

Studies of High Temperature Hydrogen Related Damage in
Welded Carbon Steel Components used in
Refineries

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Abstract

Five materials encompassing various grades of carbon steel were received from retired and ex-service petroleum refinery equipment for root-cause evaluation of High Temperature Hydrogen Attack (HTHA) damage at UTK. These materials were submitted by three contributors: Irving Oil Refinery (IOR #1110-2), Valero (#67 & #1252134), and Phillips 66 (#555-S1 & #555-S2) on behalf of American Petroleum Institute (API). These materials originated from various flange-to-pipe welded components that were exposed in hydrogen pressure environment at elevated temperatures ($> 640^{\circ}\text{F}$ and >70 psia).

A singular crack originating at the flange inside surface just outside of the visible HAZ was observed in IOR #1110-2 and Valero #67, respectively. Cracking in IOR #1110-2 was $1/4''$ long in the circumferential direction and $\sim 3/8''$ deep ($3/4$ of the flange wall) in the sample received at UTK. A singular crack $5/8''$ long in the flange circumferential direction and $3/4$ deep was found only in one quadrant in the flange base metal just outside of the visible HAZ. However, the cracks in these components (IOR #1110-2 and Valero #67) were different from traditionally accepted HTHA morphology, i.e. no decarburization, no residual methane, and no evidence of cavitation were observed adjacent to crack areas. Cracking in

these two components showed a mixture of intergranular and transgranular cracking morphology. No evidence of cracking or microstructural damage was observed in Valero #1252134.

The Phillips 66 component, #555-S1 showed the evidence of the beginning stage of HTHA damage with grain boundary microfissures in the flange base metal just outside of the visible heat-affected zone (HAZ); no apparent decarburization was observed adjacent to microfissures. The presence of methane cavities were observed along pearlite/ferrite and ferrite/ferrite boundaries. A residual methane content of 28 ppm was measured in the damaged region of P66 #555-S1 (from the most damaged area). No evidence of fissuring or decarburization was observed in the second component received from P66 #555-S2. The results showed two of the components exhibited non-traditional form of HTHA damage, two components did not exhibit any damage, and one component from Phillips 66 exhibited traditional HTHA damage.

Executive Summary

HTHA is a type of hydrogen damage observed in steels in which atomic hydrogen (H^+) from service environment diffuses into steel to react with carbon in solution or carbides at elevated temperatures and pressure to form molecular methane (CH_4). Methane bubbles grow in size with continued diffusion of hydrogen and internal methane pressure. This leads to methane bubble coalescence, grain boundary fissuring, cracking, blistering, and hence possibly causing unexpected failure of the component.

The metallurgical characterizations and root cause assessments of ex-service carbon steel components operating in petroleum refining equipment exposed to hydrogen containing environments at elevated temperatures were undertaken under the auspices of the American Petroleum Institute (API) Recommended Practice (RP) 941 Committee. The Materials Properties Council (MPC) assumed the role of a facilitator in the funding and advising of the efforts conducted at the University of Tennessee by the Metallurgy and Materials Joining Group. API RP 941 Committee members submitted components that had suffered leaking or exhibited NDE indications, which were considered potentially detrimental to continued operation of the refining equipment. A total

of five components were evaluated using various metallurgical testing and characterization techniques and the data obtained was considered in light of the equipment operating conditions to provide an assessment of the causes for the occurrence of the material conditions found by the equipment operators. The initial request for HTHA damaged materials was couched in terms of potential damage to the equipment by High Temperature Hydrogen Attack (HTHA) as defined in API RP 941 *“Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants”*. The results of the examination and assessments of the five components/samples submitted are contained within this document.

These materials originated from various contributors extracted from flange-to-pipe welds, which were exposed in hydrogen environments (70-83 psia) at elevated temperatures (640°F-670°F). The operating conditions of the five components, when positioned on the API RP 941 Nelson diagram (2008), are located to the left and below the knee of the carbon steel curve (within the API RP 941 safe operating region). Thus, HTHA damage should not have occurred in any of the components.

All components were evaluated for HTHA damage using metallography (optical & scanning electron microscopy), AWS/ISO diffusible hydrogen

measurements & methane (by dissociation to hydrogen) determination using gas chromatography. Fractographic crack surface evaluations using SEM were enhanced by the “Cryo-Cracking” technique. The mechanical properties were determined using hardness, Charpy impact toughness, and ASME Section IX bend tests.

A component received from Phillips 66 (#555-S1) exhibited traditional HTHA, but others showed singular cracks originating at the inside diameter surface in the flange base metal, just outside of the visible HAZ were observed in flange-to-pipe welded components received from Irving Oil and Valero Energy (#1110-2 and #67, respectively). A singular crack, (only a partial length provided to UTK [1/4” long and 3/8” deep] in the thru-wall direction) from the 5/8” long crack at the ID surface of the flange-to-pipe weld in the circumferential direction was provided. This IOR flange-to-pipe welded component (#1110-2) was removed from service due to leakage, and was previously examined by Wayland Engineering. The 5/8” long crack in Valero Flange #67 was found only in one quadrant adjacent to the flange-to-pipe weld. This 5/8” long crack was located in the flange base metal just outside the visible HAZ. The crack in Valero Flange #67 was oriented circumferentially along the weld at the ID surface and extended to a depth of 75% of the flange wall. The cracks in IOR #1110-2 and

Valero #67 exhibited a mixture of intergranular and transgranular propagation, and no evidence of decarburization or grain boundary cavity/bubble/void formation was observed. The cracks in these samples (IOR #1110-2 and Valero #67) were different from traditionally defined HTHA damage, i.e. no decarburization, no residual methane content, and no evidence of cavitation/voids/bubbles. The second flange-to-pipe welded component received from Valero Energy (Flange #1252134) did not exhibit any cracking and did not show any evidence of microstructural damage (such as decarburization, fissuring, or loss in hardness). No cracking or evidence of traditional HTHA damage was observed in the pipe base metal or the weld deposit in IOR #1110-2, Valero #67 and Valero #1252134.

The Phillips 66 flange-to-pipe welded component (#555-S1) showed evidence of the beginning stage of HTHA damage with grain boundary microfissures in the flange base metal just outside of the visible HAZ. No decarburization was observed in any area of this component. A methane content of 28 ppm was measured in the base metal just outside of the flange HAZ (the most damaged area). The presence of cavities was observed along pearlite/ferrite and ferrite/ferrite boundaries when evaluated by Cryo-Cracking. The second flange-to-pipe welded component received from Phillips 66 (#555-S2) did not

exhibit cracking or show evidence of microstructural damage (decarburization, fissuring, or reduction in hardness).

The samples received from Phillips 66 (#555-S1) exhibited traditional HTHA damage. However, the cracked components from Irving Oil (#1110-2) and Valero (#67) are considered a result of other than the traditional high temperature hydrogen attack mechanism. The remaining two components, Valero #1252134 and P66 #555-S2, did not exhibit any microstructural damage.

It is important to note that the definition of HTHA, as provided in API RP 941, is that *“hydrogen reacts with the carbon in the steel to cause either surface decarburization or internal decarburization and fissuring, and eventually cracking. This form of hydrogen damage is called high temperature hydrogen attack (HTHA).....”*. However, only one of the five components supplied exhibited these characteristics and thus these three should be classified, in terms of type of damage occurrence, as “Traditional HTHA”. That is not to say that hydrogen did not play a role in the damage occurrence in the remaining components samples nor does it minimize their importance in terms of potential operational difficulties. Therefore, some serious thought should be given to changing or expanding the API RP 941 HTHA definition to encompass the “Non-Traditional” damage mechanisms as well.

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Nomenclature and Abbreviations

API	American Petroleum Institute
AW	As-Welded
AWS	American Welding Society
CS	Carbon Steel
C -½ Mo	Carbon – ½ Molybdenum
CGHAZ	Coarse-Grained Heat Affected Zone
CH ₄	Methane
CSB	Chemical Safety Board
FGHAZ	Fine-Grained Heat Affected Zone
HAZ	Heat Affected Zone
HTHA	High Temperature Hydrogen Attack
IOR	Irving Oil Refinery
MJG	Materials Joining Group at the University of Tennessee
MPC	Materials Properties Council
MPa	Mega Pascal (10 ⁶ Pa)
NDE	Non Destructive Examination
OLM	Optical Light Microscopy
PWHT	Postweld Heat Treatment
psia	Pounds per square inch absolute
ppm	parts per million
RP	Recommended Practice
P66	Phillips 66 Alliance Refinery
SEM	Scanning Electron Microscope
SAW	Submerged Arc Welding
SMAW	Shielded Metal Arc Welding
UTK	University of Tennessee, Knoxville
VE	Valero Energy
WRC	Welding Research Council
Weldment	Weld Deposit, Base Metal and Heat Affected Zone

Chapter 1 – Introduction

Carbon steels are widely used in the various stages of refining of complex hydrocarbons in crude oil to produce everyday consumable products such as gasoline, kerosene, solvents, and diesel ¹. Crude oil is a complex mixture of hydrocarbon chains. During the first step of petroleum refinery, crude oil is pumped to a distillation column where crude oil is separated based on their molecular weights and boiling points. The small hydrocarbon chains with low molecular weight move to the top and longer hydrocarbon chains are left in the bottom of the distillation column. A schematic illustration of a petroleum distillation tower is shown in Figure 1. Once the different petroleum fractions are separated based on their molecular weight in the distillation tower they are sent to catalytic reformers, hydrocrackers, hydrotreating, desulfurization, isomerization units for further purification of impurities and to obtain day to day usable product with greater efficiency and increased octane ratings ².

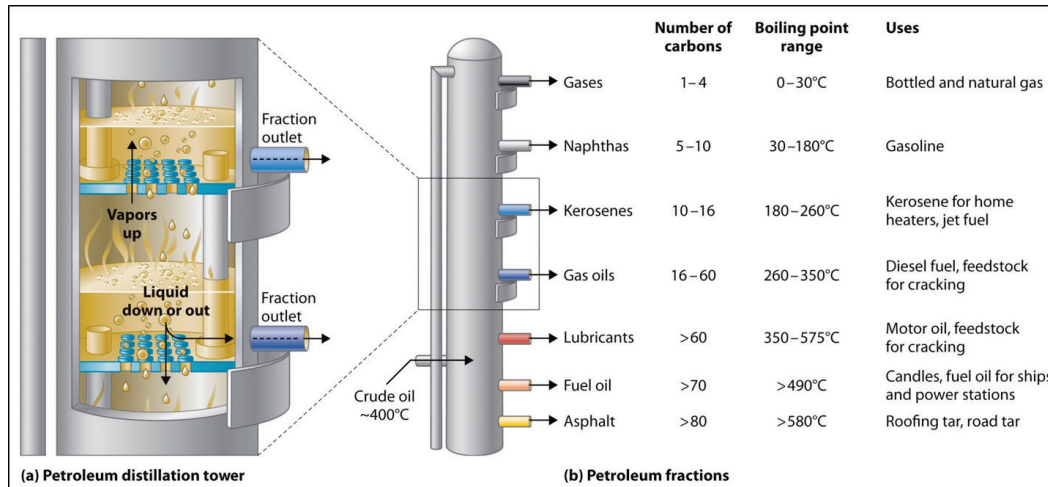


Figure 1. Schematic Illustration of a) Petroleum Distillation Tower and Petroleum Fractions Based on Molecular Weight ³.

Carbon steels are commonly used in the various stages of petroleum refinery because of their availability and affordability. The operating conditions for carbon steels are usually in the temperature range of 450°F-750°F (232°C-399°C) with a hydrogen partial pressure of 50 psia-1000 psia (0.34 MPa-6.90 MPa) in petroleum industries and refineries ^{4,5}. However, carbon steels are found to be susceptible to High Temperature Hydrogen Attack (HTHA) when exposed to a hydrogen pressures environment greater than 70 psia (0.48 MPa) at elevated temperatures greater than 450°F (232°C) ^{4,6,7}. Thus, hydrogen damage in these steels operating in petroleum refineries and petrochemical plants has been a

topic of intensive research for the last 70-80 years. However, the true mechanisms of hydrogen damage are not completely understood^{4, 6-22}.

HTHA is a type of hydrogen damage in which atomic hydrogen (H^+) from service environment diffuses into steel to react with carbon in solution or carbides at elevated temperatures and pressure to form molecular methane (CH_4). The methane bubbles generally form along grain, sub-grain boundaries, inclusions, ferrite-cementite interfaces, or grain boundary triple points. Methane molecules are too large to diffuse through steel, and thus accumulate along grain boundaries forming cavities and building methane pressure. Methane bubbles grow in size with continued diffusion of hydrogen and internal methane pressure leading to methane bubble coalescence. The methane bubble coalescence generates internal stresses resulting in grain boundary fissuring, cracking, blistering, and hence possibly causing unexpected failure of the component. HTHA is an irreversible phenomenon and causes permanent damage in steels ^{4, 6, 23}.

Hydrogen damage in carbon steels was first recognized by Johnson in 1875 ²⁴. The various incidents of HTHA damage were observed between 1930s-1940s in steels operating at elevated temperatures in hydrogen pressure

environment^{9, 25-29}. Extensive research was undertaken in the 1940s by G.A. Nelson for the Shell Oil Development Company to design a set of curves using empirical data obtained from laboratory and plant operating conditions to provide safe operating guidelines for steels in hydrogen service. These curves were first published in 1949 in the API proceeding in a diagram called “Nelson diagram”. The 1949 Nelson diagram is shown in Figure 2⁴. The Nelson diagram was based on components exhibiting satisfactory vs. unsatisfactory performance (go - no go basis) in hydrogen atmosphere at elevated temperature. However, the diagram does not provide information on the extent, location, or morphology of HTHA damage observed. The samples showing satisfactory performance were operating for atleast one year; however, unsatisfactory performances were plotted on the diagram regardless of the hydrogen exposure period. Nelson curves provides operating guidelines (service temperature and hydrogen pressure limit for safe operation) for carbon steel, C-1/2 Mo, 1-1/4 Cr-1/2 Mo, 2-1/4 Cr-1 Mo, 2-1/4 Cr-1 Mo-V, 3 Cr-1 Mo (with or without vanadium), 6 Cr-1/2 Mo (with or without tungsten and vanadium) steels. The Nelson diagram in Figure 2 shows the upper operating limits for different steels and represent the

tendency of steels to exhibit surface decarburization (shown by dashed lines) and internal decarburization or fissuring (shown by solid lines).

After the publication of the first Nelson curves in 1949, occasional failures of carbon and low alloy steels when exposed to hydrogen environments in petrochemical plants continued to be a concern despite the fact that the plants had been operating within the guidelines suggested by the Nelson curves. The American Petroleum Institute's (API) Division of Refining made further updates to the original Nelson diagram and the updated diagram was published in 1970 by API as Recommended Practice 941 (1st edition) "*Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*" [5]. API RP 941 has been used by various industries as guidance for operating in high-pressure hydrogen environments at high temperatures. The position of various curves in the API RP 941 Nelson diagram has been periodically updated over years based on operating experiences and accidents or incidents in the petroleum refineries ^{4, 16, 30-35}. Figure 3 shows the Nelson curves from the most recent revision of API RP 941 (7th edition published in 2008, however, the Nelson curves were not changed since 5th edition in published in 1996). Figure 4 shows

an illustration of the change in the position of carbon steel curve in the Nelson diagram from 1949 to the most recent diagram in API RP 941 (7th edition) ^{4, 35}.

Several incidents of failures involving HTHA in steels continued to be reported by the petrochemical plants even when components were operated below their applicable Nelson curves. A recent incident in the hydrogen environment at elevated temperature occurred in 2010 at Tesoro Refining (Anacortes, Washington) which resulted in expelling of hot hydrogen from a carbon steel component leading to fire and causing seven fatalities ³⁶⁻³⁹. The heat exchanger at Tesoro was operating within the guidelines suggested by the API RP 941 Nelson diagram [operating at a temperature of 504°F (262°C) and hydrogen partial pressure of 291 psia (2.01 MPa). The rupture location in the Tesoro Refinery heat exchanger is shown Figure 5 ^{38, 40}. Based on Figure 3 in API RP 941 (2008) “Time for Incipient Attack of Carbon Steel in High Temperature Hydrogen Service”, the damage on Tesoro Refinery vessel should have not occurred, since it was operating in the “no attack” region as shown by red point in Figure 6. Failures of carbon steel components even when operating below the Nelson curve have prompted engineers and designers to address the current position of carbon steel curves in the Nelson diagram.

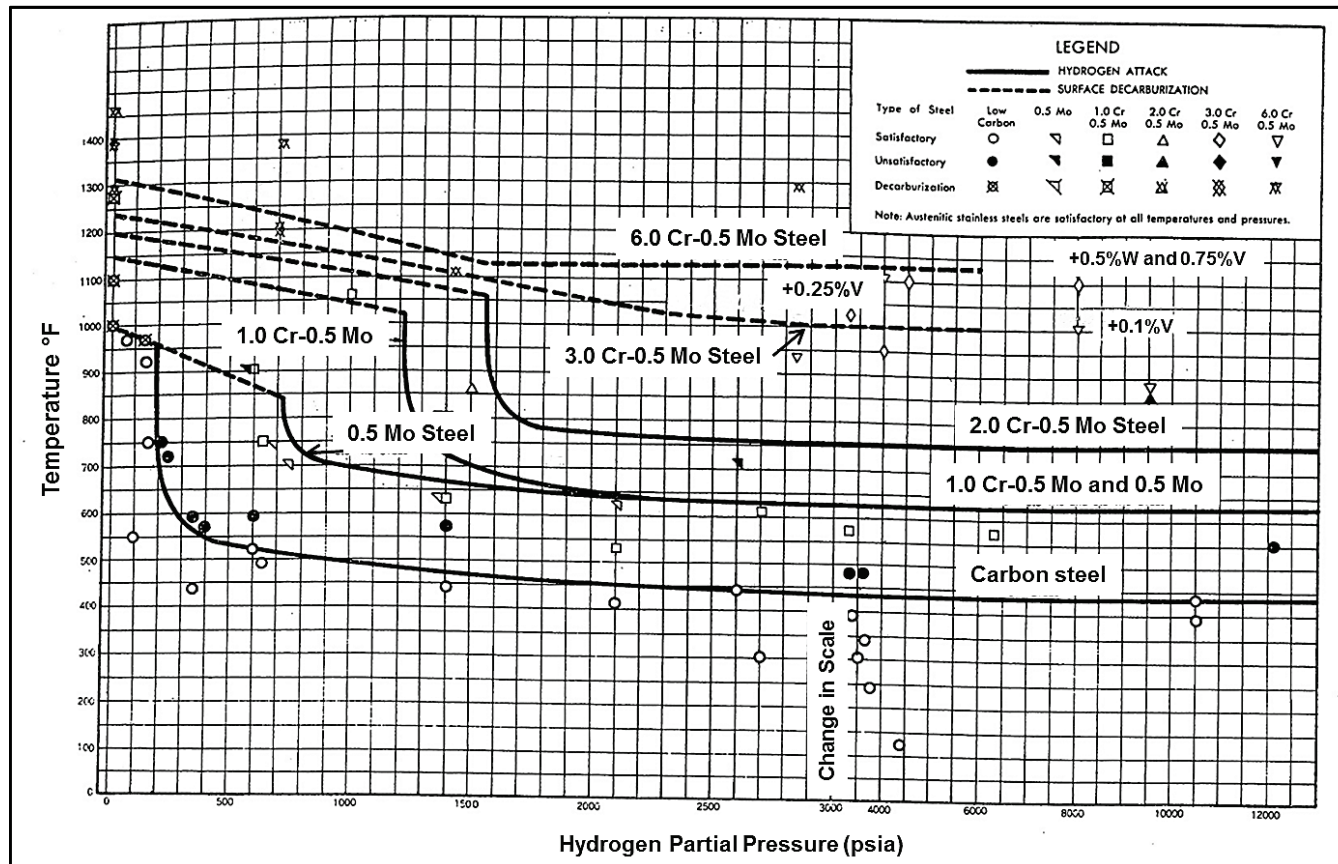


Figure 2. Operating Guidelines for Steels in Petroleum Refineries for Hydrogen Service at Elevated Temperatures and Pressures by G.A. Nelson (Extracted from Nelson's 1949 Paper) ⁴.

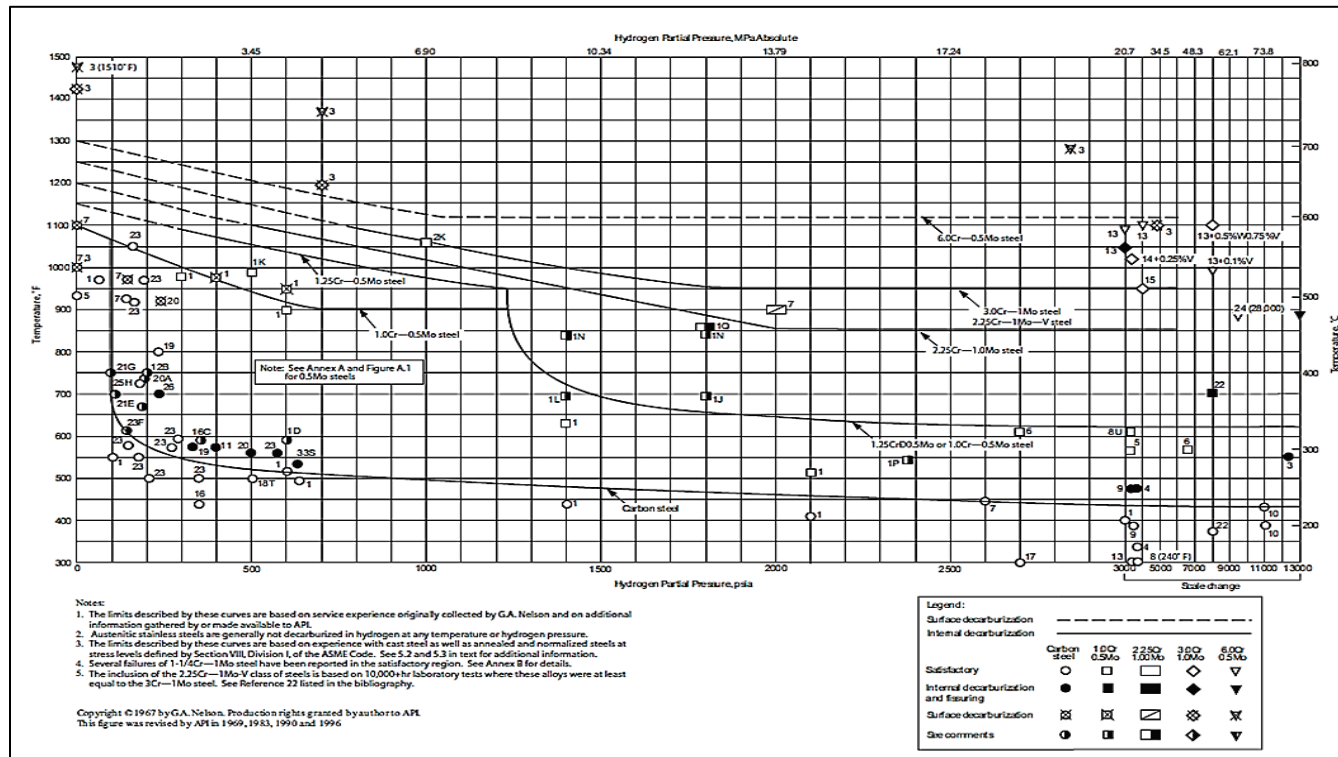


Figure 3. Operating Guidelines for Steels in Petroleum Refineries for Hydrogen Service at Elevated Temperatures and Pressures from API RP 941 (7th Edition, 2008). The last Revision to this Nelson Diagram was Made in 1996 ³⁵.

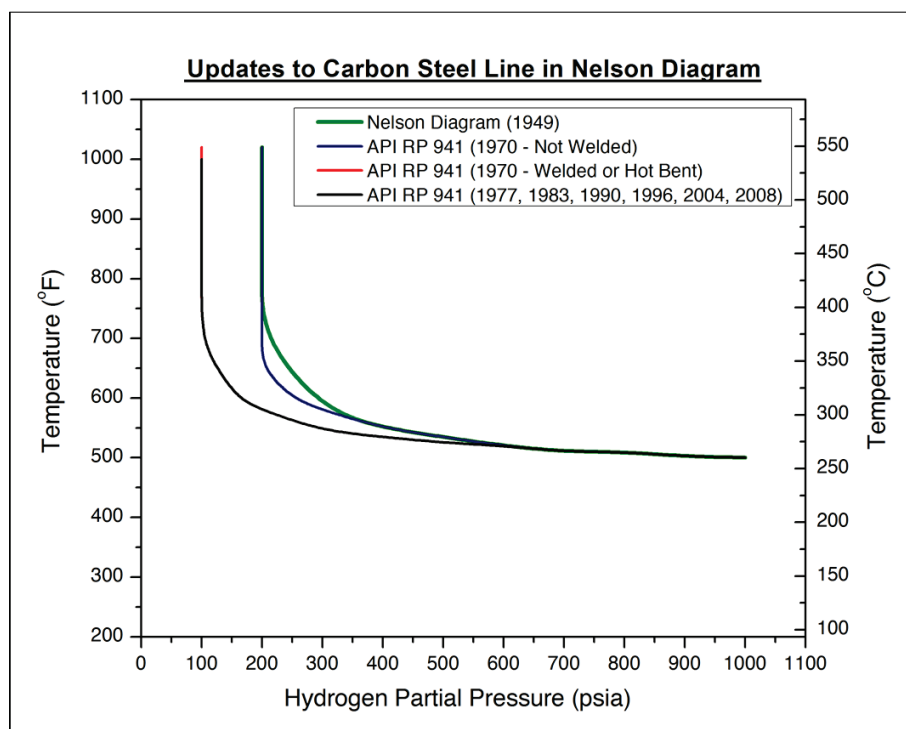


Figure 4. Updates to the Position of the Carbon Steel Curve in the Nelson Diagram from 1949 to 2008 ^{4, 16, 30-35}.

The Chemical Safety Board (CSB) investigated the Tesoro incident and recommended against using the carbon steel component above a hydrogen partial pressure of 50 psia and temperature of 400°F. Figure 7 shows the positions of the CSB carbon steel curve (as shown by the blue dashed lines) with comparison to the current position of carbon steel in API RP 941 Nelson diagram (2008) ^{37, 38}.

Cracking in a non-postweld heat treated (PWHT'ed) carbon steel piping component immediately below the Nelson curve was studied by McLaughlin et. al. in 2010. This study provided inspection guidance for the non-PWHT'ed carbon steel component operating in the area highlighted by red as indicated in Figure 8. The position of the operating conditions of the Tesoro Refinery vessel is shown in Figure 7 by the red square. Thus, this approach of re-inspection should be re-visited as damage was observed in the non-PWHT'ed carbon steel vessel from the Tesoro Refinery operating at the lower end of the inspection area provided by McLaughlin ³⁷. Cracking in a non-PWHT'ed carbon steel component from ExxonMobil (2010) did not reveal traditional HTHA damage, a singular crack initiating at the inside diameter surface propagating towards

outside diameter surface was observed. Decarburization, or cavitation was not associated with the singular crack ³⁷. Methane content was determined in the ExxonMobil component ³⁷. Thus, it is important to recognize currently (traditionally) accepted HTHA damage morphologies in contrast to cracking from other mechanisms.

Hydrogen damage in steels, specifically HTHA is a complex and has been a recurring issue in the petroleum services. One of the primary reasons for the recurrence of these failures despite of operating within the suggested API RP 941 guidelines is due to the lack of industries/refineries support in providing accurate processing information (like service temperature, hydrogen partial pressure, time in service, service-environment, prior thermal, mechanical, and metallurgical history, etc.). The comprehensive and accurate knowledge of a component's in-service condition, prior thermal and mechanical history is important to characterize the extent of hydrogen damage and predict the remaining life of a vessel or a component. The work herein by the Materials Joining Group at the University of Tennessee provides important data, which is

intended to assist engineers/designer's to the further understand HTHA morphologies.

