommendations/guidance on fracture performance in gaseous hydrogen environments. This ranking system is a first step in developing a screening tool to assess the potential of existing pipelines for hydrogen service. In addition, this information can be used to aid design of new pipelines and potentially make modifications to existing codes.

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