In this study, the Materials Joining Group at The University of Tennessee (UTK) in a joint collaboration with the American Petroleum Institute (API) and the Materials Properties Council (MPC) has made an effort to develop further understanding of HTHA damage. The materials submitted in this study were characterized with regard to HTHA damage morphology and extent of damage using metallography (using both optical and scanning electron microscopy), diffusible hydrogen and methane determination (using gas chromatography), and methane bubble and crack surface evaluation (using the "Cryo-Cracking" technique). The mechanical properties of the materials received in the study were also evaluated using Charpy impact testing, hardness testing, and bend testing. This study provided additional empirical data points along with detailed metallurgical characterizations, which will be beneficial to further understand HTHA damage in carbon steel components and to assist in mitigating future failures and predicting the service life of components when used in hydrogen environments at elevated temperatures.

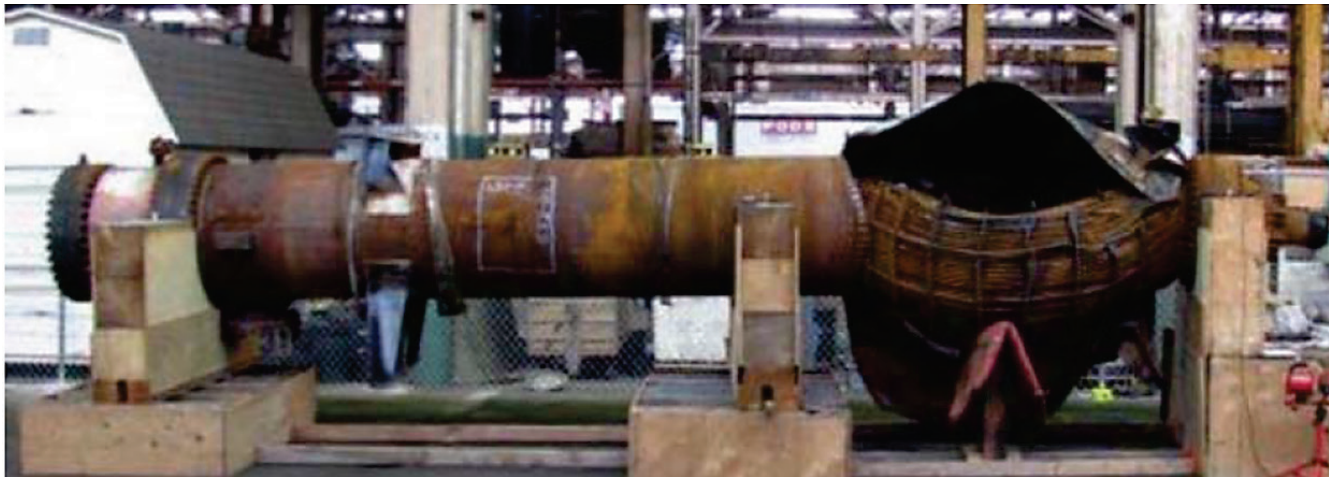


Figure 5. Tesoro Anacortes Heat Exchanger E (NHT-6600E) showing Rupture and Subsequent Fire which resulted in Seven Fatalities on April 2, 2010 ^{38, 40}.

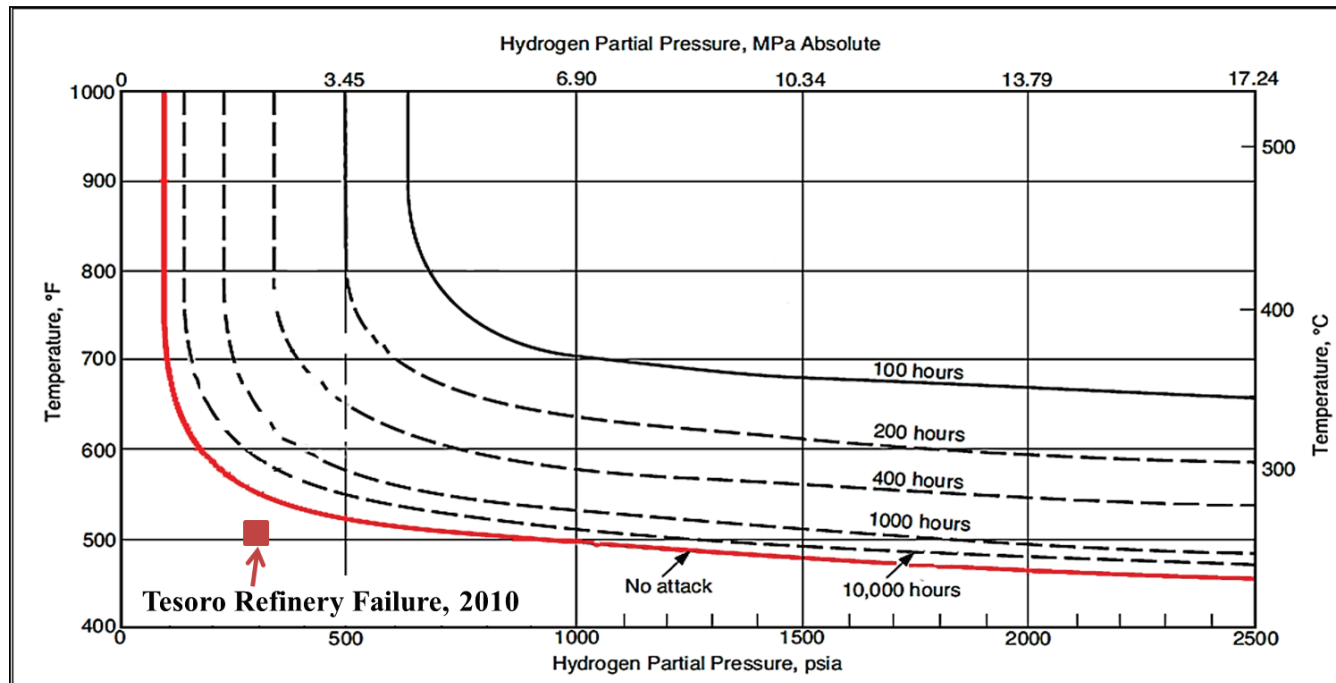


Figure 6. Time for Incipient Attack of Carbon Steel Components in High Temperature Hydrogen Service based on Figure 3 in API RP 941 (2008). Red Curve shows the Carbon Steel Line Below which Carbon Steel is not Susceptible to HTHA Damage. Hydrogen Related Damage was observed in the Tesoro Refinery Component in the No HTHA Susceptible Zone (Indicated by Red Point) ^{23, 38}.

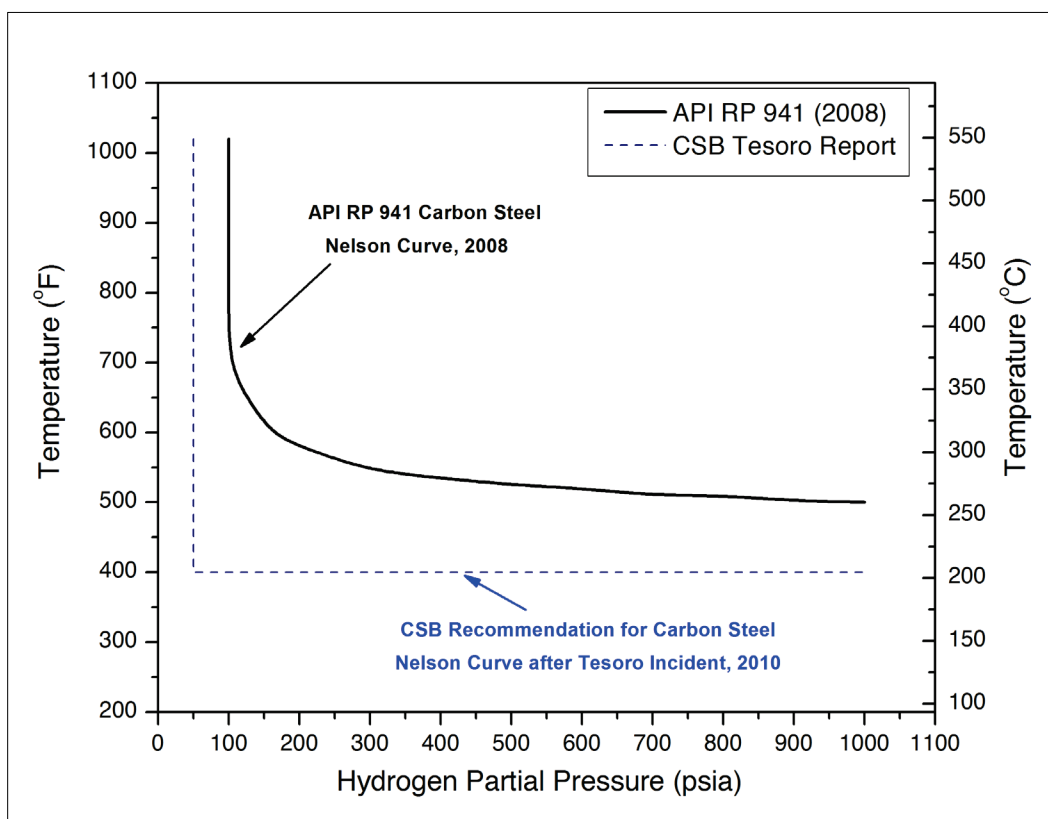


Figure 7. Recommended Move of the Carbon Steel Nelson Curve by the Chemical Safety Board (CSB) after Tesoro Refinery Incident in 2010 shown by Blue Dashed Lines with respect to the Current Position of the API RP 941 Carbon Steel Nelson Curve ³⁸.

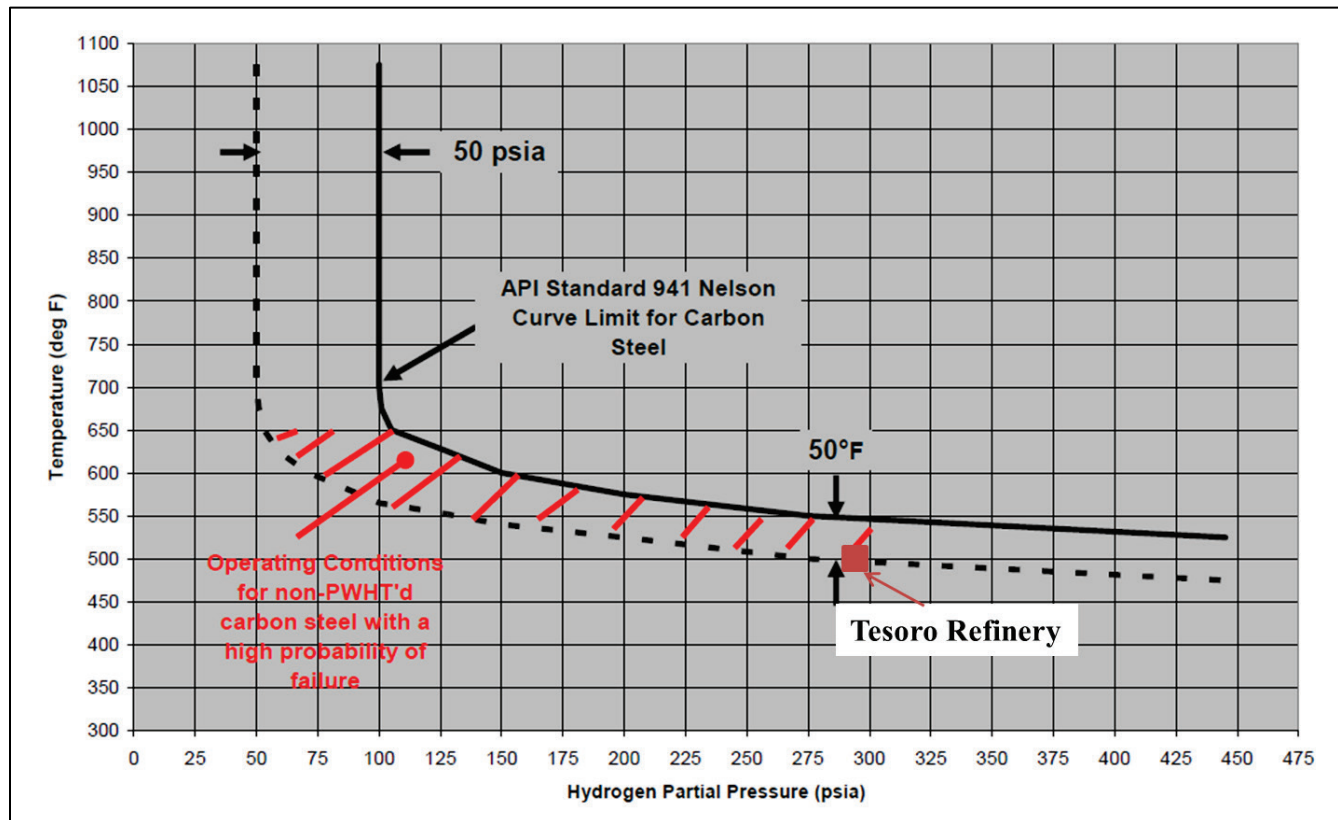


Figure 8. Inspection Guidance Diagram for Non-Postweld Heat Treated (non-PWHT'ed) Carbon Steel Components as published by McLaughlin³⁷; Shorter Inspection Intervals are Recommended for Components Operating Within the Red Cross-Hatched Region. The Position of the Tesoro Refinery Heat-Exchanger with Respect to the Inspection Region Suggested is also shown by the Red Square.

Chapter 2 – Literature Review

Carbon steels vessels has been widely used in the various stages of the refining process of complex hydrocarbons in crude oil or naphtha to produce everyday consumable fuel products like gasoline, kerosene, solvents, diesel, etc. in presence of high temperature and pressure for more than 100 years ¹. Carbon steels are susceptible to high temperature hydrogen attack (HTHA) in petroleum refinery vessels when exposed to a hydrogen environment at elevated temperatures greater than 450°F (232°C) and hydrogen partial pressures greater than 70 psia (0.48 MPa). HTHA is a type of hydrogen damage in which atomic hydrogen (H⁺) permeates into the steel to react with carbon in solution or carbides at high temperature and pressure to form methane (CH₄) as shown by following equations 1-2.



The formation of methane results in surface decarburization, internal decarburization, and fissuring/cracking in steels. HTHA is an irreversible

phenomenon, which can result in a loss in mechanical properties, decarburization, fissuring, cracking, blistering, leakage and other catastrophic failures that may result in fire and explosion ^{4, 6, 23}.

2.1. History of Nelson Curves and API RP 941

Hydrogen damage in steels has been a subject of interest ever since and it has been one of the complex and widely studied topic in last 100 years. The effects of hydrogen on steel and iron was first studied by Johnson in 1875 by introducing iron and steel wire in the aqueous environments (HCl, H₂SO₄, etc.) ²⁴. But, it was not until 1930s and 1940s the hydrogen damage was most frequently observed in steels in Europe and America ^{25, 26}. The early work hydrogen damage was performed by Naumann, however his most of his work was short-term laboratory based work, which was cut short because of the Second World War ⁸. Extensive research was done in 1940s by G.A. Nelson for Shell Development Company to design a set of curves for steels to provide safe operating guidelines. These curves were first published in 1949 in a diagram called Nelson curve ⁴. The Nelson curves are a set of curves that utilizes service temperature and hydrogen partial pressure to provide limits for operating conditions for carbon

steel, C-0.5 Mo, 0.5Mn-Mo, 1.25Cr-0.5 Mo, 2.25Cr- 0.5Mo, 3.0 Cr - 0.5 Mo steel (with or without vanadium), 6.0 Cr - 0.5 Mo steel (with or without tungsten and vanadium). The first Nelson Curve published by Nelson in 1949 is shown on Figure 2 ⁴. These curves are applicable to the equipment used in the petrochemical industries, refineries, hydrogenation plants, etc. The Nelson curve was developed based on the information gathered by Nelson from the commercial process and laboratory experiments since 1940s and also by Schuyten, Allied and Germans ^{4, 41}. The Nelson diagram was based on components exhibiting satisfactory vs. unsatisfactory performance in hydrogen atmosphere at elevated temperature. However, the diagram does not provide information on the extent, location, or morphology of HTHA damage observed. The samples showing satisfactory performance were operating for at least one year; however, unsatisfactory performances were plotted on the diagram regardless of the hydrogen exposure period.

After the publication of the first Nelson curves in 1949, occasional failures of carbon and low alloy steels when exposed to hydrogen environments in petrochemical plants continued to be a concern despite the fact that the plants

had been operating within the guidelines suggested by the Nelson curves. The American Petroleum Institute (API) continued Nelson's early work with Dr. F.H. Vitovec at the University of Wisconsin in 1960s to revise the Nelson diagram published in 1949¹³. API published a revised Nelson diagram in 1970 as Recommended Practice 941 (1st edition) "*Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*" [5]. API RP 941 is used by various industries as guidance for operating in high-pressure hydrogen environments at high temperatures and studies have been done to understand the hydrogen attack below the "Nelson Curve" to assist in keying the damage mechanism for operational life prediction and longevity of these components. The position of various curves in the API RP 941 Nelson diagram has been periodically updated over years based on operating experiences and failures or incidents in the petroleum refineries^{4, 16, 30-35}. The seven editions of API 941 have been published to date with various updates to introduce conservatism to the curves^{4, 30-35, 42}. The second edition was published in June 1977, third in May 1983, fourth in April 1990, fifth in January 1997, sixth in February 2004 and seventh in August 2008³⁰⁻³⁵. The eighth edition is most

likely to be published in July 2015. Figure 3 shows the Nelson curves from the most recent revision of API RP 941 (7th edition published in 2008, however, the Nelson curves were not changed since 5th edition in published in 1996).

However, the last update to the carbon steel curve in the Nelson diagram was performed in 1977 (second edition). Figure 4 shows an illustration of the change in the position of carbon steel curve in the Nelson diagram from 1949 to the most recent diagram in API RP 941 (7th edition) ^{4, 35}.

The dashed lines in the Nelson Curves (See Figure 2) show the tendency for steels to decarburize through surface when in contact of hydrogen atmosphere, if the operating conditions are above the line. Surface decarburization causes steels to lose their strength and an increase in ductility. Solid lines represent the tendency of steels to decarburize internally, fissuring and methane formation when steels are operating over the line ^{4, 30-35}.

2.2. High Temperature Hydrogen Attack (HTHA)

High Temperature Hydrogen Attack (HTHA) is a most common form of hydrogen damage observed in steels in the petrochemical industries used in hydrogen atmosphere at elevated temperatures. Carbon steels exhibit surface

decarburization, internal decarburization, methane bubble formation, and cracking in steels when exposed at high temperature and high hydrogen partial pressure^{4-6, 10, 15, 26, 28}. API RP 941 considers that HTHA in steels are generally observed in two forms: 1) Surface Decarburization, and 2) Internal Decarburization and Fissuring.

2.2.1 Surface Decarburization

Surface decarburization is observed in steels at the inside diameter surface (hydrogen-exposed surface) when atomic hydrogen (H^+) from the operating environment reacts with carbon in solution or carbides at elevated temperatures to form molecular methane (CH_4). Surface decarburization in steels is generally observed at high temperature greater than 450°F (232°C) and low hydrogen pressure of less than 70 psia (0.48 MPa) combinations. Surface decarburization is generally controlled by the carbon activity (carbide dissolution) in steels and the diffusion of atomic hydrogen from the service environment. The carbon activity is greater at high temperature and the diffusivity of atomic hydrogen (H^+) into the steel wall is lower at low hydrogen partial pressure^{14, 22}. Thus, methane is generally formed at the hydrogen-exposed surface, which escapes to the

atmosphere resulting in decarburization. Carbon is continually supplied to the surface from within the steel for thermodynamic stability. Surface decarburization is considered to happen by a similar mechanism as when steels are decarburized or carburized by other gases. Figure 9 shows a typical example of surface decarburization in steels at 100X and 500X (Note: unaffected base metal toward the top of 100X micrograph) ⁴³. Since, HTHA damage in this morphology is primarily at the hydrogen-exposed surface, it does not have a significant effect in the load bearing capability of the component. The operating conditions that are susceptible to surface decarburization are shown by the dashed lines in API RP 941 Nelson diagram (see Figure 3) ³⁵.

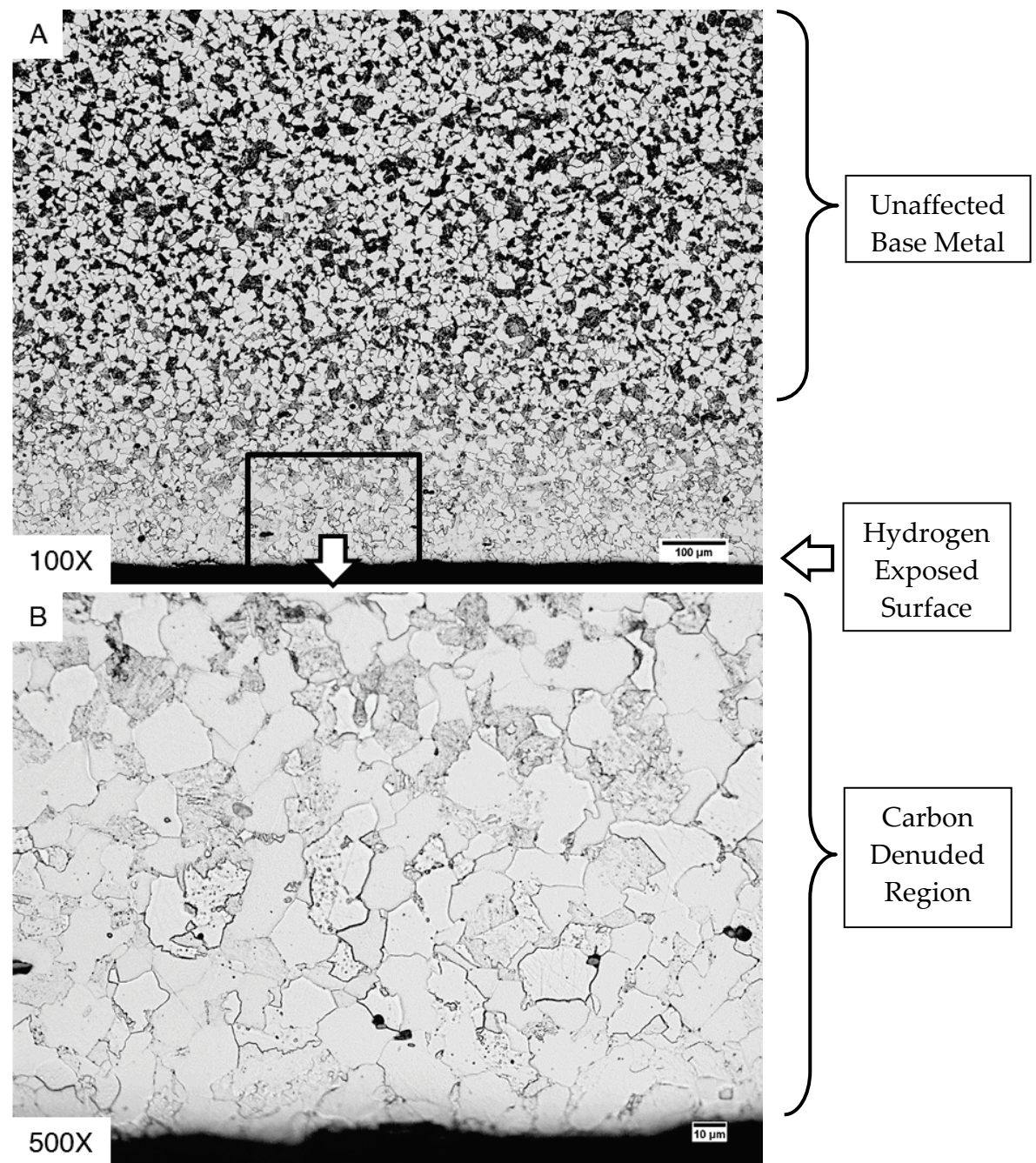


Figure 9. Photomicrographs showing a Typical Example of Surface Decarburization from HTHA Damage, (A) 100X and (B) 500X, 2% Nital Etch ⁴⁴.

2.2.2 Internal Decarburization and Fissuring

Internal decarburization occurs when atomic hydrogen (H^+) from the service environment diffuses into the steel and reacts with carbon in solution or carbide to form molecular methane. Internal decarburization is generally observed at high hydrogen partial pressure greater than 70 psia (0.48 MPa) and low temperature (but greater than 430°F) combinations. At low temperature, the mobility of carbon to the surface is reduced and the reaction takes place internally in the steel wall. At increased hydrogen pressure (> 70 psia); the solubility of hydrogen in steel is also increased causing propensity for internal attack. At higher hydrogen pressure, the atomic hydrogen diffuses into the steel wall and reacts with carbon and carbides to form methane ^{14, 22}.

Methane molecule is too large to diffuse through the steel wall, and thus accumulate generally along grain boundaries or sub-grain boundaries creating methane bubble or cavities. The continuous formation of methane bubbles over time leads to methane bubble accumulation. The accumulation of methane bubbles leads to methane bubble coalescence, thus concomitantly creates a high level of internal stress, resulting in cracking and blistering in steels ^{4, 6, 7, 10, 15}. The

loss of carbon atom from the formation of methane results in decarburization of steel. Internal decarburization leads to loss in strength and toughness, which is more detrimental to the load bearing capabilities of the component when compared with surface decarburization. An earlier study on a service-exposed C-1/2 Mo steel by Lundin et. al, revealed that more than 60% reduction in tensile strength when steels are hydrogen attacked ¹⁵. The operating temperature defining the susceptibility to internal decarburization and grain boundary fissuring is shown by solid lines in the API RP 941 Nelson diagram (see Figure 3). Figure 10 depicts a typical example of HTHA damaged surface showing evidence of internal decarburization at 100X and 500X ⁴⁴. Figure 10 shows typical example of grain boundary fissuring in the coarse-grained heat affected zone (CGHAZ).

2.3. Methane Formation

HTHA damage occurs when atomic hydrogen (H^+) diffuses into the steel and reacts with carbon in solid solution and with carbides forming methane as shown in Equations 3 and 4.



The rate of methane formation is controlled by the formation of CH radical as shown by following equations 5 to 8 ⁴⁵. Therefore, the methane formation is primarily controlled by the diffusivity of hydrogen, solubility of hydrogen, carbon concentration, operating temperature, and carbide stability.



The standard free energy (cal./mole) for methane formation is shown by Equation 9 below ⁴⁶. The change in free energy must be negative to drive the chemical reaction forward to form methane. Figure 12 shows the relation between the change in the standard free energy of methane formation (ΔG_{CH_4}) versus the temperature, and shows that the free energy increases with an increase in temperature.

Figure 12 also shows that methane is not thermodynamically stable when the temperature is above 1025°F (552°C). Thus, hydrogen attack by methane

formation should not occur in steels when the operating temperature is above 1025°F (552°C).

$$\Delta G_{\text{CH}_4} \rightarrow -691200 + 51.25T \log T - 65.35T \quad \text{Equation 9}$$

where, T is in Kelvin

The formation of methane causes decarburization in steel both at the hydrogen exposed surface and internally resulting in the loss of strength and mechanical properties. Figure 9 and Figure 10 shows typical example of showing decarburization in steels resulting from methane formation. Methane when formed is trapped as bubbles generally along grain boundaries or at the interfaces like lath boundaries, or triple point junctions. Methane molecule (CH_4) is unable to diffuse through the steel because of its size, thus gets accumulated creating internal stresses. Figure 13 shows typical micrographs of cavity formation from methane along grain boundaries and sub-grain boundaries ⁴³. The methane formed along boundaries is examined using a fracture surface of a HTHA damaged material.

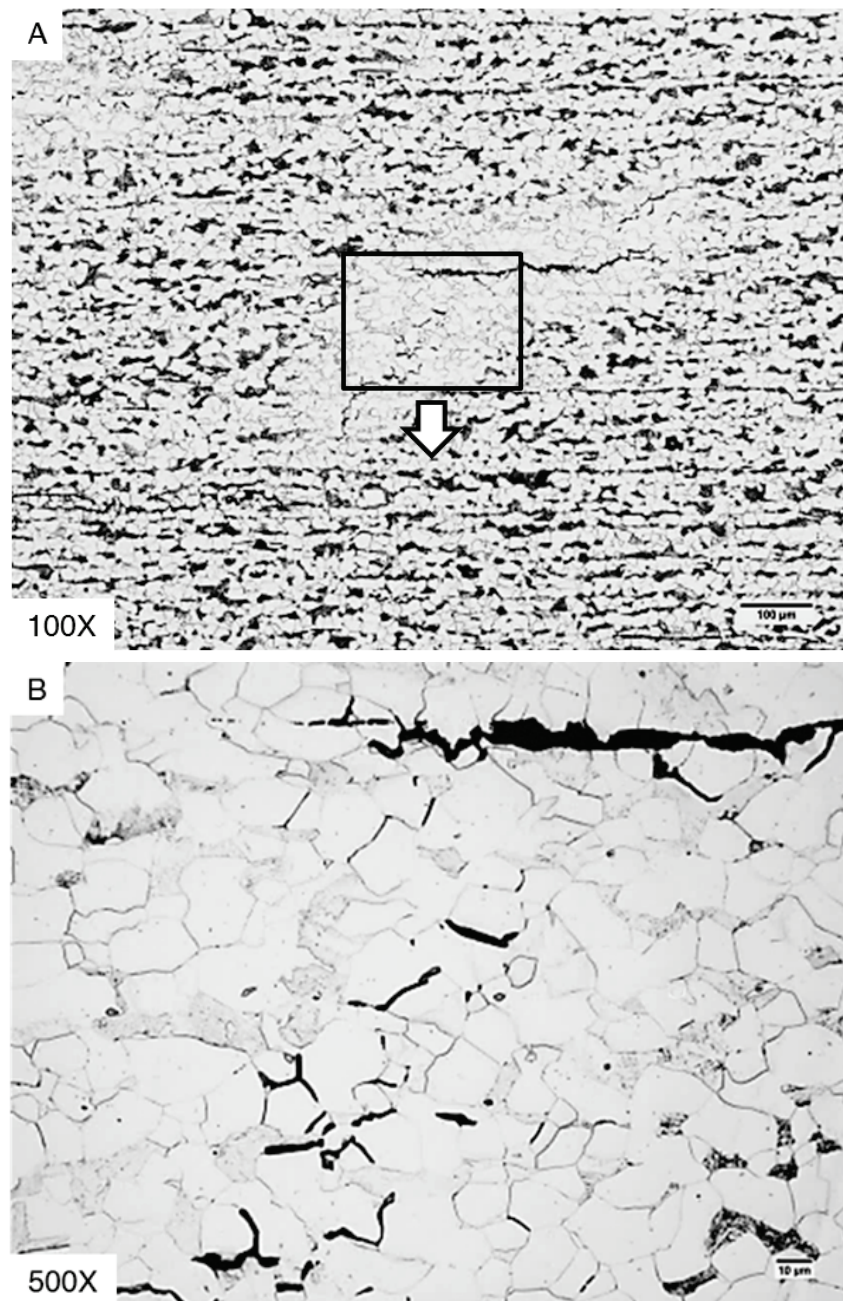


Figure 10. Photomicrographs showing a Typical Example of Internal Decarburization and Intergranular Fissuring from HTHA Damage, (A) 100X and (B) 500X, 2% Nital Etch ⁴⁴.

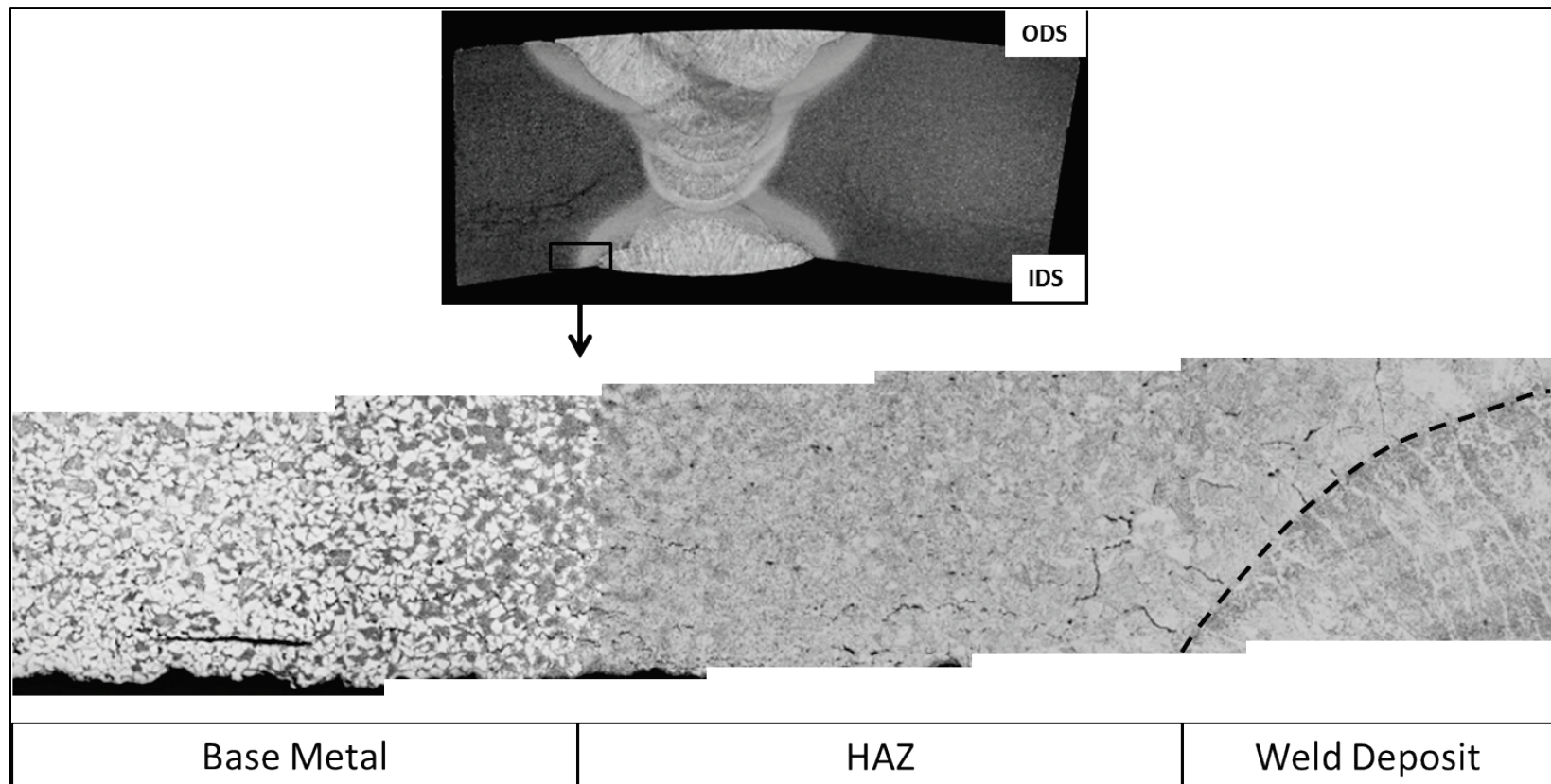


Figure 11. Hydrogen Attack Adjacent to ID Surface in the Base Metal and HAZ (micrograph location of the panoramic view is shown by the boxed region in above macrograph) No Damage Seen in Weld Deposit ⁴⁴.

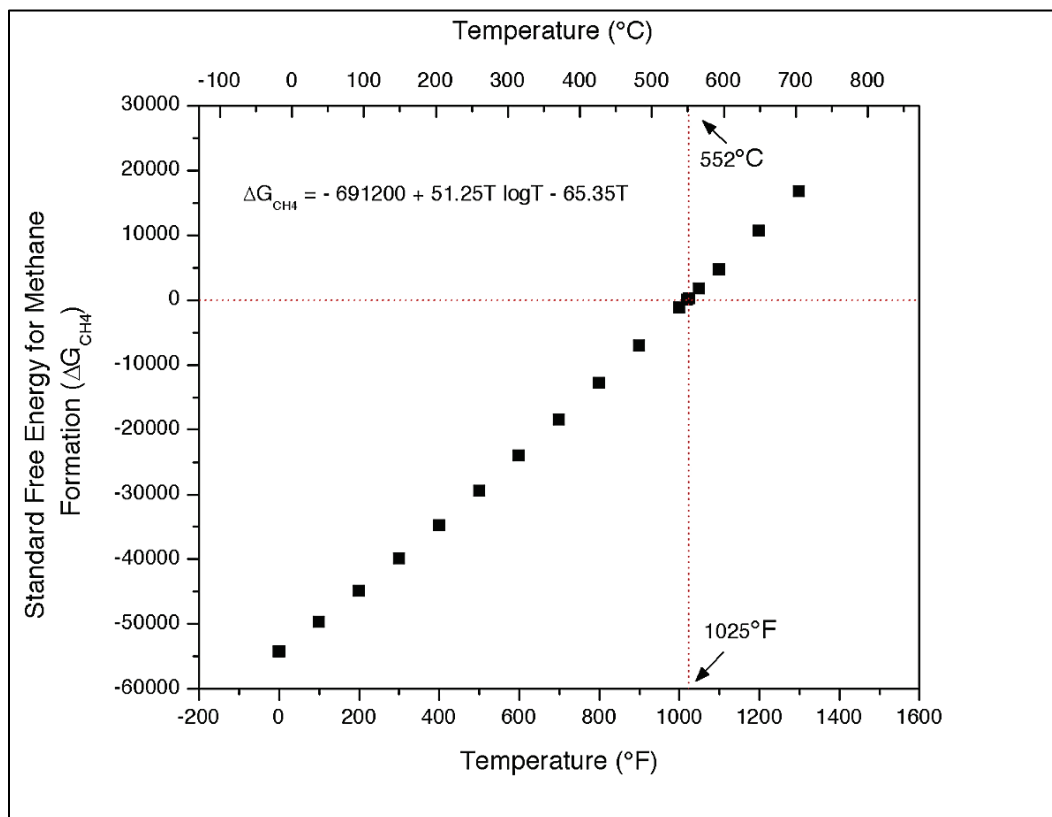


Figure 12. Standard Free Energy Change for Methane Formation (ΔG_{CH_4}) as a function of Temperature ⁴⁶ showing that Free Energy Increases with Increasing in Temperature. Standard Free Energy is Zero at 1025°F (552°C), and thus Methane should not form above 1025°F (552°C).

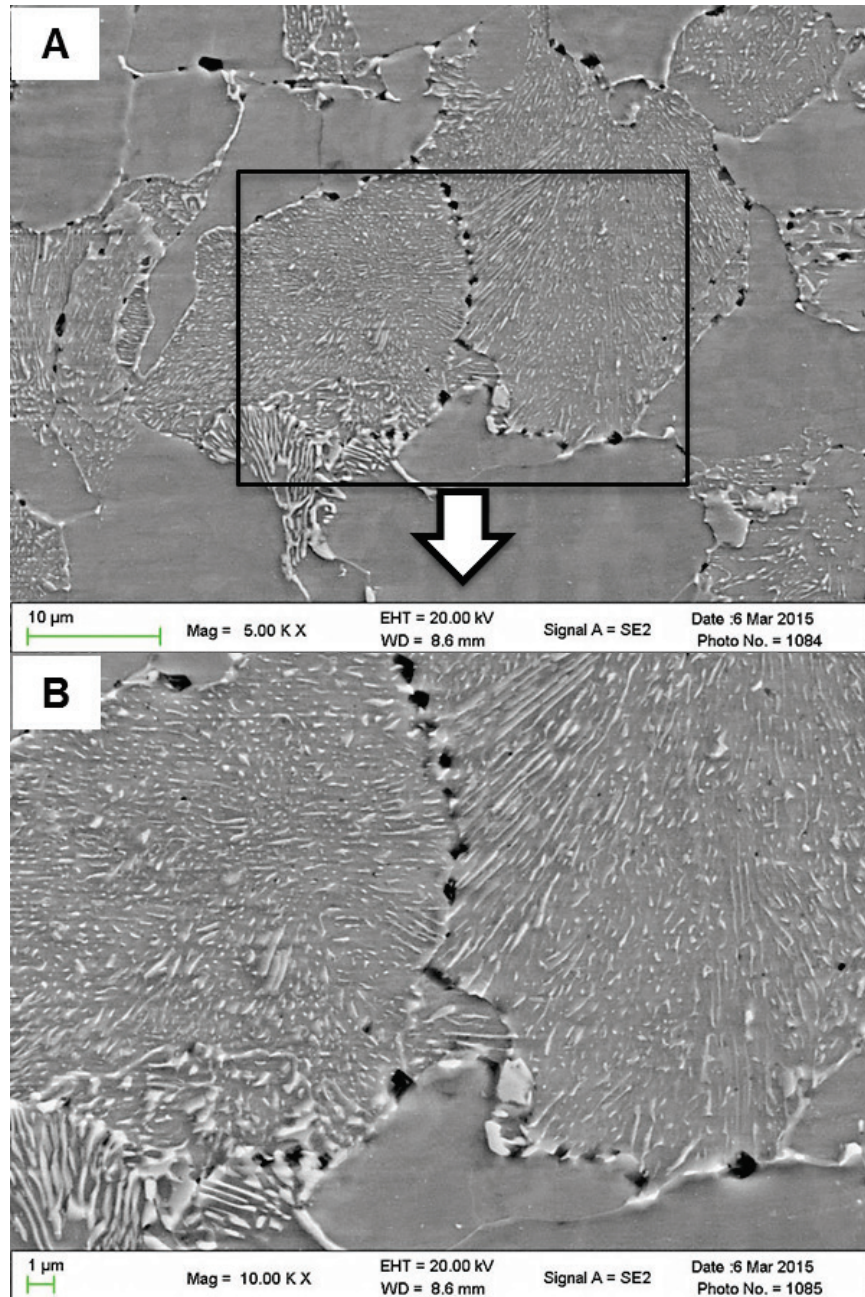


Figure 13. SEM Micrographs showing a Typical Example of Methane Bubble Formation along Grain Boundaries and Sub-Grain Boundaries ⁴³.

In order to expose a grain surface and examine the fracture morphology of a HTHA damaged sample, a technique called “Cryo-Cracking” is used in which steel is cooled to a liquid nitrogen temperature ($-320^{\circ}\text{F}/-196^{\circ}\text{C}$)⁴⁷. At liquid nitrogen temperature, steel becomes embrittled, and thus, when a crack is imposed on a sample by using a rapid force, the fracture surface will only develop cleavage facets and reveal grain boundaries characteristics. “Cryo-Cracking” technique preserves pre-existing crack as no plastic deformation is produced during crack propagation⁴⁷. Figure 14 shows a typical example of a fracture surface with grain boundary bubbles formation resulting from methane along with some cleavage facets³⁹. Figure 15 shows a comparative “Cryo-Cracked” fractographs of a sample exhibiting no evidence of HTHA damage with the fracture path revealing 100 % transgranular cleavage morphology (with no cavities or bubbles).

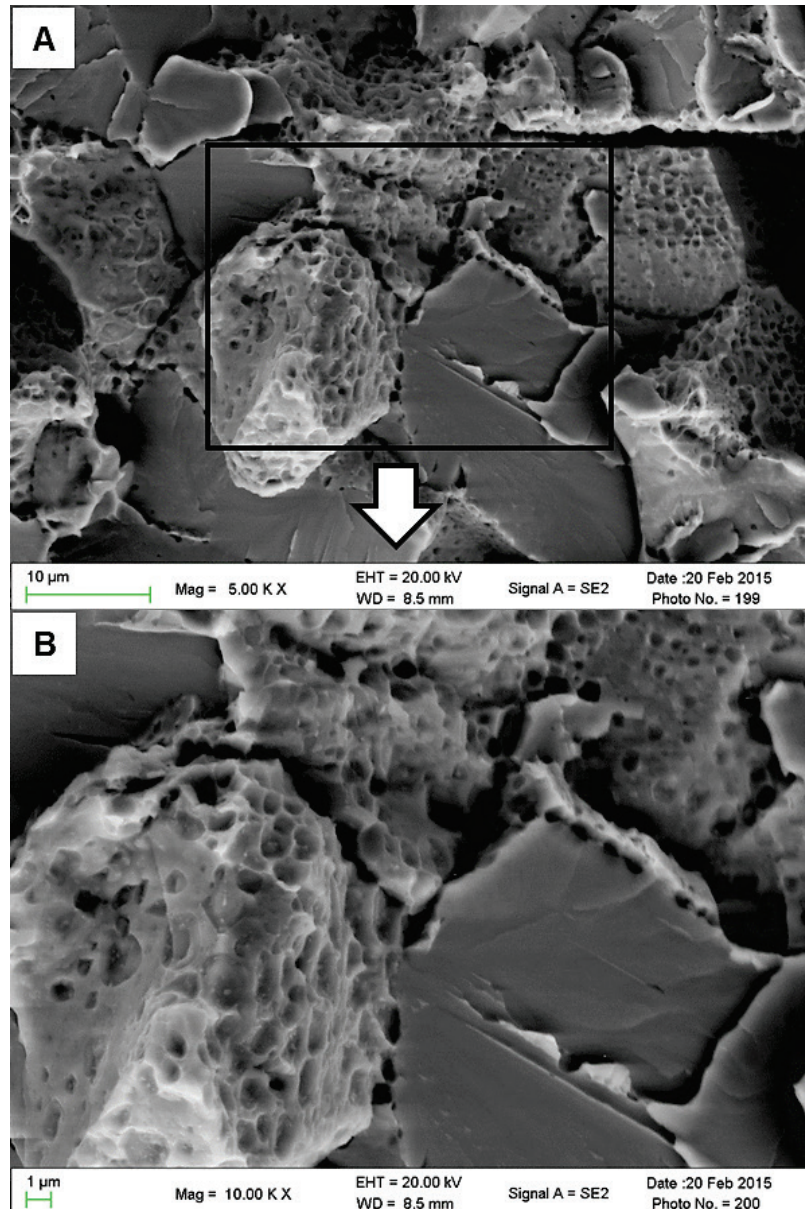


Figure 14. SEM Fractographs obtained using a "Cryo-Cracking" technique showing a Typical Example of Intergranular Separation due to Methane Bubble Formation on Grain Faces and also Along the Grain Boundaries resulting from HTHA Damage ⁴³.

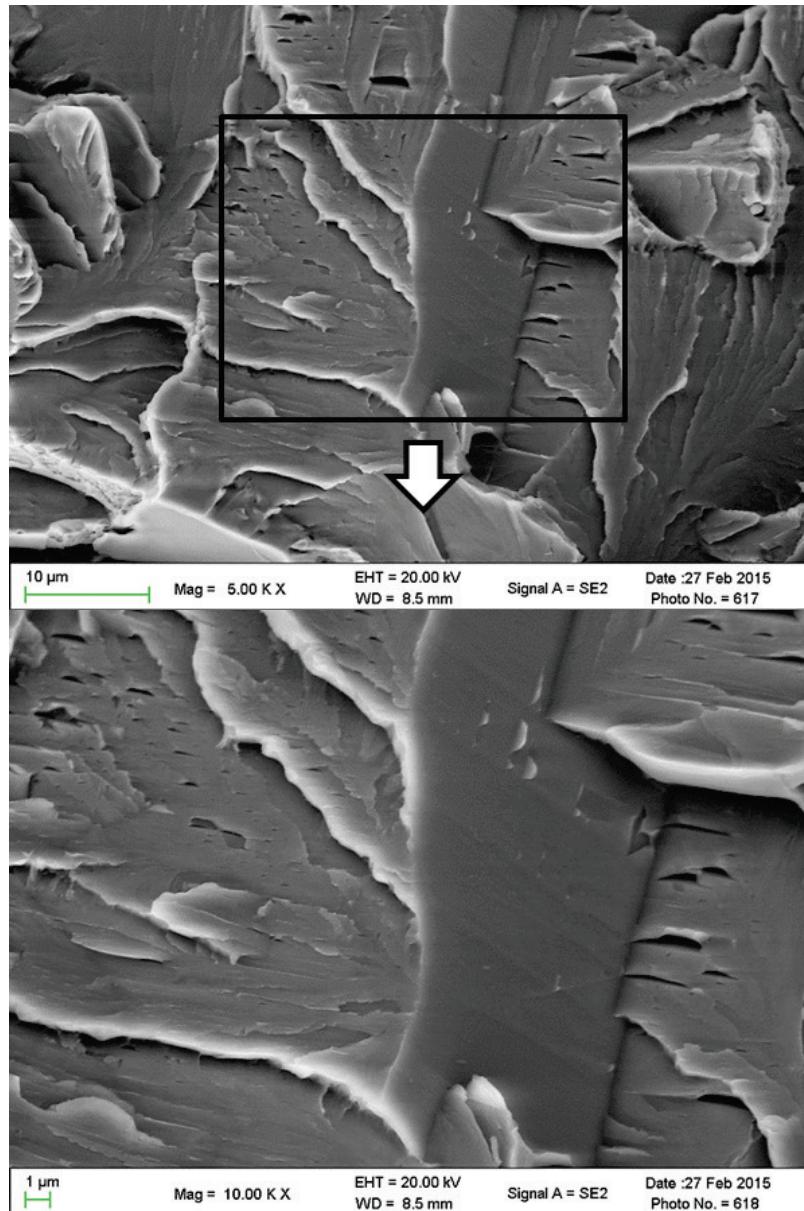


Figure 15. SEM Fractographs showing Typical Fracture Surface of a "Cryo-Cracked" Sample with No HTHA Damage⁴³. Note- Compare with HTHA Damaged Surface in Figure 14, Transgranular Cracking Morphology.

2.4. Hydrogen Damage Mechanisms

The hydrogen attack is driven by the reaction of atomic hydrogen (H^+) with carbon to form methane generally along grain boundaries, sub-grain boundaries, triple point junctions, or at inclusions. The formation of methane generates internal methane pressure resulting to subsequent growth and coalescence of methane bubbles. The coalescence of methane bubbles lead to fissuring and cracking. The loss of carbon by decarburization results in loss of mechanical properties (strength and toughness). This eventually leads in a failure of your component or a vessel.

The hydrogen attack in steels are known to happen in different stages and the most commonly proposed mechanism of HTHA damage by various studies^{13, 17, 48} occurs in three stages: 1) Incubation Stage, 2) Rapid Attack Stage, and 3) Saturation Stage. Each of these commonly known stages is believed to have sub-stages during the progress of HTHA damage. Each of these various stages is discussed in more detail in the next section^{49, 50}.

2.4.1 Progression of HTHA Damage in Steels

During the incubation period, methane bubbles start to nucleate heterogeneously and no noticeable change in the mechanical properties are observed. The nucleation and growth of cavities generally takes place in the grain boundaries, sub-grain boundaries, triple point junctions or at inclusions^{48, 51-53}. The incubation time decreases rapidly with the increase of operating temperature. The incubation period generally consumes large part of equipment life and this stage can only be observed using scanning electron microscope or transmission electron microscope, and is not detected by optical or current NDE techniques^{21, 49}. At the incubation stage of hydrogen damage, mechanical properties or load bearing capability of the component is not affected and thus is unnoticeable.

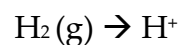
After an initial incubation period, which varies with the operating conditions and the chemical composition of steel, loss of mechanical properties is observed (toughness/ductility) during the rapid attack stage. During this stage methane cavities coalesce and grow to form microfissures along the grain boundaries¹⁷. Various studies has been done in past to understand the bubble

growth mechanism^{13, 19, 48, 52, 54-57}. Dr. Vitovec at the University of Wisconsin performed comprehensive study on the growth of methane bubble and he suggested that the bubbles grow initially by vacancy diffusion followed by dislocation creep^{13, 58}. Shewmon suggested that bubble growth is primarily controlled by the grain boundary diffusion⁵⁴. The steel depicts internal decarburization and loss in strength and hardness properties during this stage.

During the saturation stage, crack grows to a final failure. Final failure can be observed in two modes: 1) Progressive linkage of microfissures to cracks leading up to leakage during service (could take several years), and 2) Rapid separation resulting from loss of toughness/ductility⁴⁹.

The progression of hydrogen damage in steel is known to happen in seven stages as shown below:

Stage 1. Dissociation of molecular hydrogen H_2 (g) into nascent hydrogen (H^+)



Stage 2. Adsorption of Nascent Hydrogen (H^+) adjacent to the hydrogen exposed surface.

- Stage 3.** Diffusion/absorption of nascent hydrogen (H^+) into the steel wall
- Stage 4.** Reaction of nascent hydrogen (H^+) with carbon in solution or carbides to form molecular methane (CH_4)
- Stage 5.** Accumulation and coalescence of methane bubble. This results in decarburization and loss of strength and toughness
- Stage 6.** Methane bubble formation and bubble coalescence concomitantly develops tremendous amount of internal stress and results in the formation of fissures/cracks
- Stage 7.** Cracks propagate over time/temperature/stress causing ultimately in the failure of the component/vessel

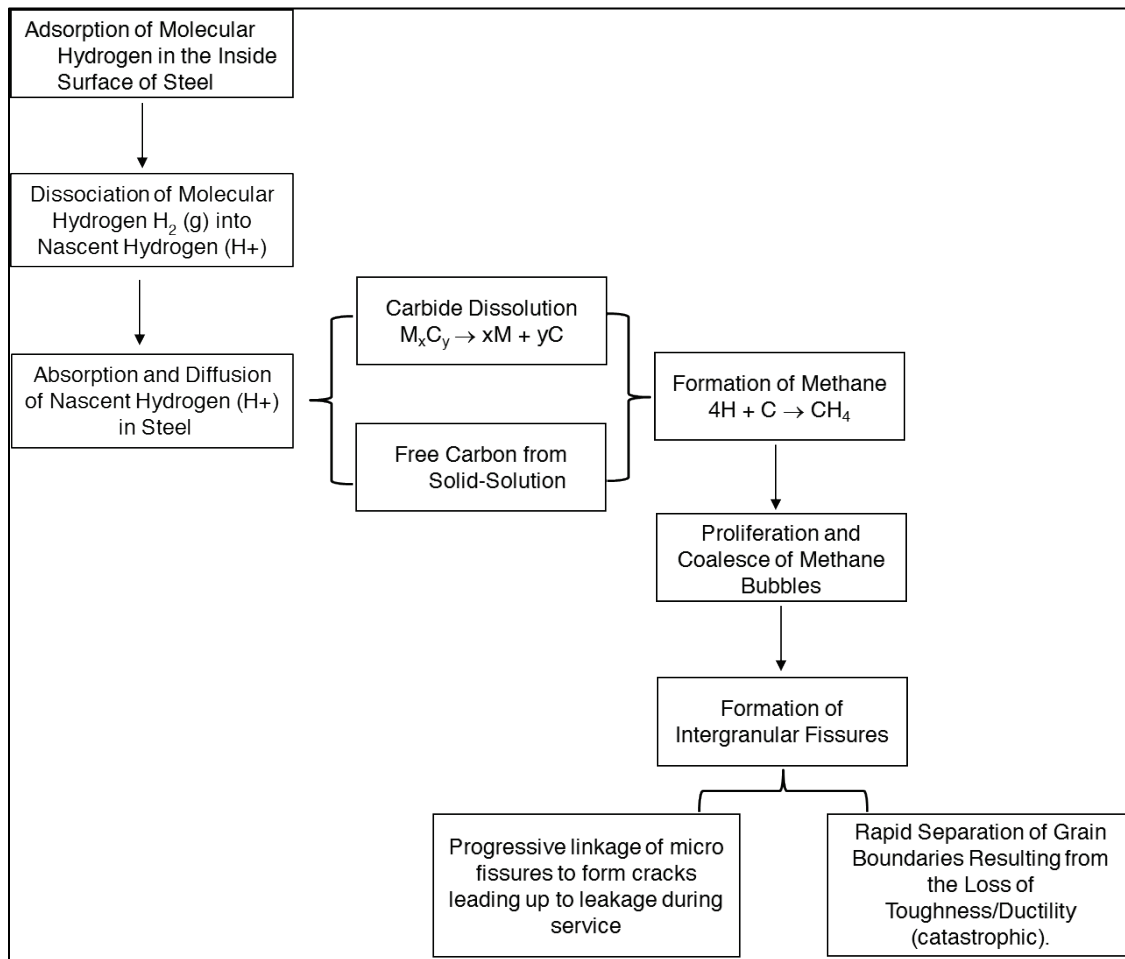


Figure 16. Flow Chart showing the Typical Progression of Hydrogen Damage in Steels. The Schematic Representation of these Seven Stages is shown in Figure 17.

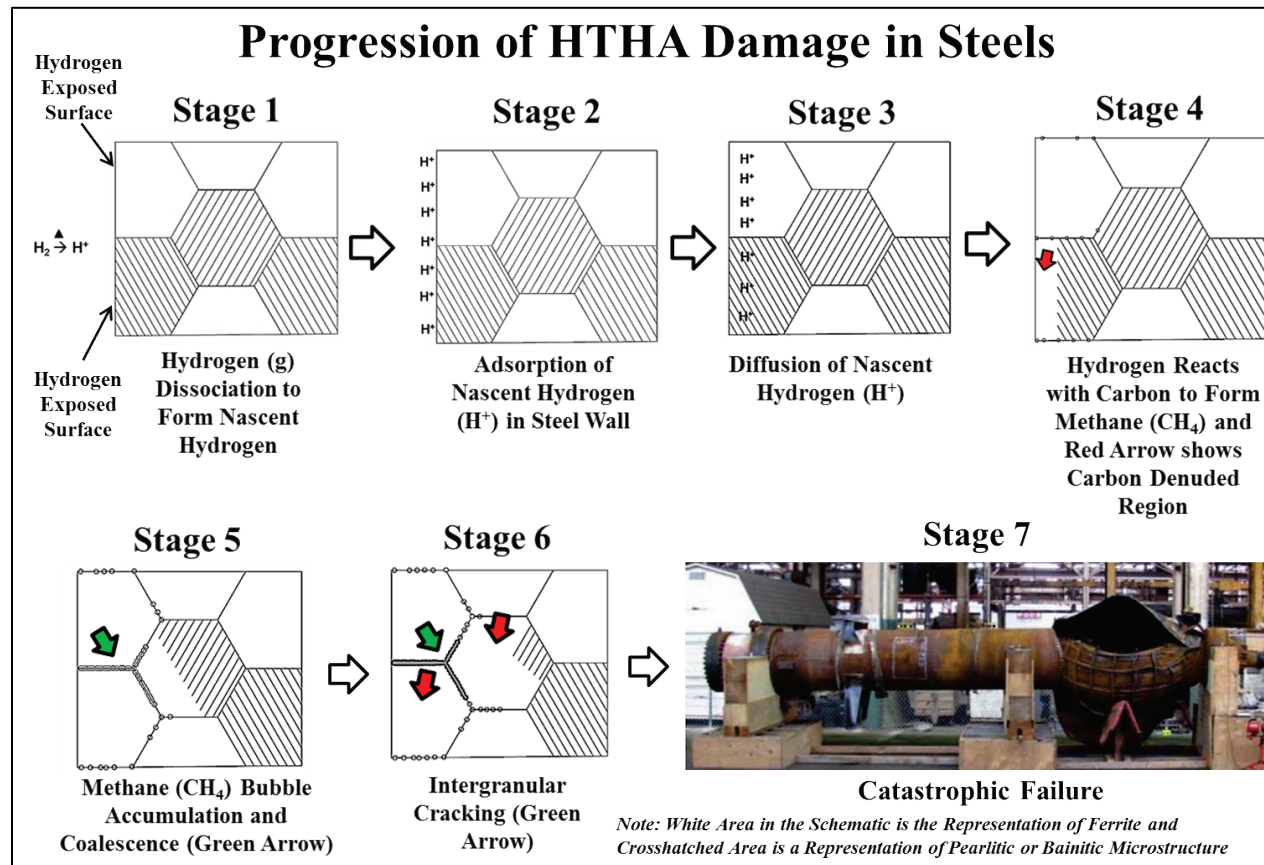


Figure 17. Schematic Representation of the Progression of Hydrogen Damage in Steels from Stage 1 to Stage 7. Red Arrows show the Location of Internal Decarburization and Green Arrows depict evidence of Intergranular Fissuring Resulting from HTHA Damage.

Hydrogen attack is caused by reaction of hydrogen from service environment with free carbon available in steels, plus carbon supplied by carbide thus it is important to discuss diffusivity of hydrogen, solubility of hydrogen and carbon activity to further understand progression of HTHA damage^{4, 10, 59, 60}.

2.4.2 Solubility of Hydrogen

The solubility of hydrogen is an important topic to be considered to understand the rate of hydrogen attack in steels. The solubility of hydrogen in carbon or alloy steels is given by the Sievert's law in the following equation (Equation 10). The solubility of hydrogen in steels primarily depends on the temperature and hydrogen partial pressure (as shown by the equation 10). Apart from these factors, the solubility of hydrogen also depends on the carbon content, alloying element, and the microstructure of steels.

$$C_H = A e^{-Q/RT} p_{H_2}^{1/2} \quad \text{Equation 10}$$

where,

C_H = Solubility of Hydrogen in Steels

A = Constant

Q = Activation Energy

P_{H_2} = Hydrogen Partial Pressure

Figure 18 shows the equilibrium phase diagram of Iron-hydrogen system showing the solubility of hydrogen as a function of temperature and pressure. The solubility of hydrogen in the FCC phase is greater than that of BCC (alpha) phase. Studies by Groeneveld and Elsea show that the solubility of hydrogen in a AISI 347 austenitic stainless steel is approximately 15 times of the 2-1/4 Cr-1 Mo steel at 700°F (371°C) and 1500 psia (10.3 MPa) ⁶¹. An earlier studies by Johnson and Hill have found the greater amount of hydrogen when measured below 750°F (399°C) than the solubility limit, and they concluded the excess amount of hydrogen was trapped at various trapping sites ⁶². These trapping sites could include inclusion sites, carbide interfaces or any defects present in steels. A virgin steel product with no prior exposure to hydrogen environment may contain trapped or molecular hydrogen greater than 1 ppm which could have resulted from melting and steel processing steps ²².

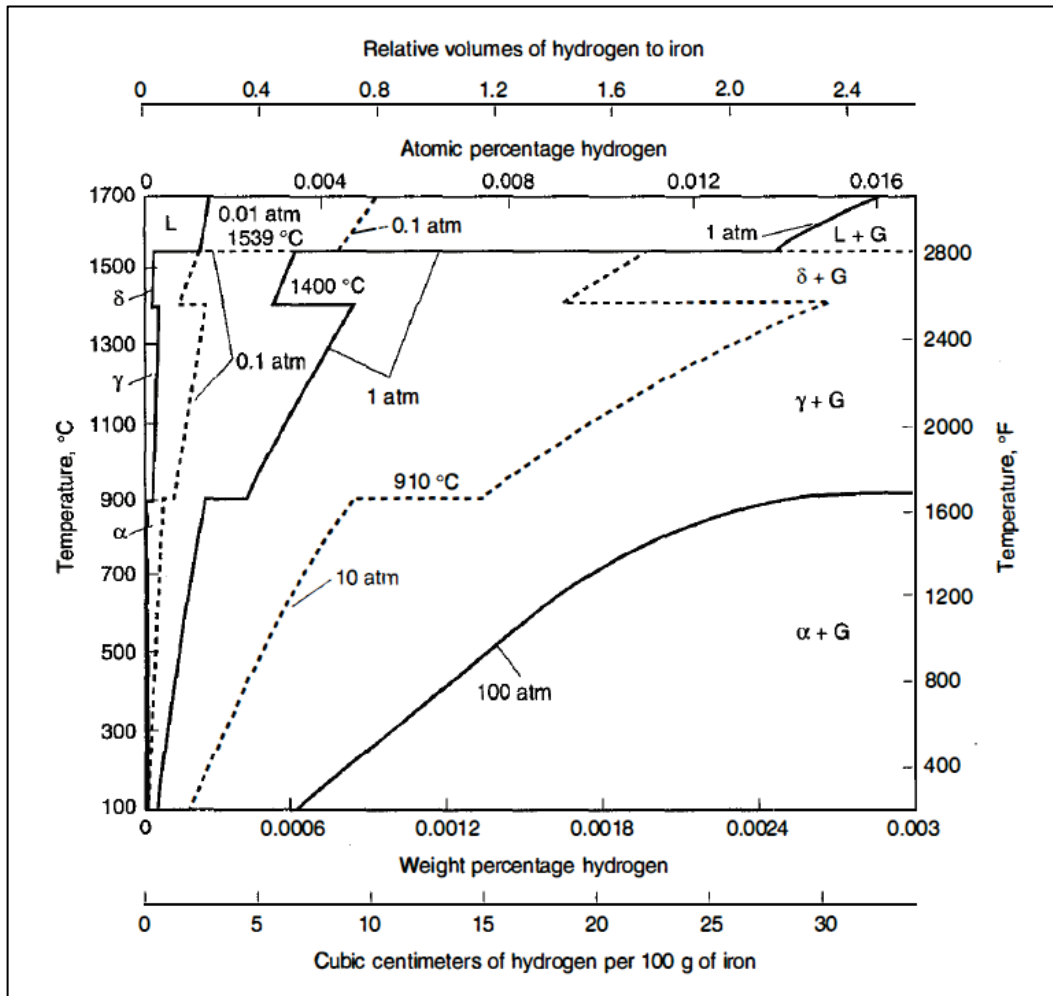


Figure 18. Equilibrium Diagram of Iron - Hydrogen System Showing the Solubility of Hydrogen as a Function of Temperature and Pressure ⁶³.

2.4.3 Diffusivity of Hydrogen

The diffusivity of hydrogen in metals depends in the chemical potential and gas pressure differential between the surface contact with the hydrogen gas and inside the steel wall. The hydrogen diffuses through steel lattice in the atomic form (H^+) during HTHA damage. The diffusivity of hydrogen through the metals was first studied by Borelius and Lindblom in 1927 and their results show that the diffusivity can be more closely represented by Equation 11 ⁶⁴.

$$D = \sqrt{P} - \sqrt{P_t} \quad \text{Equation 11}$$

where,

P = Hydrogen Pressure

P_t = Threshold Pressure Below which there will be No Hydrogen Diffusion

Smithelss and Ransley further studied the diffusivity of hydrogen through metals and generalized Borelius and Lindblom equation in 1934 to $D = \sqrt{P}$ ⁶⁵. Diffusion is generally preceded by adsorption of hydrogen in the metal surface, and the rate of diffusion is proportional to the rate of gas adsorption. When adsorption coefficient was introduced to the diffusion equation, the result showed close agreement with Borelius and Lindblom equation ^{64, 65}.

The various studies have been performed to understand the diffusivity of hydrogen in steels as a function of temperature and these studies have shown wide range of values⁶⁴⁻⁶⁹. The diffusivity of hydrogen is influenced by various factors like temperature, hydrogen partial pressure, prior thermal-treatment, and microstructure. The diffusion coefficient of hydrogen in alpha and gamma iron were found by Sykes et. al in 1947. Figure 19 shows the range of diffusion coefficients of hydrogen in iron as a function of temperature. Figure 19 shows the range of diffusion coefficients of hydrogen in iron and steels as a function of temperature^{66-68, 70, 71}.

The rate of diffusion of hydrogen is increased with the increase of temperature. The rates of hydrogen attack, i.e. methane formation, bubble nucleation, and growth rate depends on hydrogen diffusivity and carbon activity (generally controlled by operating temperature and hydrogen pressure). The rate of the nucleation of methane bubble is faster adjacent to the hydrogen-exposed surface than that in a distance from the exposed surface because of the hydrogen pressure gradient (greater at the surface compared to the inside surface).

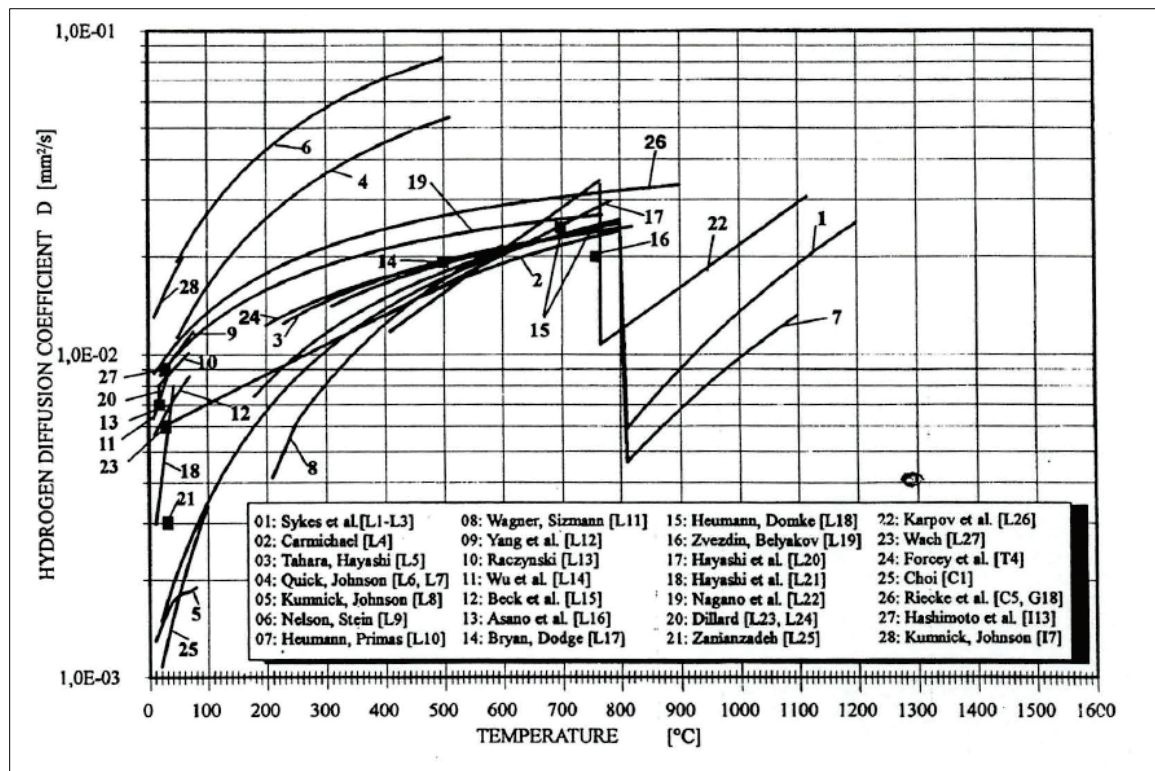


Figure 19. Diffusivity of Hydrogen in Iron and Steel as a Function of Temperature ⁷².

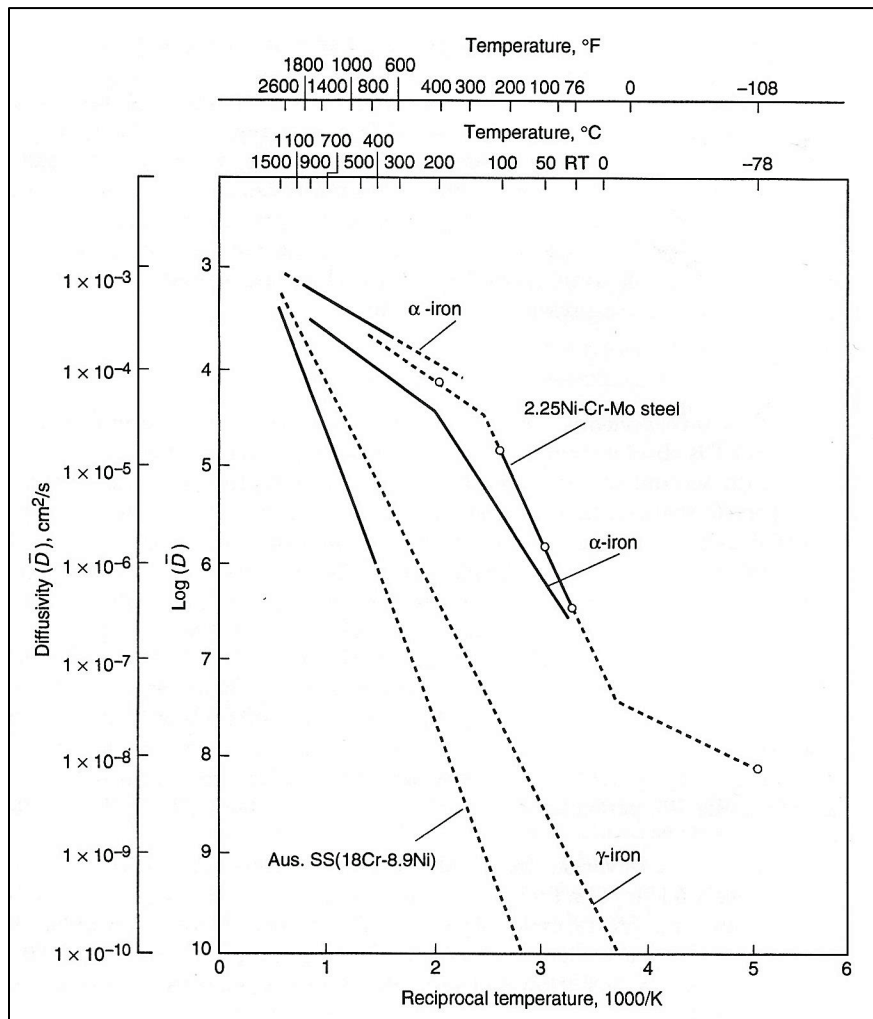


Figure 20. Diffusivity of Hydrogen in Iron and Steel as a Function of Temperature ^{66-68, 70, 71}.

2.5. Effect of Service-Temperature

The tendency of hydrogen attack increases with the increase of temperature which is also by Nelson in his diagram ^{4, 30-35}. At a lower temperature, the rate of methane formation is lower; however, the methane pressure is greater at the lower temperature. Figure 21 shows the equilibrium methane pressure as a function of service temperature and hydrogen pressure for carbon and low alloy steel. The Hydrogen attack is generally not observed at temperatures lower than 450°F (232°C). The rate of carbide dissociation and carbon diffusion increases with the increase of temperature thus increases the tendency for carbon/carbides in steels to react with atomic hydrogen. This will result in surface decarburization than internal decarburization ²¹.

2.6. Effect of Hydrogen Pressure

The extensive research done by G. A. Nelson in 1949 who empirically determined that the hydrogen attack is not observed when the hydrogen pressure is lower than 150 psia ^{4, 30}. However, there has been several instances after 1949 when HTHA damage in steels was observed when the hydrogen

partial pressure lower than 150 psia³⁵. The increase of hydrogen pressure increases the equilibrium methane pressure as shown by Figure 21, which subsequently increases the propensity of steels to decarburize internally and form intergranular fissures.

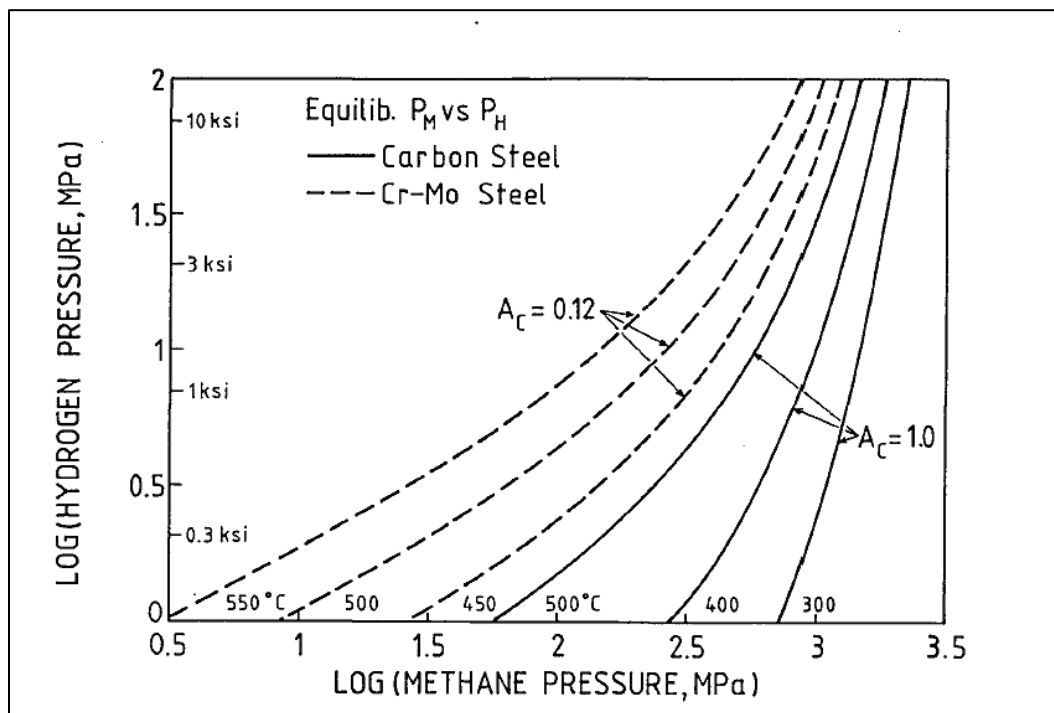


Figure 21. Methane Pressure as Function of Hydrogen Pressure and Temperature for Carbon Activity 1 and 0.12²¹.

2.7. Effect of Alloying Elements

Hydrogen attack is related to hydrogen permeating in steel and reacting with carbon in solution or carbide to form methane. Figure 15 shows the

Naumann's early findings on the effect of alloying elements on HTHA resistance⁸. The tendency of hydrogen attack on steels can be mitigated by an addition of the carbide stabilizing elements: like manganese, molybdenum, chromium, vanadium, titanium, and columbium^{4,8}. The presence of vanadium and titanium provides increased resistance to HTHA if present in small amount because of the formation of carbides stable at an elevated temperatures⁸. The earlier studies by Nelson has showed that steels were free from hydrogen damage when titanium to carbon and vanadium to carbon ratio were 4:1 and 5.7:1, respectively⁴. The addition of chromium significantly increases the steels ability to resist hydrogen attack, and allows the vessels to operate at higher operating temperatures. An addition of 1% Cr to a carbon steel, allows an increase of operating temperature by ~200F° at the hydrogen partial pressure of 600 psia³⁵. The effect of an addition of the chromium content was studied by F.K. Naumann, and showed the increase in carbon stability with an increase of chromium content as a function of increasing temperature⁸. Shewmon suggests that the addition of chromium reduces the bubble density rather than reducing the growth rate of methane bubbles²⁷.

The presence of non-carbide forming elements like silicon and nickel has no effect in preventing hydrogen damage ^{4, 8, 28}. The presence of impurity elements such as sulfur or phosphorus increases hydrogen attack susceptibility in carbon steels ^{4, 6}. However, the effect of impurity elements sulfur, phosphorus, tin, antimony and arsenic on the hydrogen attack on C-1/2 Mo steels was studied by Japan Steel Works (JSW) and their results showed a negligible effect on hydrogen attack ⁷³.

The increase in the carbon content increases the tendency for steels to react with free hydrogen to form methane thus result in hydrogen damage. The lowering the carbon content minimizes the tendency for steels to have hydrogen damage; however, it is not considered an effective approach to minimize hydrogen damage by reducing the carbon content. The strength and hardness in steels is controlled primarily by its carbon content. The various studies have shown that the steels with only few hundredths percent of carbon have shown hydrogen damage ^{19, 21, 27, 74}. Rather than lowering the carbon content, it is recommended to add carbide stabilizers to tie-up the carbon atoms, so that

strength and HTHA resistance can both be met. That is why the hydrogen attack is not observed in the weld deposit (with lower carbon content).

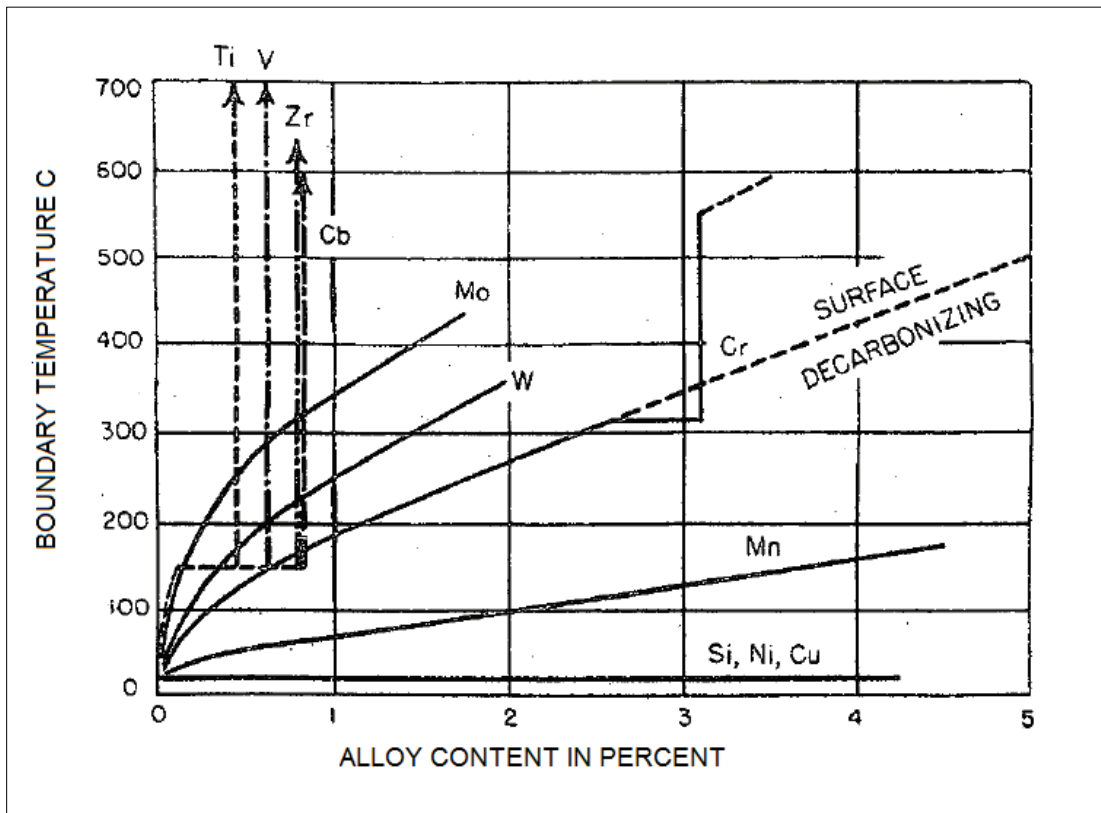


Figure 22. Effect of Alloying Elements on the Hydrogen Attack Resistance. Si, Ni, and Cu showed No Effect on Hydrogen Resistance. Mn, Cr, W, and Mo increased Resistance to Hydrogen Attack. Ti, V, Zr, Nb, showed no Special Effect until Certain Amount and then showed Improvement for HTHA Resistance ⁸.

2.8. Effect of Microstructure and Prior-thermal Treatment

The prior heat treatment and the resulting microstructure play an important role in the hydrogen resistance of carbon and low alloy steels. Earlier

studies at the UTK have shown that a combination of normalizing and tempering (N&T) heat-treatment have shown the greatest resistance to HTHA compared to annealed (A) or annealed and tempered (A&T) heat-treatment for C-1/2 Mo steels⁵⁰. The tempering treatment transforms the carbide type into more stable carbides. The studies by JSW on C-1/2 Mo steels also showed annealing heat-treatment have the worst resistance to hydrogen damage⁷³. This is however different for carbon steels (with no alloying elements).

Various studies have shown that the cold-worked steels are susceptible to hydrogen attack^{50, 75-77}. Hydrogen attack susceptibility of the cold worked steels is a result of the presence of localized residual stresses⁵⁰. The regions of manganese sulfide inclusion in the rolling direction create a location for hydrogen entrapment (enters in an atomic form) and builds pressure to form hydrogen cracks and blisters²⁷.

Coarse grained microstructure have showed greater susceptibility to HTHA damage than the fine grained structure as grain boundaries normally provide paths for accelerated diffusion of hydrogen^{60, 72}. The effect of average grain size on the hydrogen diffusivity in a pipeline steel was studied by

Dadfarnia et. al. and Yazdipour et. al.; and they have found similar results. The diffusivity of hydrogen is greatest at the optimal grain size as shown in Figure 23. The finer grain size has greater density of triple points which act as a potential traps for hydrogen thus reducing the diffusivity of hydrogen ⁷⁸.

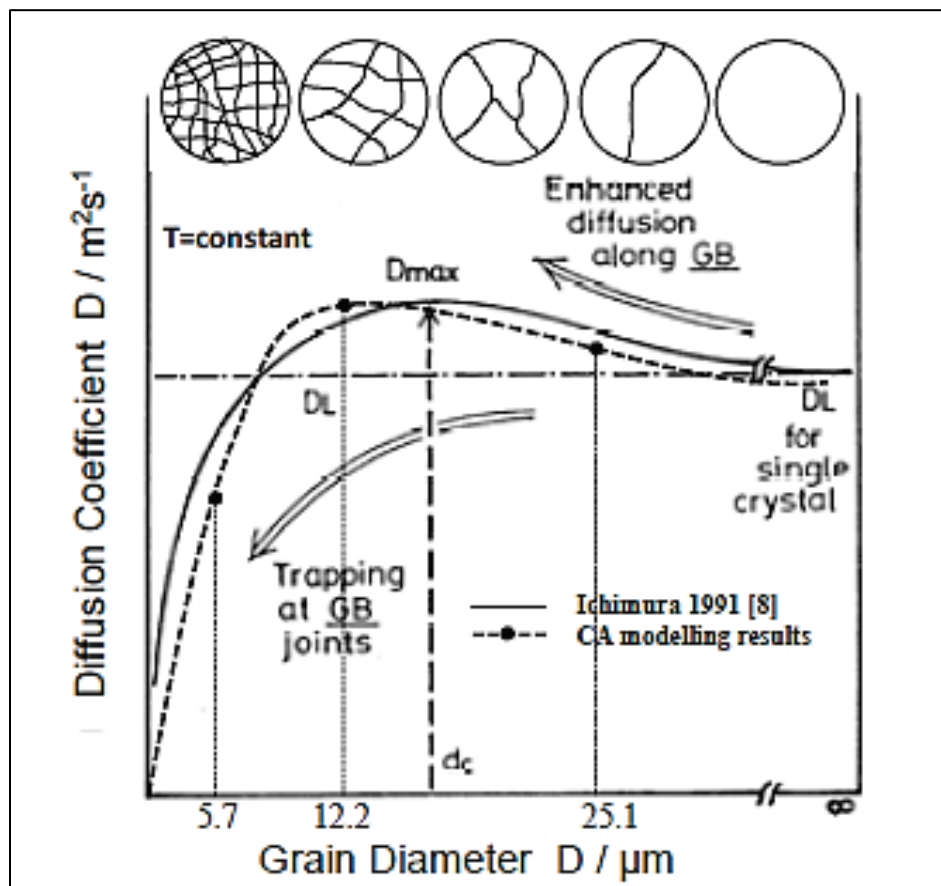


Figure 23. The Effect of Average Grain Size on Hydrogen Coefficient. Hydrogen Diffusivity is Greatest at the Optimal Grain Size and Decreases with Reduction of Grain Size ⁷⁹.

Chapter 3 – Materials

Five components for root cause examination involving various carbon steel grades originating from various components extracted from flange-to-pipe welded were received from petroleum refineries. The components selected for this study were received from three contributors: Irving Oil Refinery (IOR), Valero Energy, and Phillips 66 (P66). The sample IDs of all the five materials used this study are IOR #1110-2, Valero #67, Valero #1252134, P66 #555-S1, and P66 #555-S2. Table 1 shows the list of the materials involved in the current study.

Among the five carbon steel components received, three components (IOR #1110-2, Valero #67, P66 #555-S1) were reported to have service damage resulting from the hydrogen exposure at elevated temperature and high hydrogen pressure. Two carbon steel flange-to-pipe welded components Valero #1252134 and P66 #555-S2 received from Valero Energy and P66 respectively were not reported to have exhibited any indication of damage in service. The current study was used to characterize the type/extent and mechanism of damage for all the components. Table 1 shows the operating conditions (temperature, hydrogen

partial pressure, time, and environment) and the identification of the components used in this report ⁸⁰⁻⁸².

The operating conditions (temperature and hydrogen partial pressure) of all five components were superimposed on the API RP 941 (7th edition) as shown in Figure 24, and all the components were found to be below the carbon steel Nelson curve (within the safe operating guidelines). The position of the operating conditions for all the components were also superimposed in all the previous editions of Nelson diagram in API RP 941, and they were also positioned below the carbon steel limit line (within the safe operating guidelines). Thus, none of these components should have been reported for HTHA damage when operating at these conditions. Figure 25 shows the position of each components received at UTK with respect the carbon steel curve developed by G.A. Nelson in 1949 (green solid line), current carbon steel line in API RP 941 (2008) Nelson diagram (black solid line), and relocation of carbon steel line suggested by Chemical Safety Board (dashed blue lines) ^{37, 38}. Note: The positions of all the components are higher than the CSB suggested relocation of carbon steel line in the Nelson diagram in the HTHA susceptible region. The

location of the operating conditions of the Tesoro refinery failed heat-exchanger component is also superimposed in the same figure for a reference (shown by maroon point).

Table 1. List of Industry Contributors, Sample IDs, and Operating Conditions for All Materials Received at UTK ⁸⁰⁻⁸².

Industry Contributor	Sample ID	Temperature	Hydrogen Partial Pressure	Service Time (Years)	Reactor/Plant Output
Valero Energy	Flange #67	650°F (343°C)	71 psia (0.49 MPa)	8.2	Desulfurized Gasoline
	Flange #1252134	650°F (343°C)	71 psia (0.49 MPa)	8.2	Desulfurized Gasoline
Irving Oil Refinery	Flange #1110-2	641°F (338°C)	85 psia (0.59 MPa)	8	Liquid Hydrocarbon
Phillips 66	Flange #555-S1	670°F (354°C)	83 psia (0.57 MPa)	6	Liquid Gasoline
	Flange #555-S2	670°F (354°C)	83 psia (0.57 MPa)	6	Liquid Gasoline

Table 2. Chemical Composition of the Base Metal (BM) Regions for all the Components.

Elements	Valero Flange #67		Valero Flange #1252134		IOR Flange #1110-2		P66 Flange #555-S1		P66 Flange #555-S2	
	Flange BM	Pipe BM	Flange BM	Pipe BM	Flange BM	Pipe BM	Flange BM	Pipe BM	Flange BM	Pipe BM
C	0.220	0.237	0.222	0.214	0.18	0.23	0.237	0.197	0.231	0.165
Mn	0.88	0.90	0.88	0.64	1.23	0.88	0.86	1.05	1.12	0.54
P	0.012	0.006	0.012	0.007	0.02	0.016	0.009	0.009	0.016	0.009
S	0.003	0.005	0.003	0.001	0.017	0.010	0.029	0.002	0.009	0.001
Si	0.30	0.28	0.29	0.22	0.25	0.28	0.26	0.46	0.27	0.21
Cu	0.36	0.23	0.37	0.07	0.18	0.01	0.27	0.12	0.07	0.07
Ni	0.16	0.09	0.16	0.01	0.11	0.02	0.06	0.08	0.06	0.03
Cr	0.07	0.08	0.07	0.02	0.15	0.02	0.06	0.07	0.10	0.05
Mo	0.049	0.029	0.047	0.009	0.03	<0.01	0.02	0.071	0.009	0.014
V	0.004	0.009	0.003	0.002	<0.01	<0.01	0.004	0.004	0.002	<0.001
Nb	0.009	0.006	0.006	0.007	--	--	0.01	0.013	0.002	<0.01
Ti	0.002	0.004	0.001	0.003	--	--	0.002	0.003	0.001	0.001
Co	0.011	0.006	0.011	0.003	--	--	0.006	0.007	0.003	0.004
Al	0.028	0.045	0.026	0.024	<0.01	<0.01	0.003	0.04	0.032	0.026
B	0.0004	0.0004	0.0003	0.0003	--	--	0.0007	0.0006	0.0001	0.0001
W	0.01	0.01	0.01	0.01	--	--	0.01	0.01	<0.01	<0.01
Sb	0.005	0.003	0.003	0.002	<0.01	<0.01	0.005	0.004	0.001	<0.001
As	0.013	0.007	0.012	0.003	--	--	0.007	0.009	0.004	0.004
Sn	0.012	0.012	0.012	0.005	--	--	0.01	0.012	0.005	0.005
Zr	0.003	0.003	0.003	0.003	--	--	0.004	0.004	0.002	0.001
Pb	0.004	0.002	0.003	0.002	<0.01	<0.01	0.003	0.003	0.001	<0.001
N	0.011	0.012	0.014	0.008	--	--	0.022	0.072	0.018	0.011
O	0.010	0.008	0.014	0.009	--	--	0.009	0.092	0.022	0.008
IIW. Carbon Eq.	0.43	0.43	0.43	0.33	0.44	0.39	0.42	0.41	0.45	0.27

Note: Chemical Analysis was Performed using Optical Emission Spectroscopy (OES).
 Flange and Pipe Base Metals meet the Chemical Composition Requirements of their respective ASTM Standards A105 and A106-Gr. B. (See Appendix A and B for their respective ASTM Standards)
 $IIW\ Carbon\ Equivalent = \%C + \%Mn/6 + (\%Cr + \%Mn + \%V)/5 + (\%Cu + \%Ni)/15$

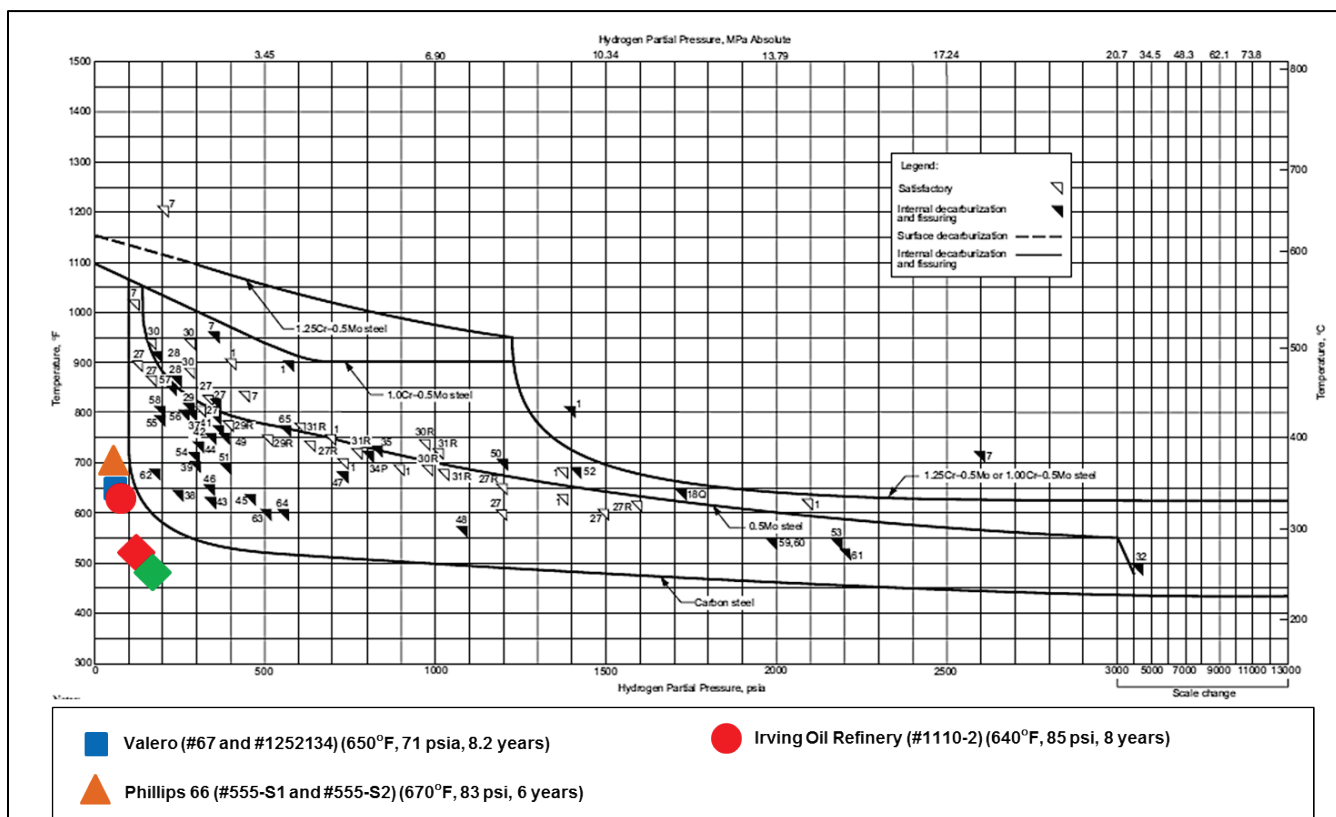


Figure 24. API RP 941 Nelson Diagram shows all the Heats used in the Current Study are below the Knee of the Carbon Steel Limit Line. Complete Operating Conditions for all the Heats used in the Current Study are shown in Table 1.

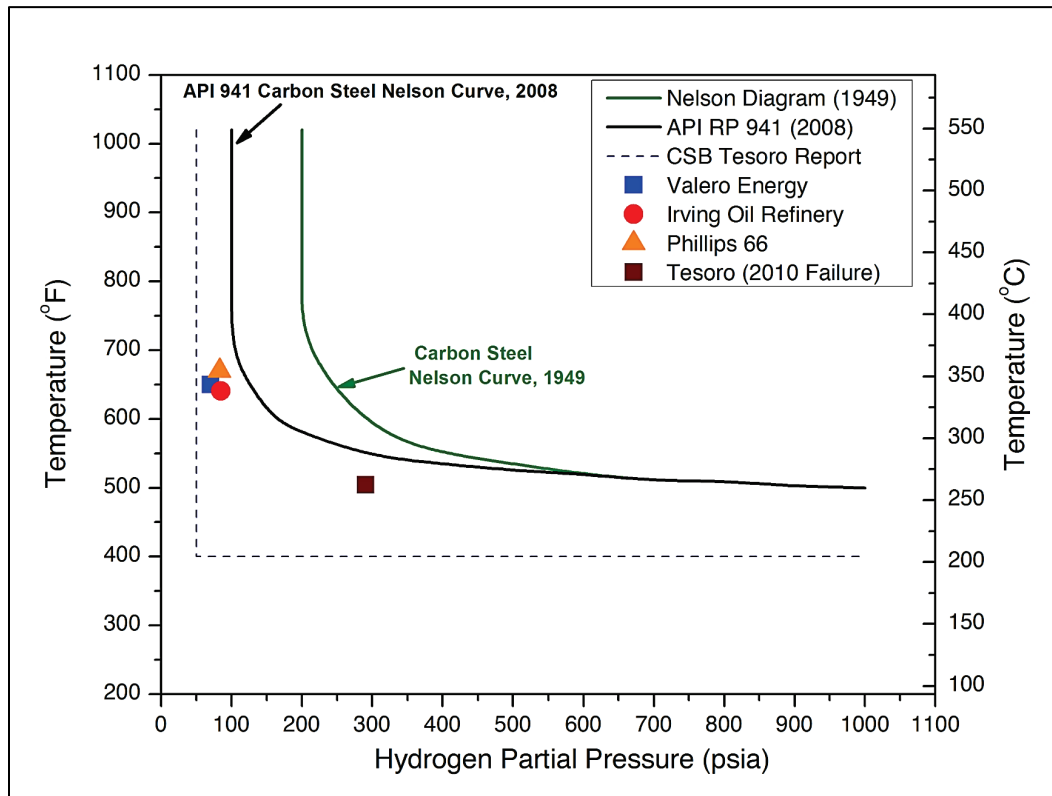


Figure 25. Operating Conditions of all Components Received at UTK with Respect to the Carbon Steel Nelson Curves (1949 and API RP 941 - 2008). The Plot also shows the Position of these Components with Respect to the Suggested Repositioning of the Nelson Curve by the CSB after Tesoro Refinery Incident in 2010^{23, 37, 38}. Complete Operating Conditions for all the Components used in the Current Study are shown in Table 1.

3.1. Valero Energy (Flange #67 and Flange #1252134)

Two carbon steel flange-to-pipe welded components (Flange #67 and Flange #1252134) were proactively removed from service (no known damage at the time of removal) by Valero Energy. There were six other instances of failures in Valero Energy flange-to-pipe welded components between 2008 and 2011, which prompted in the proactive removal of these two components for metallurgical analysis ⁸². Flange-to-pipe welded components #67 and #1252134 were inspected using ultrasonic techniques by Valero Energy, and a UT indication of service damage was observed in one quadrant (270° location) only on Flange #67. Flange #1252134 was determined to be clear of any UT indications around the full circumference of the component (no service damage observed). The location of ultrasonic indication on Valero Flange #67 was subsequently confirmed using metallography by Valero Energy ⁸². Both of these components were operating under the same conditions as shown in Table 1. Flanges #67 and #1252134 were sent to UTK for further metallurgical examination.

As-Received photographs of the Valero flange-to-pipe welded components #67 and #1252134 are shown in Figure 26A and Figure 26B,

respectively. The red arrow in Figure 26A shows an approximate location of a crack in Flange #67 (270° location - found by Valero Energy ultrasonic technique and presence of damage confirmed using metallography). These flange-to-pipe welded components (#67 and #1252134) received from Valero Energy were not given a postweld heat treatment (PWHT) prior to being placed in service.

Scaling was observed from service exposure at the inside diameter surface of both Valero components. Flange-to-pipe welded components #67 and #1252134 had a scale thickness of 0.060" (1.5 mm) and 0.089" (2.2 mm), respectively.

The flange and pipe has a wall-thickness of 0.55" (14 mm) and 0.60" (15.2 mm), respectively [Note- the flange (damaged) component is thinner than the pipe]. The wall-thickness of flange is 0.45" (11.4 mm) and pipe is 0.43" (11 mm) for the flange-to-pipe welded component #1252134, which did not show any damage is approximately same. Detailed dimensional information for each component is shown in Table 3.

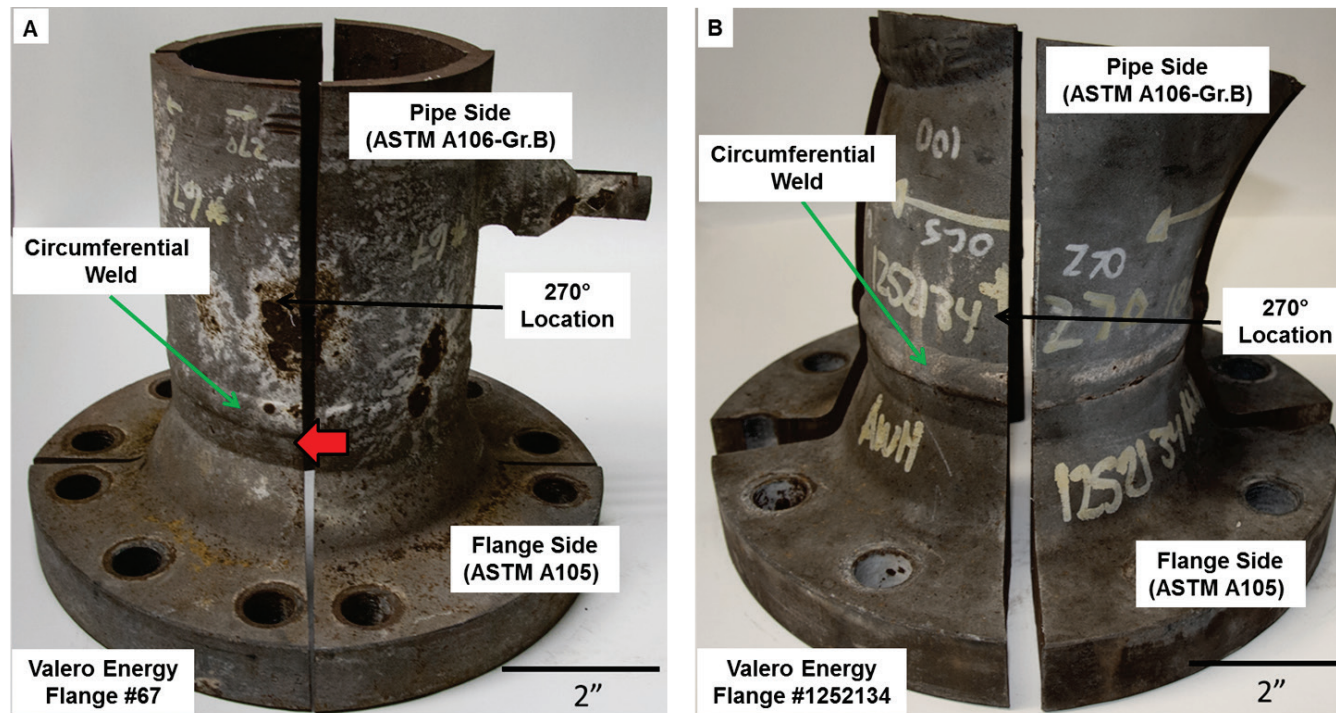


Figure 26 Valero Energy Flange-to-Pipe Weld Components As-Received by UTK, (A) Flange #67 and (B) Flange #1252134. (A) Cracking was observed in the Flange Base Metal of Flange #67 as indicated by the Red Arrow at the 270° Location when Evaluated by Valero Energy (using ultrasonic inspection). (B) Valero Flange #1252134 was indicated not to have any Service-Damage, based on Ultrasonic Inspection by Valero Energy ⁸².

3.2. Irving Oil Refinery (Flange #1110-2)

A carbon steel flange-to-pipe welded section removed from the line P425-3185 CAA5-H because of leakage during service was sent to the University of Tennessee (UTK) by Irving Oil Refinery (IOR) for HTHA damage evaluation⁸⁰. IOR flange-to-pipe welded component was sent to Wayland Engineering for metallurgical failure analysis prior to sending the components to UTK⁸⁰. The line transports liquid hydrocarbons from hydrodesulphurization (HDS) column to the reheat furnace⁸⁰. Figure 27 shows a photograph of the IOR flanges-to-pipe welded component #1110-2 before it was sectioned and sent to UTK for a HTHA damage evaluation. Magnetic particle inspection (MPI) by Wayland Engineering showed the presence of damage 0.93" (23.6 mm) long in the circumferential direction in the flange base metal of the flange-to-pipe welded component #1110-2 (as shown by red arrow in Figure 27).

The locations of two circumferential flange-to-pipe welds on IOR components are shown by green arrows. Figure 28A and Figure 28B shows the as-received photographs of the flange-to-pipe welded component #1110-2 and the section extracted from IOR Flange #1110-2, respectively. Red arrow shows

the approximate crack location per Wayland Engineering's finding in the flange base metal as shown in Figure 28B.⁸⁰

The IOR flange-to-pipe welded component was operating at 641°F and a hydrogen partial pressure of 70 psig⁸⁰. The service life, operating temperature, and hydrogen partial pressure for the Irving Oil Refinery (IOR) component is shown in Table 1 (component was operating below the carbon steel curve in API RP 941, 2008 Nelson diagram). The IOR flange-to-pipe welded component #1110-2 was not postweld heat-treated (PWHT'ed). Initial dimensional measurements at various regions of the Flange #1110-2 were obtained and the wall-thickness of the flange is 0.54" (13.7 mm) and that of the pipe 0.61" (15.5 mm) (note the cracked flange is thinner than the pipe component). Scaling approximately 0.019" (0.5 mm) thick on the inside diameter surface (hydrogen exposed surface) was observed in Flange #1110-2 (see Table 3 for detailed measurements).

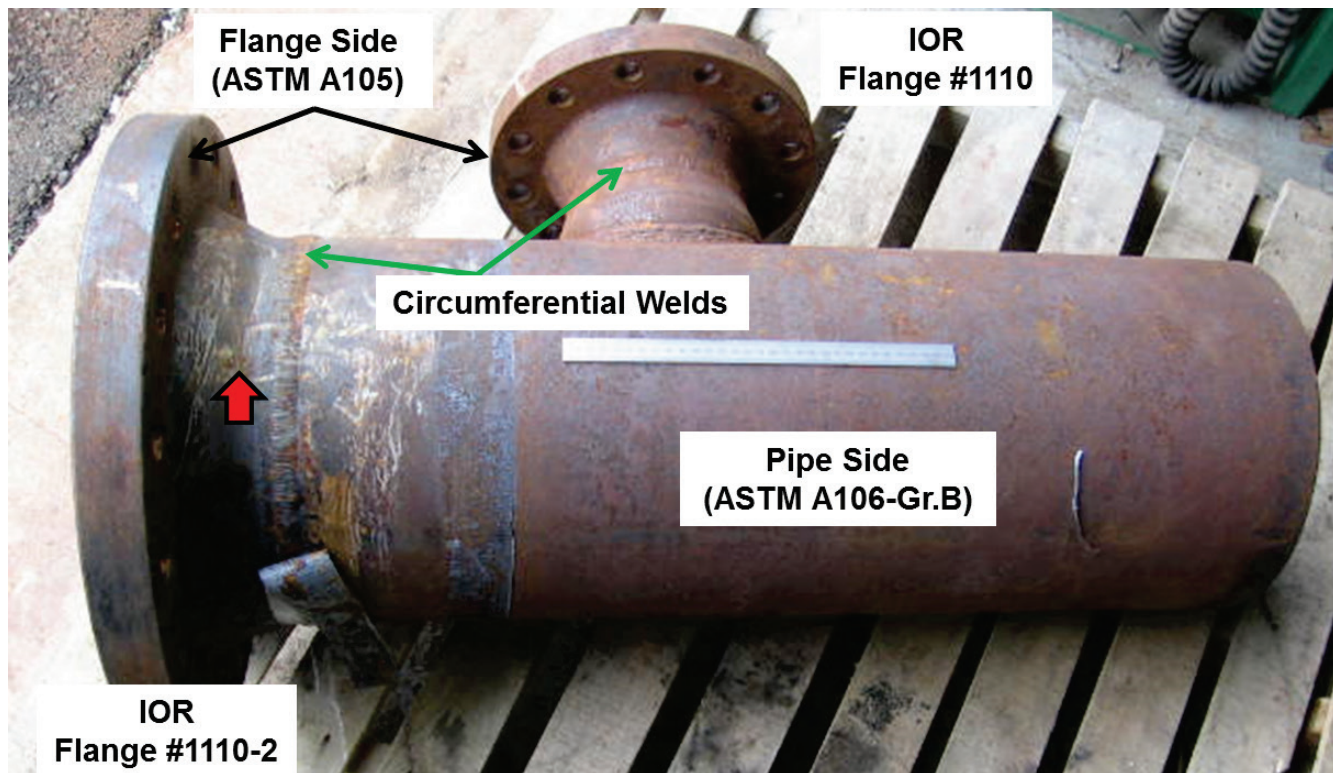


Figure 27. Photograph of Irving Oil Refinery Flange-to-Pipe Welded Component #1110-2 prior to the Receipt by UTK. Photograph Extracted from the Failure Analysis Report Prepared by Wayland Engineering⁸⁰. Cracking was observed in IOR Flange #1110-2, as shown by the Red arrow.

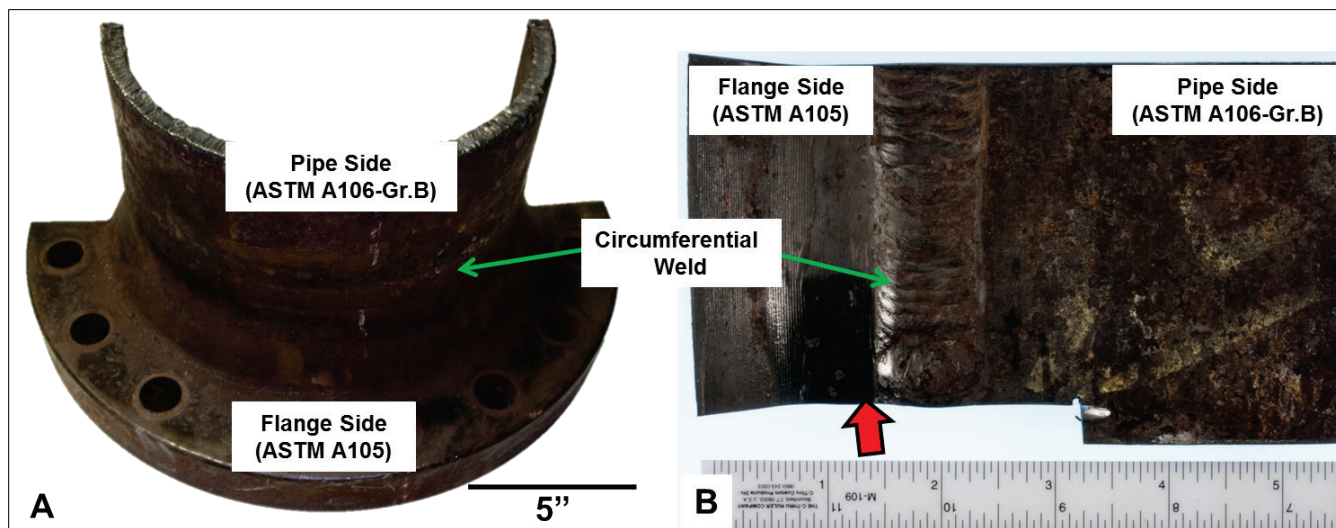


Figure 28. As-Received Photographs of the Irving Oil Refinery Flange-to-Pipe Welded Component received from Wayland Engineering for HTHA Evaluation, (A) #1110-2, and (B) Section #1110-2-1 extracted from Flange-to-Pipe Welded Component #1110-2 by Wayland Engineering. Green Arrows show the Location of the Flange-to-Pipe Circumferential Weld. Red Arrow Indicates the Approximate Crack Location in the Flange Base Metal. The Exact Location of Section #1110-2-1 with respect to the Flange-to-Pipe Welded Component #1110-2 is Unknown.

3.3. Phillips 66 (Flange #555-S1 and Flange #555-S2)

Two carbon steel flange-to-pipe welded components #555-S1 and #555-S2 were received by the Materials Joining Group at the University of Tennessee (UTK) from Phillips 66 Alliance Refinery (P66) for an evaluation of service damage and any evidence of High Temperature Hydrogen Attack (HTHA). Flange-to-pipe welded components #555-S1 and #555-S2 were proactively removed from service by P66 due to a leakage of a nearby flange, and the whole system was upgraded to 1-1/4 Cr ⁸¹. The leaked component was unavailable for this study. The ultrasonic inspection techniques by P66 using Advanced Ultrasonic Backscatter Technique (AUBT), Spectrum Analysis, Velocity Ratio, and Phased Array techniques however did not detect the presence of any damage in these flange-to-pipe welded components #555-S1 and #555-S2. The ultrasonic inspection by UTK using the Linear Phased Array and Focused Phased Array techniques also failed to detect the presence of any damage in P66 flange-to-pipe welded components #555-S1 and #555-S2.

As-Received photographs of the P66 flange-to-pipe welded components #555-S1 are shown in Figure 29A. Samples #555-S1-A and #555-S1-B, shown by red arrows in Figure 29A (Flange #555-S1), were evaluated by P66 for damage to

the weld/flange location prior to shipping the components to UTK. The green arrows in Figure 29A show the location of the circumferential weld for both flange-to-pipe welded components. Figure 29B shows an as-received photograph of the flange-to-pipe welded component #555-S2. Approximately half of the flange-to-pipe weld ($\sim 180^\circ$) of #555-S2 was received by UTK (see Figure 29B). The outside diameter (OD) surface of Flange #555-S2 (see Figure 29B) had been ground smooth to contour the weld and the inside diameter (ID) surface of the weld had been ground flush prior to the receipt of the components by UTK. From the appearance of the inside and outside surfaces of flange-to-pipe weld component #555-S2, it appears that the inside and outside surfaces of the weld regions were ground prior to the service installation. Both P66 flange-to-pipe welded components #555-S1 and #555-S2 were in non-postweld heat-treated (PWHT'ed) condition.

Both P66 flange-to-pipe welded components #555-S1 and #555-S2 were in service at the same operating conditions (Temperature of 670°F and Hydrogen Partial Pressure of 83 psia). The service life, operating temperature, and hydrogen partial pressure are shown in Table 1 ⁸¹. The operating temperature and hydrogen partial pressure for flange-to-pipe welded components #555-S1

and #555-S2 were superimposed on the Nelson curve from API RP 941 7th edition as shown in Figure 24 ³⁴. It should be noted that the service conditions of both P66 components are positioned to the left of the carbon steel curve at the “knee” of the Nelson diagram (within safe operating limits). Both flange-to-pipe welded components #555-S1 and #555-S2 are also positioned to the left of the carbon steel limit line at the “knee” of the Nelson curve (within safe operating limits) when superimposed on all the previous editions of API RP 941 Nelson curves. Thus, the damage resulting from high temperature hydrogen attack (HTHA) was not expected to have occurred at these temperatures and pressures ³⁴.

Initial dimensional measurements at various regions of the P66 flange-to-pipe welded components #555-S1 and #555-S2 were obtained, and the wall-thickness of the flange and pipe base metals is same for both components (0.48”- wall and 8”- outside diameter). Scale, if present on the ID surface was removed from both the P66 flange-to-pipe welded components prior to receipt at UTK. Detailed information on the dimensional measurements for flange-to-pipe welded components #555-S1 and #555-S2 are shown in Table 3.

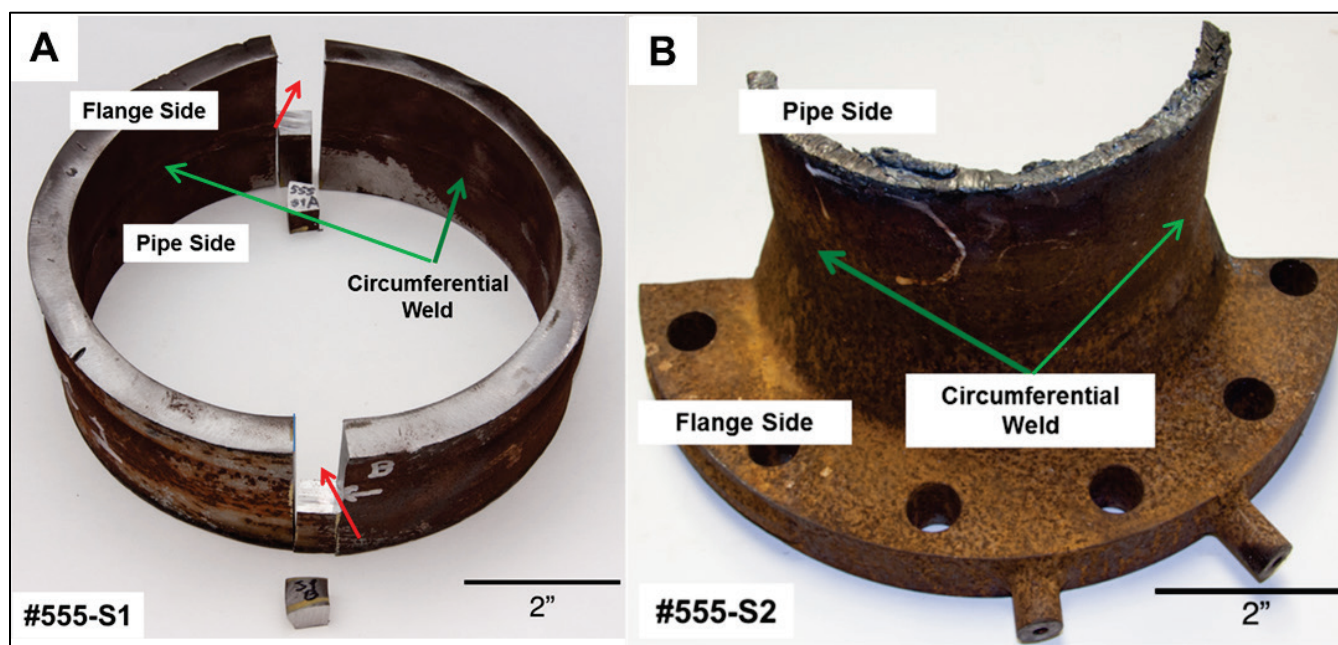


Figure 29. As-Received Photographs of the Flange-to-Pipe Welded Components Received From Phillips 66, (A) #555-S1 and (B) #555-S2. Samples #555-S1A and #555-S1B (shown by red arrows in Figure 19A) were evaluated by Phillips 66 for Damage to the Weld/Flange Location prior to shipping the Components to UTK.

Table 3. Complete Dimensional Measurements on Various Regions of the Components Received at UTK for API HTHA Study.

Industry Contributor	Sample ID	Wall-thickness (inches)			Outside Diameter (inches)		Scale Thickness (inches)
		Pipe	Flange	Weld ^(a)	Pipe	Flange ^(b)	
Valero Energy	Flange #67	0.60	0.55	0.71	6.625	12	0.060
	Flange #1252134	0.45	0.43	0.71	6.625	12	0.089
Irving Oil Refinery	Flange #1110-2	0.61	0.54	0.72	11.5	19.4	0.019
Phillips 66	Flange #555-S1	0.48	0.48	0.62	8	Unavailable	N/A
	Flange #555-S2	0.53	0.49	0.49	8	14.5	N/A

(a) Measured at the center of the weld deposit. Outside surface of the P66 flange-to-pipe welded component #555-S2 was ground to contour the weld.

(b) Measured at the outside end of the flange where the bolts are applied.

N/A- Not Applicable (If any scaling present was removed from the inside surface prior to shipping the components to UTK)

Chapter 4 – Experimental Procedures

The samples extracted from the five components involved in the current study were characterized for root cause evaluation by: 1) microstructural characterization using metallography (OLM and SEM), 2) diffusible hydrogen measurement using American Welding Society (AWS/ISO diffusible hydrogen) method using gas chromatography, 3) methane determination using gas chromatography, and 4) crack surface and methane bubble evaluation using the “Cryo-Cracking” technique. The experimental procedures are discussed in detail below:

4.1 Metallographic Sample Preparation

Samples for metallography were extracted from a desired location and mounted in epoxy for metallographic sample preparation. The metallographic specimens were ground in a sequential order using 120, 240, 600, and 1200 grit-grinding disks and were rinsed with methanol. Samples were then polished with 6 μm diamond paste on a woven napless nylon cloth (a few drops of mineral spirits can be used as a lubricant if the nylon pad becomes dry). Samples were then polished to a 0.05 μm alumina finish using micro-cloth (approximately

60 seconds). Samples were examined in the as-polished condition before etching because if the HTHA damage is in the initial stages, it will be difficult to observe the damage in the etched condition. After the initial OLM examination, samples were then etched using 2% Nital. A layer of cold-worked metal is generally formed on the specimen surface during the initial grinding and polishing process commonly referred to as “disturbed metal”⁸³. A sequence of 4-5 etch-polish cycles is required for complete removal of the “disturbed metal” from the specimen surface to observe the true microstructure for HTHA characterization. The samples were cleaned in an ultrasonic bath using high purity methanol/ethanol for 60-90 seconds between each etch-polish sequence. Samples were evaluated using the Optical Light Microscope (OLM) and Scanning Electron Microscope (SEM) at the magnifications of 50X to 10,000X for microstructure characterization.

4.2 Hydrogen Measurement and Methane Determination

Carbon and low-alloy steels, when exposed in high hydrogen partial pressure environments (> 70 psia) at high temperatures (>450°F/232°C), results in the reaction between carbon in solution or carbides in steels causing traditional High Temperature Hydrogen Attack (HTHA). HTHA damage occurs when

atomic hydrogen (H^+) diffuses into the steel and reacts with carbon in solid solution and with carbides forming methane as discussed in earlier section. The methane content measured at the surface does not reflect the true amount of hydrogen damage, as methane formed at the exposed surface may diffuse outside of steel through a path (cracks, fissures, or surface defects). Thus, the hydrogen measurement should be performed at least 1-2 mm away from the hydrogen-exposed surface to measure the maximum extent of damage. However, when methane forms internally it is trapped as bubbles and accumulates in grain boundaries since the molecular methane (CH_4) is unable to diffuse through the steel (because of the molecular size).

The molecular methane (CH_4) formed internally is non-diffusible and cannot be measured directly using standard diffusible gas chromatography. Molecular methane was dissociated according to equation 4 at a temperature of 1292°F (700°C), as methane is thermodynamically unstable above 1025°F (552°C) (as described in the literature review section). Hydrogen content dissociated from methane is thus measured using gas chromatography, and is then used to back-calculate the equivalent methane content. The detailed procedure to

measure the hydrogen and equivalent methane content for HTHA damage evaluation using gas chromatography is described in detail later in this section.



Hydrogen measurement for proper HTHA damage evaluation is performed using a gas chromatograph in two Steps (I & II):

1. **Step 1:** AWS Diffusible Hydrogen Measurement
2. **Step 2:** Hydrogen Measurement from Methane Dissociation (i.e. HTHA Hydrogen)

The measurement procedure was divided into two steps to avoid any confusion between the diffusible hydrogen and the hydrogen that reacts with carbon/carbides to form methane (i.e. HTHA Hydrogen). The gas chromatograph used in this study “Oerlikon-Yanaco Hydrogen Analyzer” is shown in Figure 30. However, hydrogen measurements can be performed using any gas chromatograph which is capable of accurately measuring to a minimum level of +/- 0.02 mL ⁸⁴.



Figure 30. Oerlikon-Yanaco Hydrogen Analyzer for Hydrogen Measurement.

4.2.1 Step 1: AWS Diffusible Hydrogen Measurement

Suitably sized samples from the damaged area were extracted, cleaned with acetone, weighed to the nearest 0.001 g using an analytical balance, and placed in the sample chambers of a gas chromatograph. A minimum weight of 6 grams is generally required for accurate hydrogen measurement upon methane dissociation⁵⁰. Samples were placed in the sample chambers of a gas chromatograph, and the chambers were flushed with high purity argon

(99.999%) for a minimum of 30-45 seconds to remove any air/moisture present. The sample chambers of the gas chromatograph are shown in Figure 31A. The sample chambers were then back-filled with high purity argon (99.999%) to create an inert atmosphere for the measurement. As recommended in AWS A4.3 (now adopted by ISO), the sample chambers are then held at a hydrogen evolution temperature of either 45°C (113°F) for 72 hours or 302°F (150°C) for 6 hours to completely evolve hydrogen gas in the measurement chamber ⁸⁴. A temperature of 113°F (45°C) for 72 hours was used in the current study. After the thermal treatment, the sample chambers were allowed to cool to room temperature before running the hydrogen measurement test. The hydrogen volume (mL) was converted to standard temperature and pressure [32°F (0°C) and 1atm (760 mm of Hg) respectively] using the combined ideal gas law (see Equation 13).

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{Equation 13}$$

The hydrogen (mL) content at standard temperature and pressure (STP) is converted to mL/100g using Equation 14.

$$\text{Hydrogen} \left(\frac{\text{ml}}{100\text{g}} \right) = \frac{\text{Measured Hydrogen at STP (ml)}}{\text{Sample Weight (g)}} \times 100 \quad \text{Equation 14}$$

The gas chromatograph (“Oerlikon-Yanaco Hydrogen Analyzer”) used in the current study also has a capability of measuring nitrogen content, which makes this instrument rather versatile. The measurement of nitrogen content allows the operator to check if there has been leakage into the sample chamber prior to testing. If the nitrogen content is above the limit specified by the manufacturer (max 0.02 mL for “Oerlikon-Yanaco Hydrogen Analyzer”), the test should be repeated to confirm the results after properly sealing the chambers. Upon completion of the AWS diffusible hydrogen measurement, the same samples used in Step I were used in Step II to measure the hydrogen content dissociated from the methane.

4.2.2 Step 2: Hydrogen Measurement from Methane Dissociation

The samples from Step 1 were re-ground to 400 grit, cleaned with acetone, weighed to the nearest 0.001 g using an analytical balance, and encapsulated in a quartz tube (as shown in Figure 31B). The quartz tube was triple pumped and back-filled with high purity argon (99.999 %) to remove all the moisture from the surface of the sample and to create an inert atmosphere inside the capsule. The

encapsulated samples (see Figure 31B) were then thermally treated at 1292°F (700°C) for 72 hours for complete methane gas dissociation based on Equation 12. Based on the standard free energy of methane formation (ΔG_{CH_4}) described earlier (see Figure 7), there is no driving force for methane to form above 1025°F (552°C). Earlier studies at the UTK by L. Peng have shown comparable results between hydrogen measurements by methane dissociation at 1292°F (700°C) for 72 hours using gas chromatography and Leco-vacuum fusion methods⁵⁰. Thus, the thermal treatment at 1292°F (700°C) for 72 hours completely dissociates all the methane trapped in the steel to determine hydrogen content using gas chromatography.

After the 1292°F (700°C) for 72 hours heat treatment, the encapsulated samples were placed in the sample chambers of the gas chromatograph. The sample chambers were then flushed with high purity argon (99.999%) for minimum of 30-45 seconds to drive away any moisture present. The sample chambers were back-filled with high purity argon (99.999%) to create an inert atmosphere during the measurement. The quartz capsules containing the samples were broken by shocking the sample chamber and releasing the gas

(Ar/H₂/N₂) from the capsule into the measurement chamber, allowing the hydrogen dissociated from methane to be measured using gas chromatography.

The volume of measured hydrogen (mL) was converted to STP using Equation 13. The hydrogen content at STP was converted to mL/100 g using Equation 14 as described in the previous section. The volume of hydrogen (mL/100 g) was converted to parts-per-million at STP using the given methods. The conversion from mL/100 g to ppm is shown in Equation 15. This conversion example uses 1 mL of hydrogen measured in a 100 g sample.

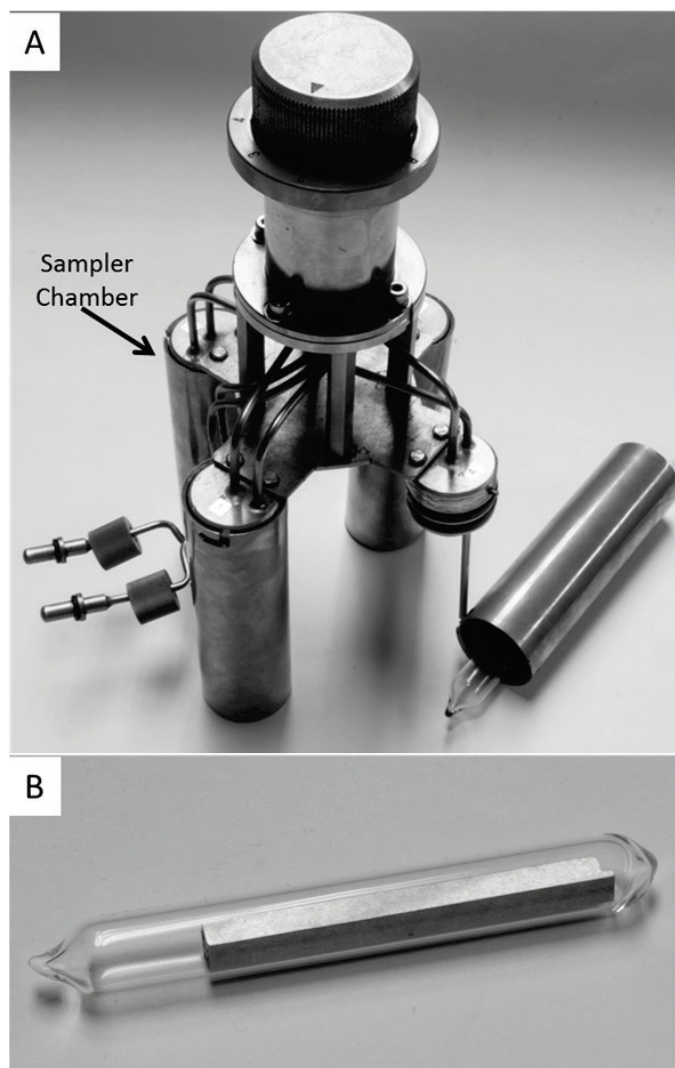


Figure 31. Oerlikon-Yanaco Hydrogen Analyzer, (A) Stainless Steel Sampler Chamber, and (B) Sample Encapsulated in a Quartz Tube for Hydrogen Measurement.

At STP,

$$\text{Volume of hydrogen (V)} = 1 \text{ mL}$$

$$\text{Density of hydrogen } (\rho) = 0.08988 \text{ g/L} = 8.988 \times 10^{-5} \text{ g/mL}$$

$$\text{Density } (\rho) = \text{mass (m)}/\text{Volume (V)}$$

$$\text{Mass of hydrogen (m)} = 8.988 \times 10^{-5} \text{ g}$$

$$\text{Parts-per-million (ppm)} = 1 \text{ g}/10^6 \text{ g} = 10^{-6}$$

$$\text{Volume of hydrogen (1 mL/100 g)} = 8.988 \times 10^{-5} \text{ g}/100 \text{ g} = 0.898 \text{ ppm}$$

$$\text{Hydrogen Content (ppm by weight)} = 0.898 \times \text{Volume of hydrogen at STP} \left(\frac{\text{mL}}{100 \text{ g}} \right) \quad \text{Equation 15}$$

The measured hydrogen content was utilized to back-calculate the methane content using methane dissociation reaction (Equation 11). Based on Equation 11, two moles of hydrogen is dissociated from one mole of methane. Thus, one ppm of hydrogen by weight is equivalent to four ppm of methane by weight. The measured hydrogen content is multiplied by a factor of four to obtain the equivalent methane content present in the sample. It is generally considered that two ppm of hydrogen is the nominal amount present in unaffected steel without causing any hydrogen damage and with the equivalent methane content of eight ppm⁵⁰.

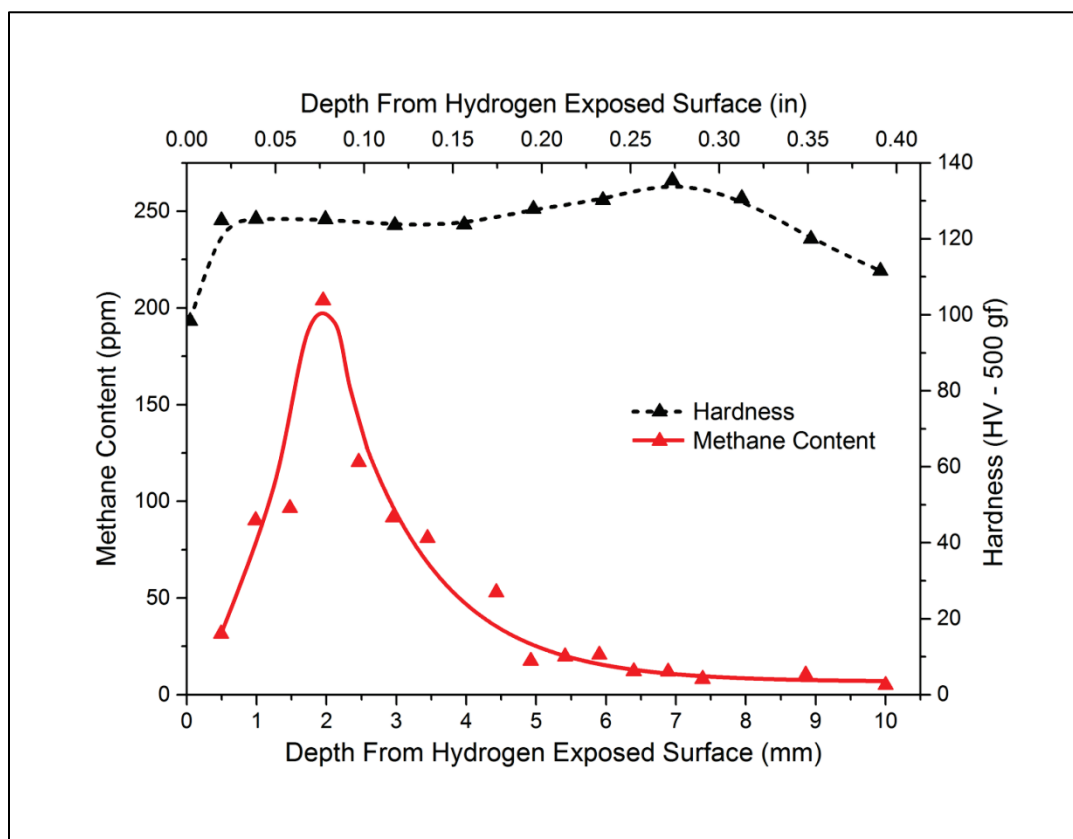


Figure 32. Methane Content (ppm) and Vickers Micro-Hardness Profile (HV-500 gf) as a Function of Distance from the Hydrogen Exposed Surface in C-1/2 Mo Steel. Methane Content (ppm) was Determination from Hydrogen Measurements using a Methane Dissociation Reaction. The plot shows the Maximum Content of Methane was Measured ~ 2 mm away from the Hydrogen Exposed Surface

4.3 “Cryo-Cracking” and SEM Examination

The “Cryo-Cracking” technique is used to induce a cracked surface at cryogenic temperature to reveal the cracking morphology along with the extent of microstructural damage. In this technique, when the steel is cooled to a liquid nitrogen temperature at -320°F (-196°C), it becomes embrittled. When the crack is imposed by using a rapid force, it will only develop cleavage facets and reveal grain boundary features. The “Cryo-Cracking” technique preserves the pre-existing crack surface as no plastic deformation is produced during crack propagation. The “Cryo-Cracked” sample is examined using high magnification microscopy (SEM) for the presence of methane bubbles and extent of HTHA damage ⁴⁷.

The sample preparation is one of the most important aspects of “Cryo-Cracking” to evaluate the hydrogen-damaged surface. Sample preparation depends upon the initial condition of the component (i.e. if the sample extracted has pre-existing cracks/fissures). If the sample has a pre-existing crack or defect, which extends for more than one-quarter of the wall-thickness, notch preparation is generally not required to produce a fracture surface. If the specimen extracted for “Cryo-Cracking” from the desired location

does not have pre-existing cracks or if the damage is limited to the microscopic level, a notch should be made on the sample to direct a fracture in the desired location with ease. A sharp notch (~1-2 mm deep) is placed using a dremel tool at the desired location. A notch is made circumferentially around the sample to direct the “Cryo-Cracking” along the desired path.

Samples for “Cryo-Cracking” were extracted from IOR #1110-2, Valero Flange#67, and P66 #555-S1. The presence of any grinding/cutting marks on the specimen could increase the stress concentration at that location and may generate fracture at the undesired location. Thus, any defects on the specimen surface, which could influence the fracture location, were removed prior to the fracture. The sample was submerged in liquid nitrogen for a minimum of 15 minutes to lower the sample temperature below the ductile-to-brittle transition temperature. The sample was placed in a vise and fractured by a hammer blow to generate a fracture in the desired location. Immediately after the fracture, the sample is placed in a methanol bath until ambient temperature is reached to prevent any oxidation/rusting on the fracture surface. The sample was then dried using hot air for SEM fractographic examination. SEM examination of the

fracture surface aids in evaluating the crack surface characteristics, fracture morphology, methane bubbles, and methane bubble sizes.

Chapter 5 – Results and Discussion

5.1 Valero Energy

5.1.1 Metallography on Valero Components (#67 and #1252134)

A sample for metallography was extracted from the 270° location in flange-to-pipe welded component #67 (see Figure 26), which was the same location identified by Valero Energy as a damage location by ultrasonic examination ⁸². A photomacrograph of the flange-to-pipe welded component #67 is shown in Figure 33. Cracking was found only in one quadrant (270° location) 5/8" (16 mm) long along the circumferential direction but isolated to the flange side of the weld and outside of the HAZ. This location of cracking was also noted by Valero Energy during their examination ⁸². During metallographic examination at UTK, the crack found on Flange #67 appeared to initiated at the inside diameter surface (IDS) and had extended to a depth of ¾ of the flange wall 0.45" (11.4 mm). Figure 34 shows a panorama of the entire crack in the flange base metal just outside of the visible HAZ. Cracking in the flange base metal appears to have initiated at the inside diameter surface and propagated towards the outside diameter surface. The crack exhibits both intergranular and

transgranular cracking morphology (~50% each). Figure 35 shows the optical micrographs of the crack adjacent to the ID surface in Flange #67 (A) 100X and (B) 500X. No evidence of decarburization was observed adjacent to the crack. Figure 36 shows optical micrographs of the crack termination location in Valero flange-to-pipe welded component #67 at (A) 100X and (B) 500X. Note that the crack terminates in the flange HAZ and does not extend into the weld deposit.

Scanning Electron Microscopy (SEM) was used to further investigate the nature of cracking in Valero flange-to-pipe welded component #67. Figure 37 shows the SEM photomicrographs at (A) 144X, (B) 2,500X, (C) 2,500X, and (D) 5,000X. The cracking shows a branching nature (a primary crack and multiple secondary cracks initiating from the primary crack). The cracking morphology is a mixture of intergranular and transgranular (~50% each) and any evidence of decarburization was not observed in a perlite colony adjacent to the crack location (see Figure 37D). Figure 38 (A) 5,000X and (B) 10,000X show SEM micrographs depicting grain boundary separation at the ferrite-ferrite triple point (shown by green arrows at the crack termination location. Internal decarburization was not observed in any areas adjacent to the crack location.

The microstructures of both the flange and pipe base metals in Valero flange-to-pipe welded component #67 are composed of ferrite and pearlite, which is typical for ASTM A105 for a flange and ASTM A106-Gr.B for a pipe material. Figure 39 shows photomicrographs of a flange base metal at (A) 100X and (B) 500X showing a typical forging microstructure with elongated grains. Figure 40 shows photomicrographs of the pipe base metal from Valero flange-to-pipe welded component #67 at (A) 100X and (B) 500X; the microstructure consists of ferrite and pearlite and exhibits a typical pipe forming/rolling texture. The directionality of the microstructural banding is normal for a forged a flange and wrought pipe material.

Two metallography specimens were extracted from the second flange-to-pipe welded component received from Valero Energy, identified as Flange #1252134; the two samples were located 180° apart along the component circumference. Figure 41 shows a photomacrograph of the flange-to-pipe welded component #1252134. Figure 42 shows photomicrographs of the flange base metal in flange-to-pipe welded component #1252134, and it shows a typical forging texture with elongated grains. No evidence of decarburization or fissuring/cracking was observed in all regions of flange-to-pipe welded

component #1252134. The microstructure consisted of ferrite and pearlite for the flange and pipe base metals. A ferritic and pearlitic microstructure is considered typical for the ASTM A106-Gr.B for pipe and ASTM A105 for flange materials.

ASTM grain size for both the installations (Flange-to-Pipe Welded Components #67 and #1252134) for flange and pipe base metal is approximately 5-7, which is a normal range for these materials.

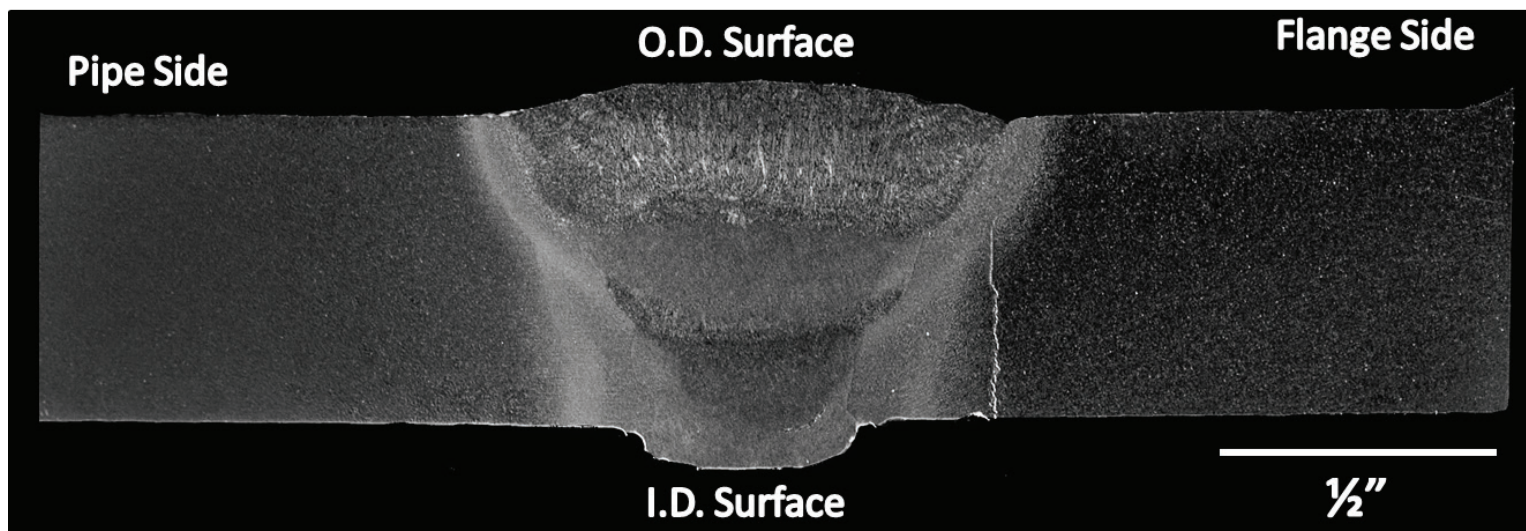


Figure 33. Photomacrograph of Valero Flange #67 showing Cracking in the Flange Side. Cracking Initiated just outside of the Visible HAZ on the Inside Diameter Surface (ID Surface) and Propagated towards the Outside Diameter Surface (OD Surface). Crack Terminated in the Heat-Affected Zone, 2% Nital Etch.

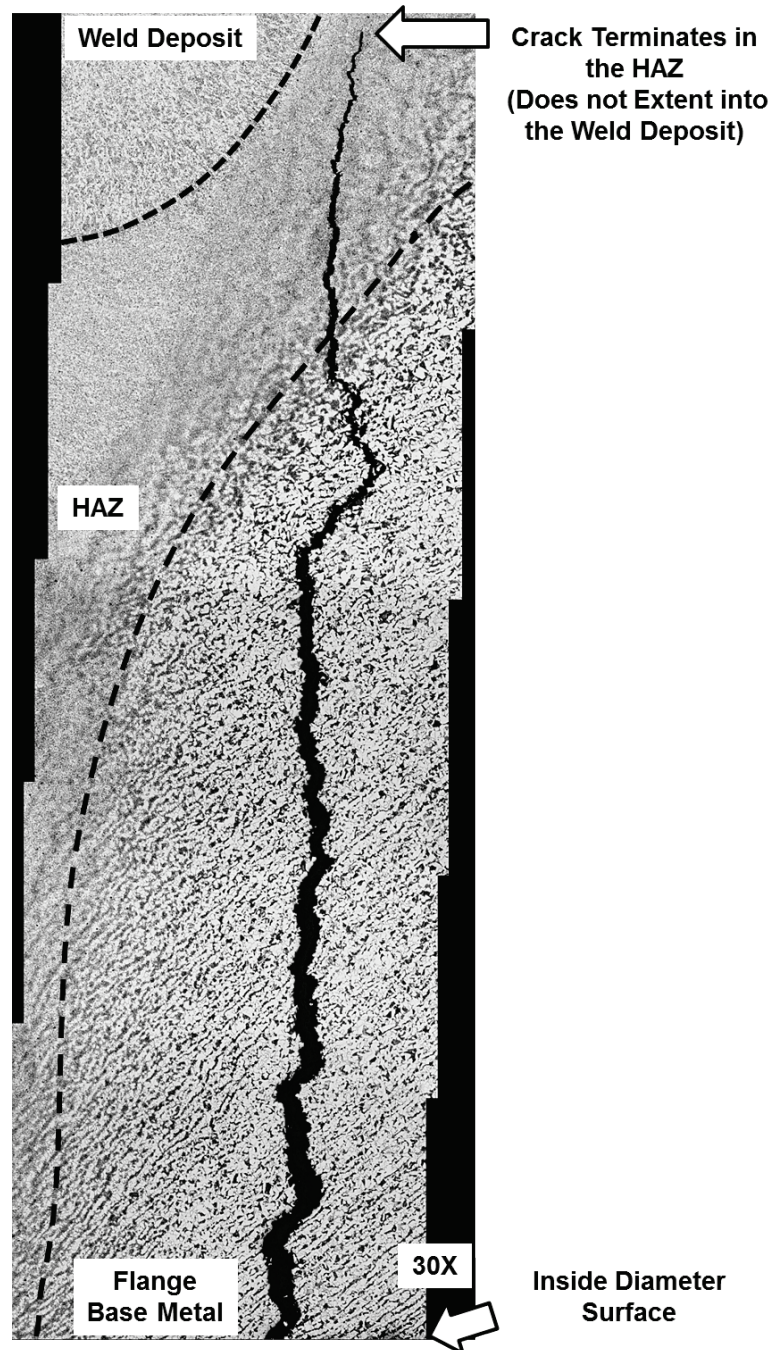


Figure 34. Panorama showing the entire Crack in the Valero Flange-to-Pipe Welded Component #67. Cracking was observed in the Flange Base Metal just Outside of the Visible HAZ and Appears to have Initiated at the Inside Diameter Surface, 2% Nital Etch.

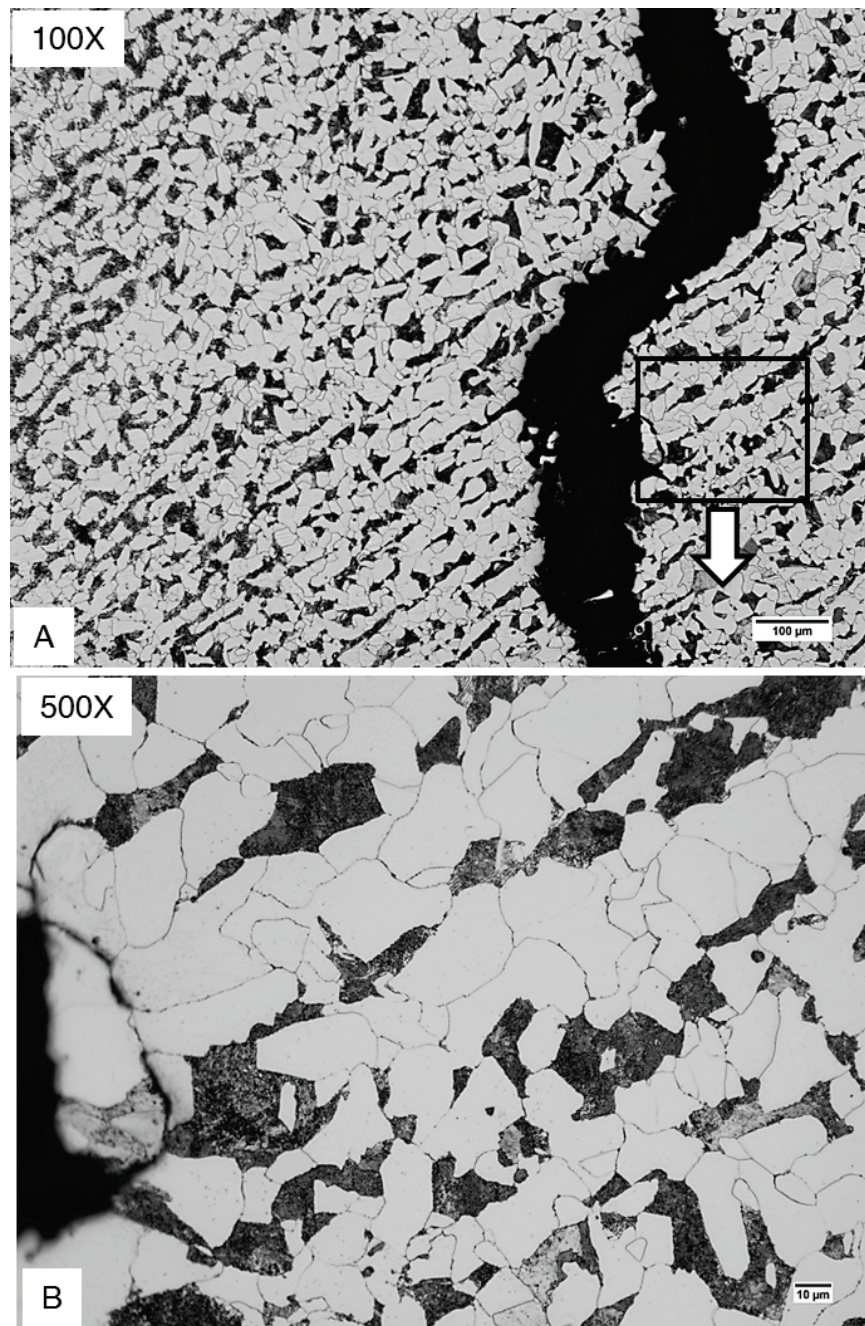


Figure 35. Photomicrographs showing the Crack Location in Valero Flange #67 adjacent to the Inside Surface in the Flange Base Metal. Internal Decarburization was not Evident, 2% Nital Etch.

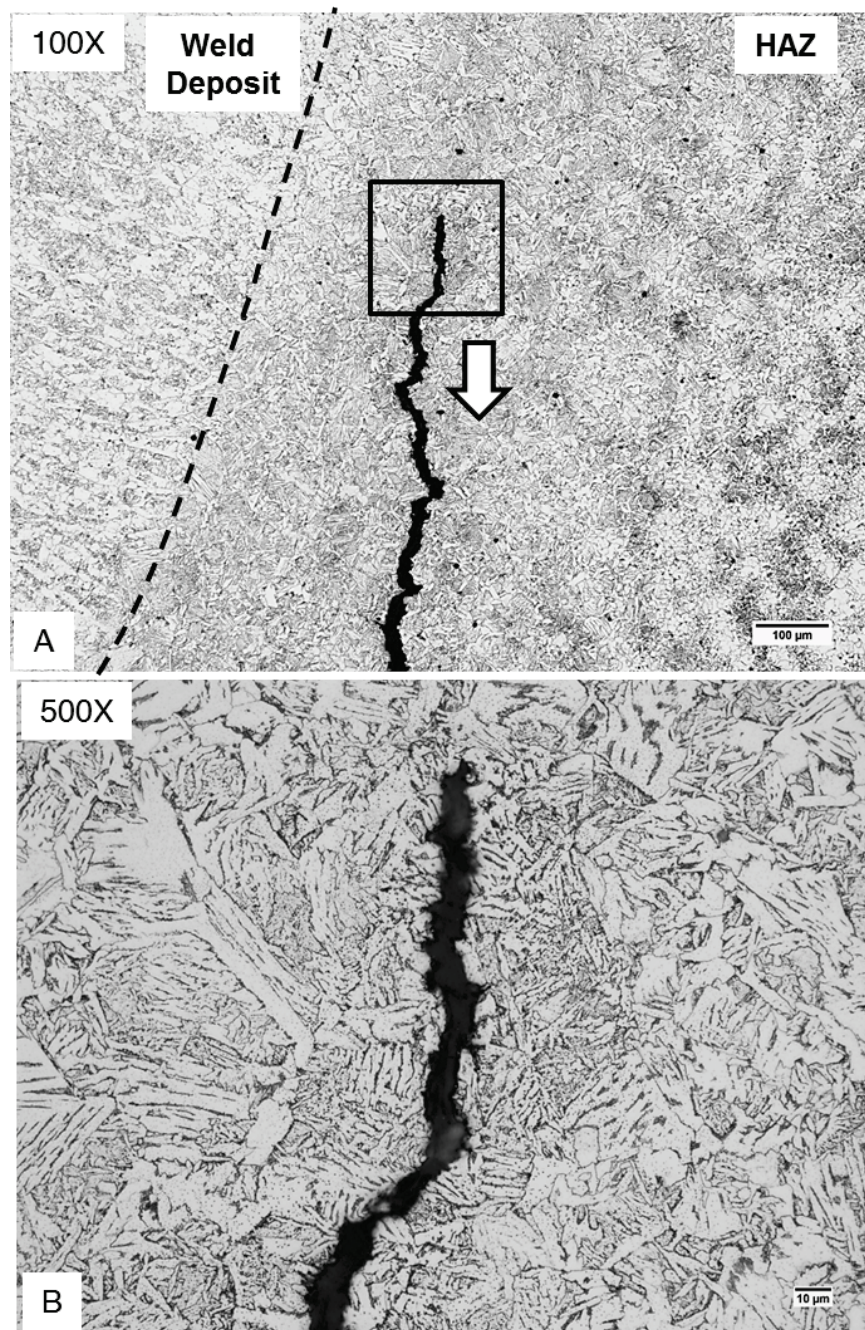


Figure 36. Photomicrographs showing the Crack Termination Location in the Flange-HAZ of Valero Flange #67. Internal Decarburization was not Observed in any Area Adjacent to the Crack, 2% Nital Etch.

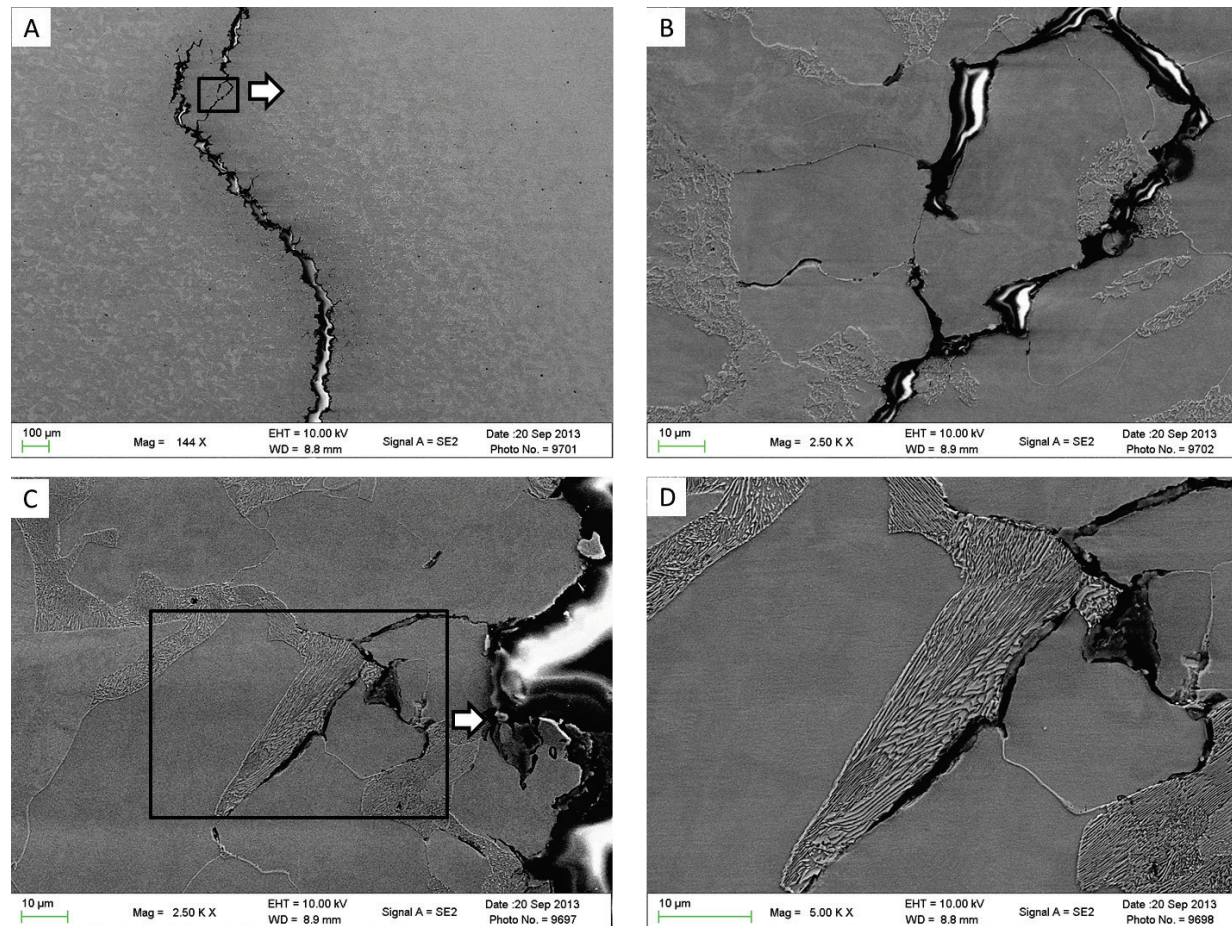


Figure 37. SEM Micrographs showing the Branching Nature of the Crack in Flange #67. Cracking Morphology was a Mixture of Intergranular and Transgranular (~50% each). No Evidence of Decarburization was Evident, 2% Nital Etch. (Note: Bright Regions inside the Crack are due to Charging of Epoxy Mounting Material during SEM Examination).

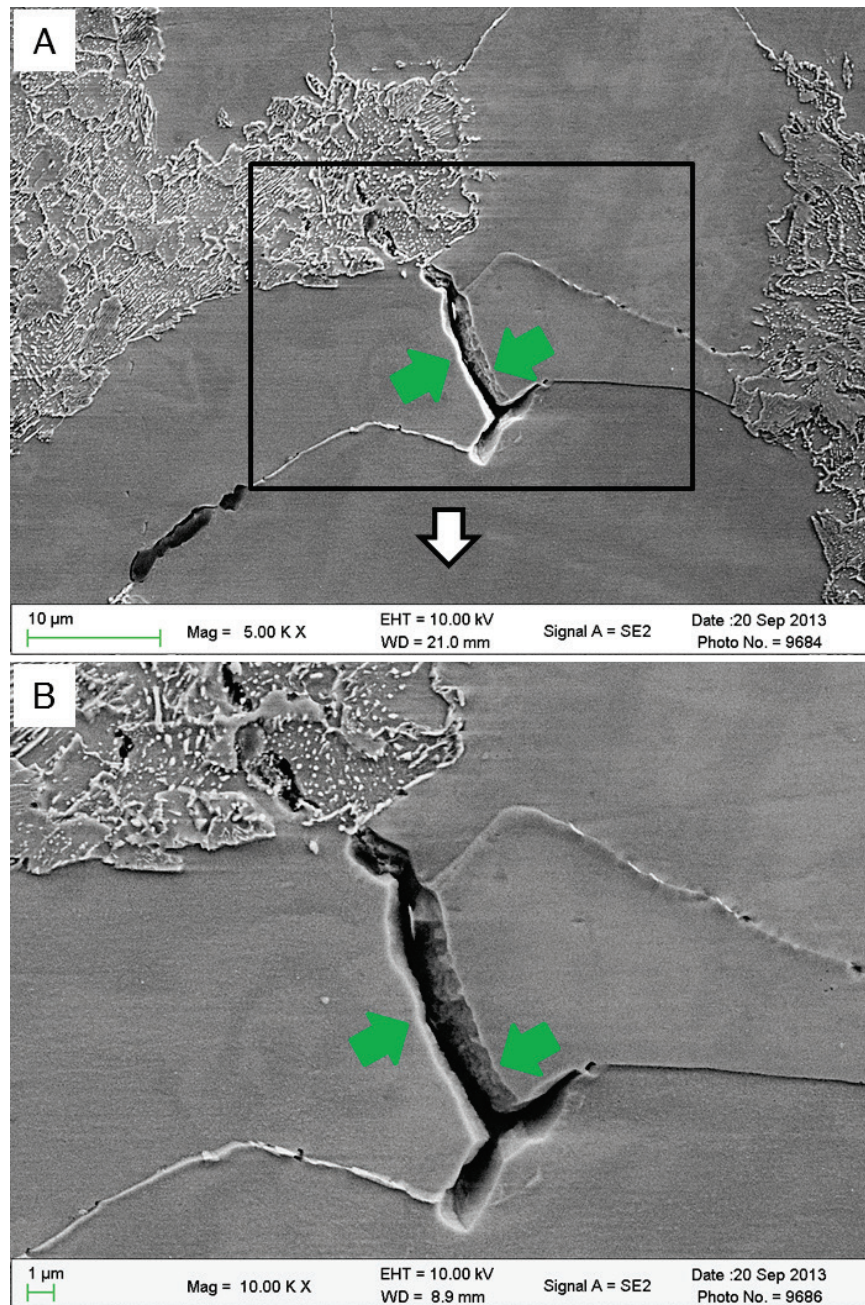


Figure 38. SEM Micrographs showing Grain Boundary Separation at a Ferrite-Ferrite Triple Point (Green Arrows) in Valero Flange #67 at the Crack Termination Location (HAZ).

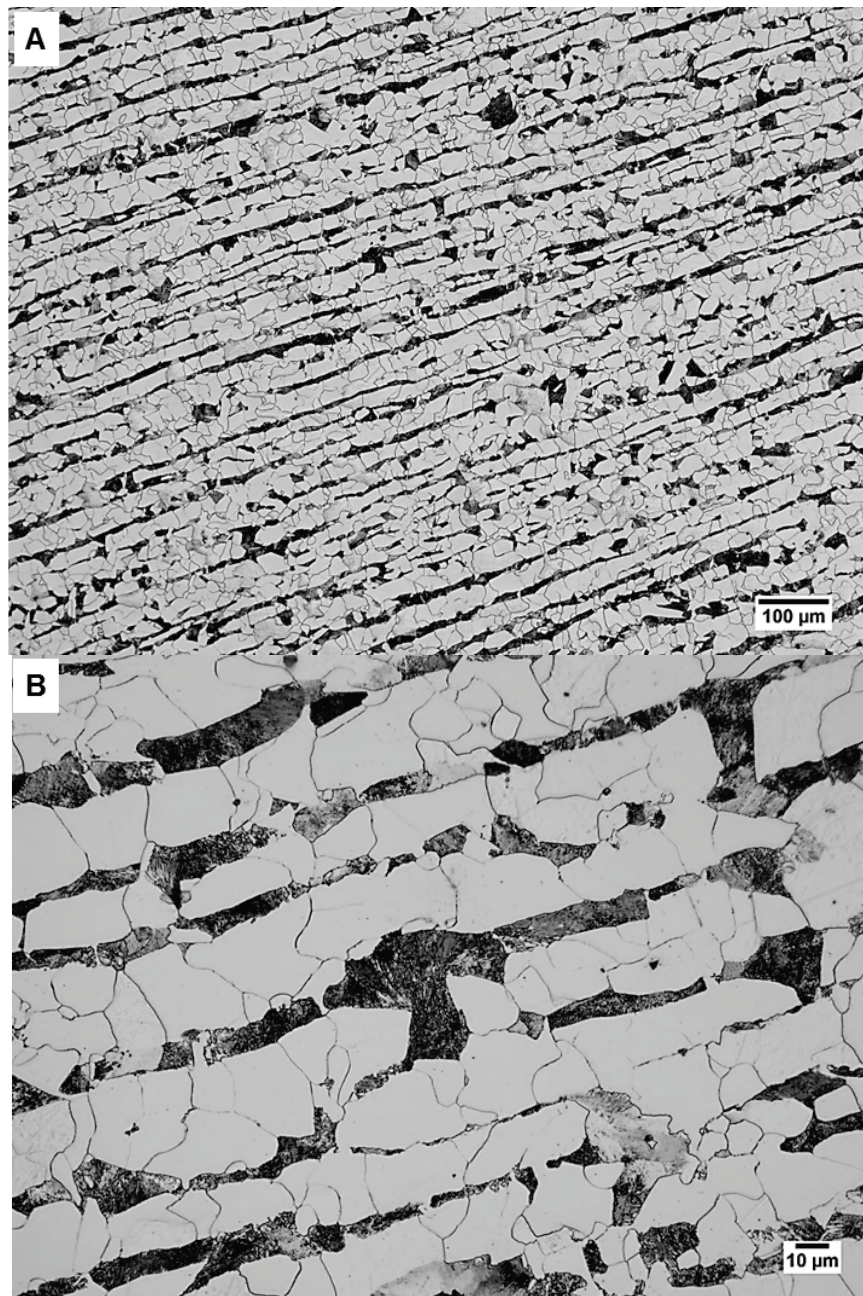


Figure 39. Photomicrographs of the Flange Base Metal showing Forging Texture in Valero Flange #67, (A) 100X and (B) 500X, 2% Nital Etch. Microstructure consists of Ferrite and Pearlite, ASTM Grain Size #6.

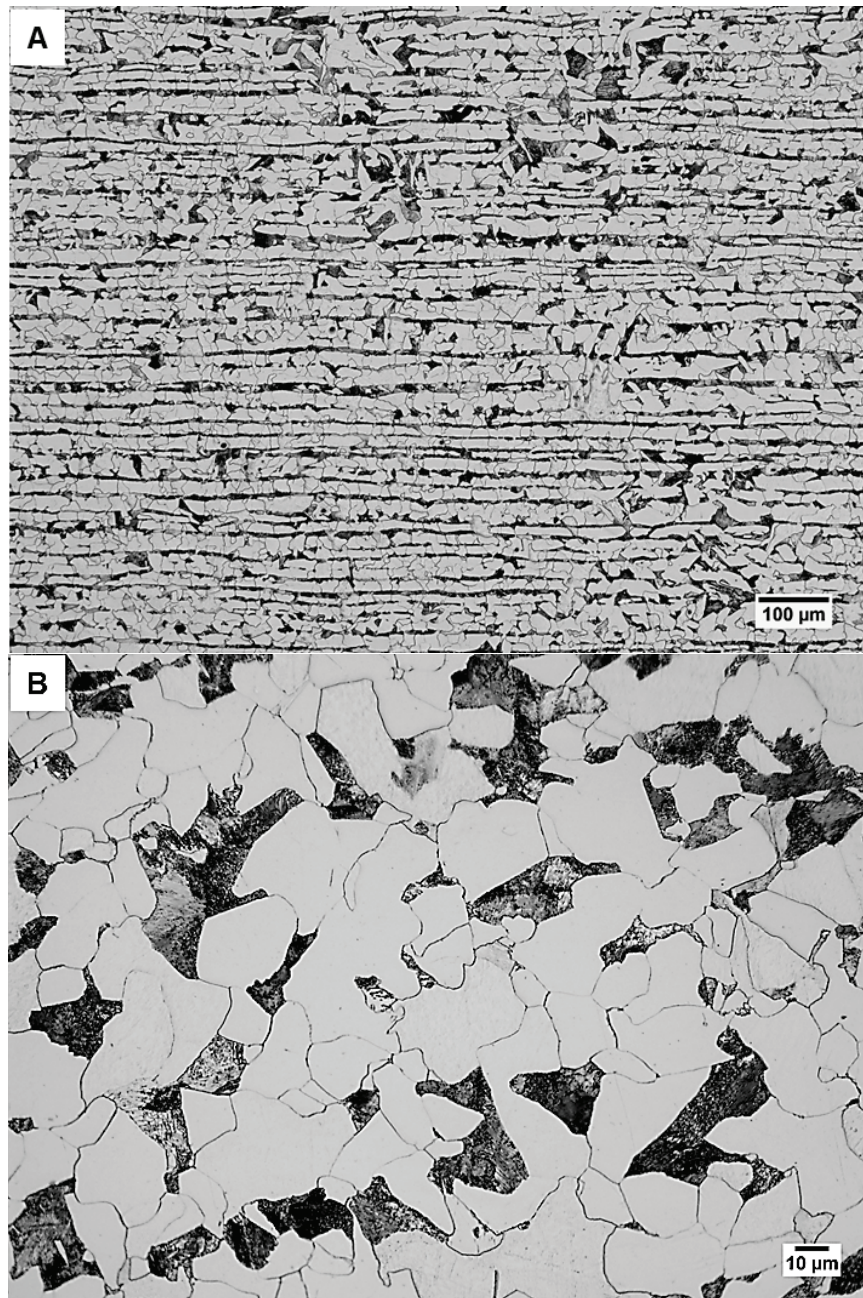


Figure 40. Photomicrographs of the Pipe Base Metal showing the Plate Rolling/Forming Texture in the Longitudinal Direction in Valero Flange #67, (A) 100X and (B) 500X, 2% Nital Etch. Microstructure consists of Ferrite and Pearlite, ASTM Grain Size # 6.

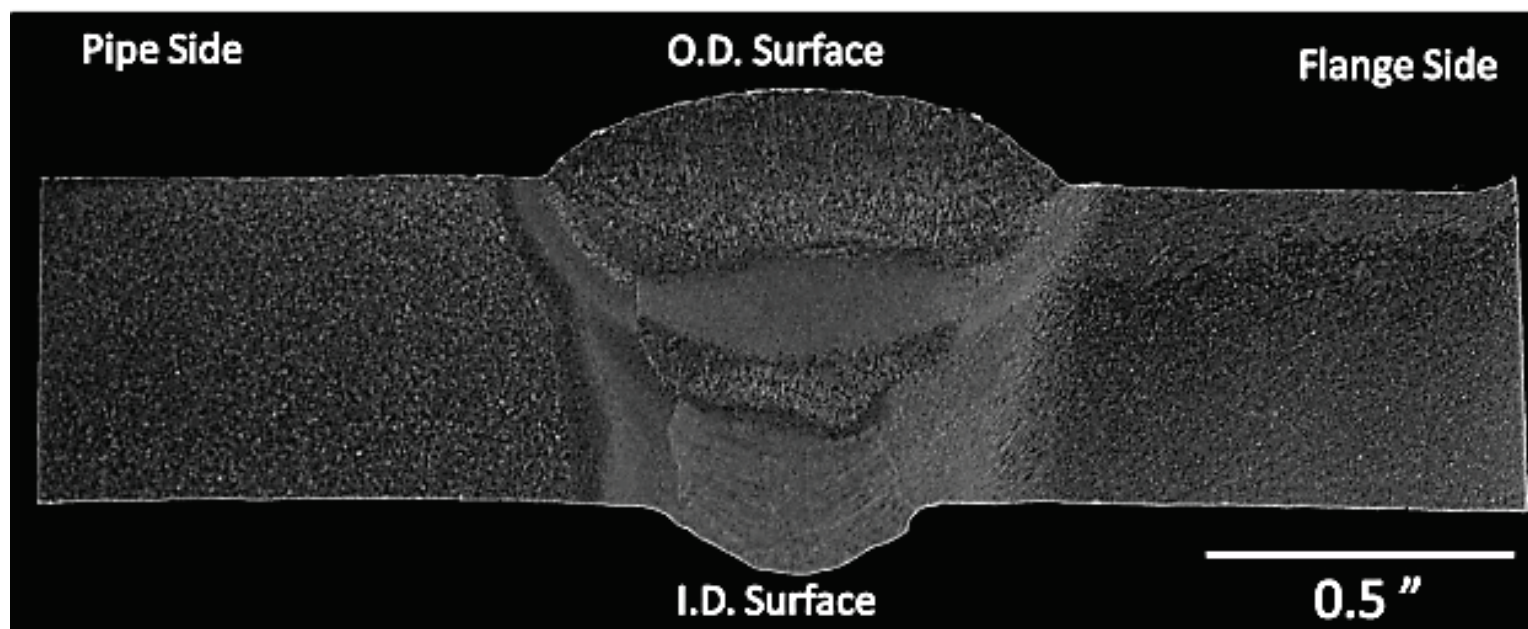


Figure 41. Photomacrograph of Valero Flange-to-Pipe Welded Component #1252134, 2% Nital Etch. No Evidence of Decarburization or Cracking was observed in any Locations in Flange #1252134.

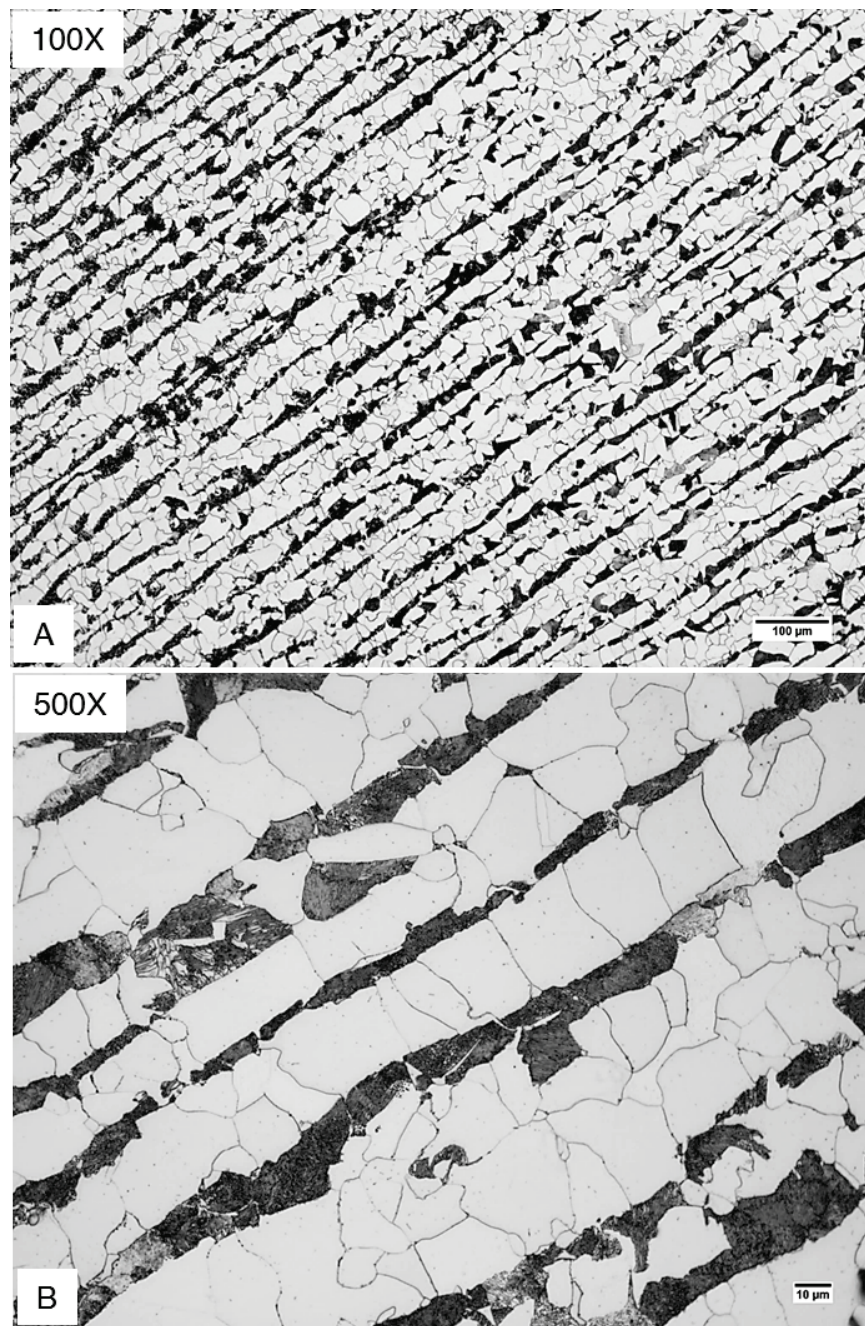


Figure 42. Photomicrographs of the flange base metal just outside of the visible HAZ showing the forging texture in Valero Flange #1252134, 2% Nital Etch, ASTM Grain Size #6.

5.1.2 Hydrogen Measurements on Valero Flange #67

AWS/ISO Diffusible Hydrogen Measurement

AWS/ISO diffusible hydrogen content was measured on 1/8" thick samples containing pipe base metal, flange base metal and weld deposit that were extracted adjacent to the inside diameter surface of Valero Flange #67 (location where cracking was observed during optical examination) and Flange #1252134 (location where cracking not observed during optical examination). The result however showed the presence of less than 1 ppm of AWS diffusible hydrogen in both Valero components. Detailed test results from the AWS diffusible hydrogen tests in Valero flange-to-pipe welded components #67 and #1252134 are shown in Table 4.

Methane Derived From Measured Hydrogen

Hydrogen content measured from methane dissociation for Valero Flange #67 and Flange #1252134 using same samples upon completion of AWS/ISO diffusible hydrogen tests. The results showed the presence of 1.1 ppm and 1.15 ppm of hydrogen on Flange #67 and Flange #1252134, respectively. The methane measurement was performed by heating the encapsulated sample at 700°C and dissociating methane to hydrogen. The measured hydrogen was used to back

calculate the methane levels. Note: If any trapped hydrogen was present in these samples, then that will also be released at 700°C to be combined with any hydrogen dissociated from methane and this will be included in methane measurement results. A virgin steel sample with no prior hydrogen exposure may contain 1-2 ppm of hydrogen (trapped or diffusible). No methane was detected at the cracked region in IOR #1110-2. Eight ppm of methane is generally considered a threshold amount for the incubation of HTHA damage in steels^{39, 50}. Thus, the methane content present in Valero Flanges #67 and #1252134 is lower than the methane content for HTHA incubation period. Detailed test results of the hydrogen measurements after methane dissociation are shown in Table 4.

5.1.3 Charpy Impact Toughness on Valero Flanges #67 and #1252134

Exploratory Charpy impact toughness tests were performed at room temperature (74°F) for the Valero Flanges #67 and #1252134 to compare the toughness level between the cracked and un-cracked component. The notches in the Charpy specimens were placed just outside of the visible HAZ for both flange and pipe base metals. The absorbed energy of the Charpy bar notched in the flange base metal was 27 ft-lbf for Valero Flange #67 and the fracture surface

exhibited a “rock-candy” appearance. However, the Flange #67 pipe base metal exhibited superior ductility/toughness with absorbed energy greater than 125 ft-lbf. Figure 43 show macrographs of broken Charpy bars extracted from (A) flange and (B) pipe base metal from Flange #67. Figure 43C shows a SEM fractograph Charpy impact specimen from the flange base metal at 500X. The fracture surface shows 100% transgranular cleavage fracture (see Figure 43C). The absorbed energies of the flange and pipe base metals for flange-to-pipe welded component #1252134 were 31 ft-lbf and >125 ft-lbf, respectively. Figure 44 shows fractographs of the Charpy bars extracted from the (A) flange and B) pipe base metals.

The impact toughness results between the cracked Flange #67 and un-cracked Flange #1252134 for both flange and pipe sides are comparable. Charpy impact toughness results for both Valero components #67 and #1252134 are summarized in Table 5.

Table 4. Measured Hydrogen Content (ppm) by AWS Diffusible Method and Methane Determination from Hydrogen Measurements using a Methane Dissociation on Valero Energy Flange-to-Pipe Welded Components #67 and #1252134.

Sample ID	AWS Diffusible Hydrogen at 45°C/72hrs (ppm)	Hydrogen Content Measured during Methane Dissociation (ppm)	Remarks
Valero Energy Flange-to-Pipe Welded Component #67	< 1 ppm hydrogen	1.1 ppm hydrogen	Methane Level Below the Traditional HTHA Incubation Limit
Valero Energy Flange-to-Pipe Welded Component #1252134	< 1 ppm hydrogen	1.15 ppm hydrogen	

Methane Dissociation Reaction: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ at 700°C/72hrs. Methane determination was performed by measuring the dissociated hydrogen and back calculating the methane content (4:1 ratio).

Note: The hydrogen content measured by the methane dissociation reaction comply with optical and SEM examinations for this component. (No Methane Present at the Cracked Location)

The hydrogen content measured was 1.04 ppm. A virgin steel sample with no prior hydrogen exposure may contain 1-2 ppm of hydrogen (trapped or diffusible).

Table 5. Room Temperature (74°F) Charpy Impact Toughness Results for Samples Extracted from the Components Received from Valero Energy (Flange-to-Pipe Welded Components #67 and #1252134).

Notch Location	Valero Energy Flange-to-Pipe Welded Component #67	Valero Energy Flange-to-Pipe Welded Component #1252134
Flange Base Metal	27 ft-lbf ^(a)	31 ft-lbf ^(a)
Pipe Base Metal	> 125 ft-lbf ^(b)	> 125 ft-lbf ^(b)

(a) Fracture surface of the Charpy Specimens Exhibited Rock Candy Appearance with Intergranular Separation Morphology.

(b) Charpy Specimens did not break and absorbed more than 125 ft-lbf of Energy.

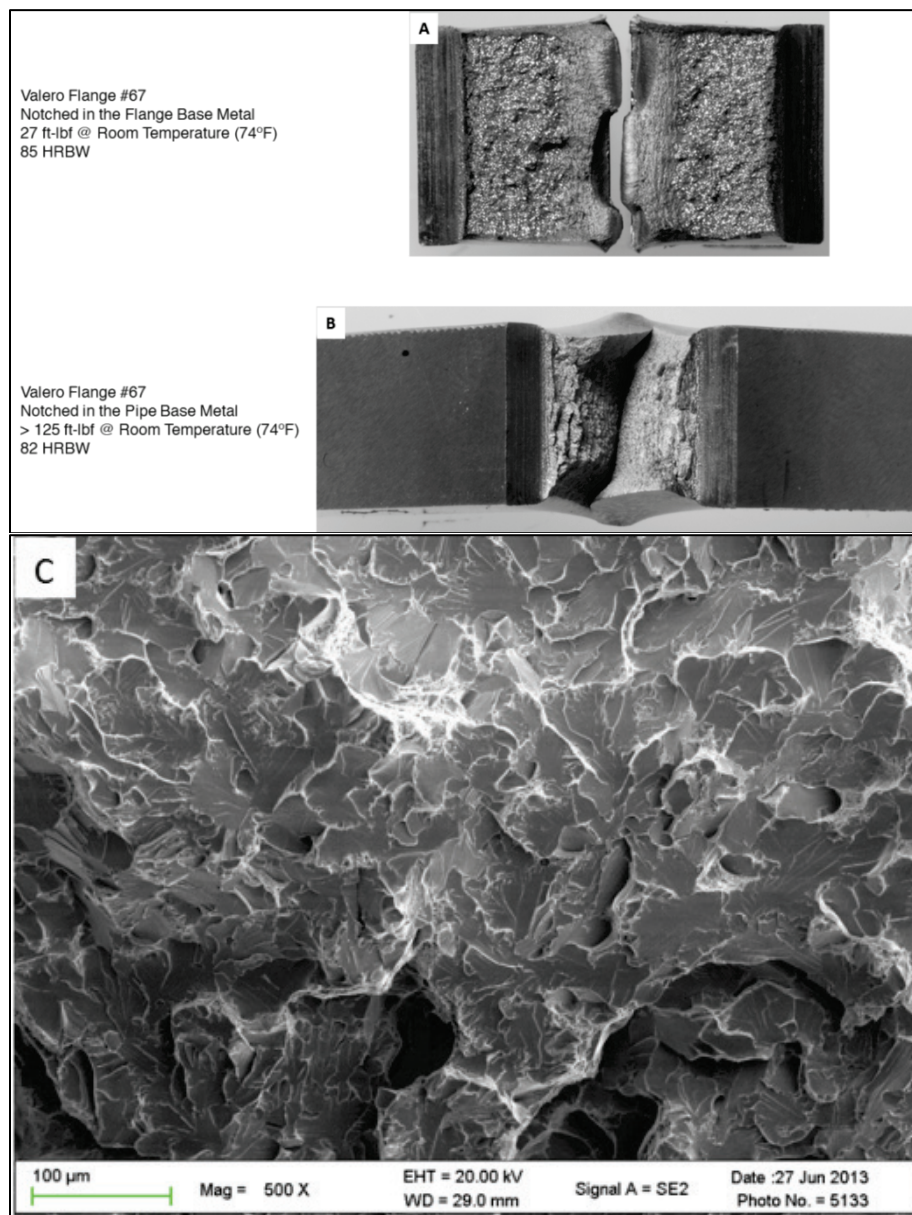


Figure 43. Fractographs of Charpy Impact Specimens Tested at Room Temperature (74°F) for Valero Flange #67, (A) Notched in the Flange Base Metal (27 ft-lbf), (B) Notched in the Pipe Base Metal (> 125 ft-lbf) and C) SEM Fractograph of Flange Base Metal from Figure 43A, 500X.

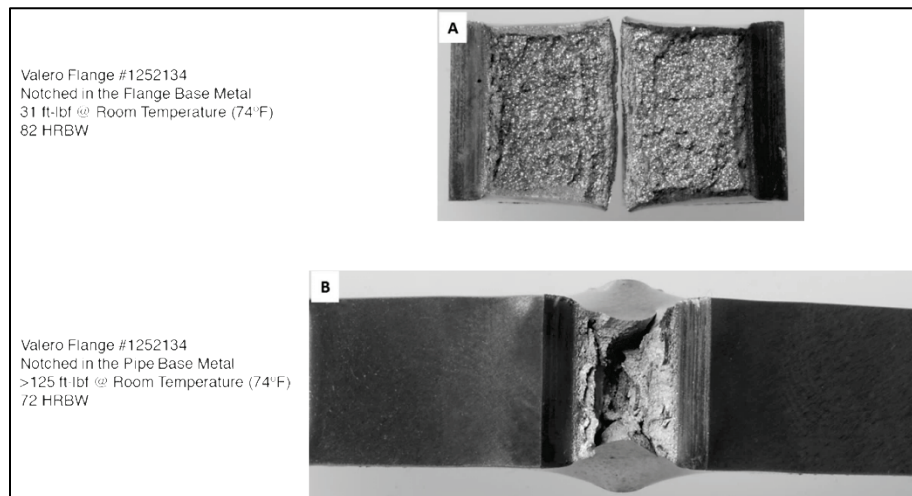


Figure 44. Fractographs of Charpy Impact Specimens Tested at Room Temperature (74°F) for Valero Flange #1252134, (A) Notched in the Flange Base Metal (31 ft-lbf) and (B) Notched in the Pipe Base Metal (>125 ft-lbf).

5.1.4 “Cryo-Cracking” and SEM Examination on Valero Flange #67

Figure 45 shows the SEM fractographs of a “Cryo-Cracked” specimen extracted from the 270° location in Valero Flange #67, (see Figure 26) illustrating the transition between the tip of the pre-existing crack and the “Cryo-Cracked” region. The pre-existing crack surface shows intergranular separation, which is partially masked by oxidation from service exposure. The “Cryo-Cracked” region exhibited clean transgranular cleavage fracture morphology. No evidence of methane bubble was observed in both pre-existing crack surface and in the “Cryo-Cracked” region. No evidence of striation or beach marks, which would be recognized as having come from fatigue propagation, was found.

Energy Dispersive Spectroscopy (EDS) analysis in the pre-existing cracked area (highlighted by green boxes) in Figure 46A and Figure 46C are shown in Figure 46B and Figure 46D, respectively. The EDS analysis shows the presence of oxygen (8 wt. %) in the pre-existing crack surface compared to the surface generated from the “Cryo-Cracking” which did not detect any oxygen. The pre-existing cracked surface exhibited intergranular separation, which was masked by partial oxidation from the service-exposure as shown by fractographs in Figure 47, (A) 20,000X and (B) 40,000X. Thus, the cracking mechanism in Valero

Flange #67 is not related to traditional HTHA (involving decarburization, residual methane content, and intergranular fissuring).

Figure 48 shows an EDS spectrum obtained from the pre-existing cracked region adjacent to the exposed surface (inside diameter surface) of Flange #67, showing the presence of chlorine (0.31 wt. %) along with iron, carbon, and oxygen. The EDS spectrum of the pre-existing cracked surface immediately below the crack tip is shown in Figure 49. Sulfur and chlorine were not detected in the region immediately below the crack tip and in the “Cryo-Cracked” region (overload).

5.1.5 Energy Dispersive Spectroscopy (EDS) on Valero Scale

Fragments

Scaling was observed on the inside diameter surface (exposed surface) of both Valero flange-to-pipe welded components #67 and #1252134. EDS analysis was performed on the scale fragments removed from flange-to-pipe welded components #67 and #1252134. EDS analysis of scale fragments removed from Valero Flange #67 (cracked) showed the presence of 17 wt. % sulfur, however did not show any evidence of manganese. EDS analysis of the scale fragments

removed from flange-to-pipe welded component #1252134 (not cracked) showed a composition similar to the scale fragments from flange-to-pipe welded component #67 (see Figure 50).

5.1.6 Hardness Assessments of Valero Flanges #67 & #1252134

The hardnesses of the pipe base metal, flange base metal, and the weld deposit for flange-to-pipe welded component #67 are 82 HRBW, 85 HRBW, and 84 HRBW, respectively. The hardnesses of flange-to-pipe welded component #1252134 are 72 HRBW, 87 HRBW, and 83 HRBW, for the pipe and flange base metal, and the weld deposit, respectively. The hardness of the pipe base metal for flange-to-pipe welded component #1252134 (un-cracked) is slightly lower at 72 HRBW. The measured hardnesses were used to estimate the tensile strength (ksi) from the appropriate tables in ASTM E370 ⁸⁵. The strength requirements of ASTM A105 for flange base metal (minimum of 70 ksi) and ASTM A106-Gr.B for pipe base metal (minimum of 60 ksi) were met by hardness to strength conversion ^{86, 87}. Table 8 shows the hardness and tensile strength results for Valero flange-to-pipe welded components #67 and #1252134.

A Vickers micro-hardness traverse (1000 gf. load) was performed across the weld and HAZ on cracked flange-to-pipe welded component #67 (from pipe

base metal to flange base metal) as shown in Figure 32. The hardness traverse did not show any hardening or softening immediately adjacent to the crack location in the flange base metal just outside of the visible HAZ. The traverses are similar and reflect the starting hardnesses of flange and pipe material.

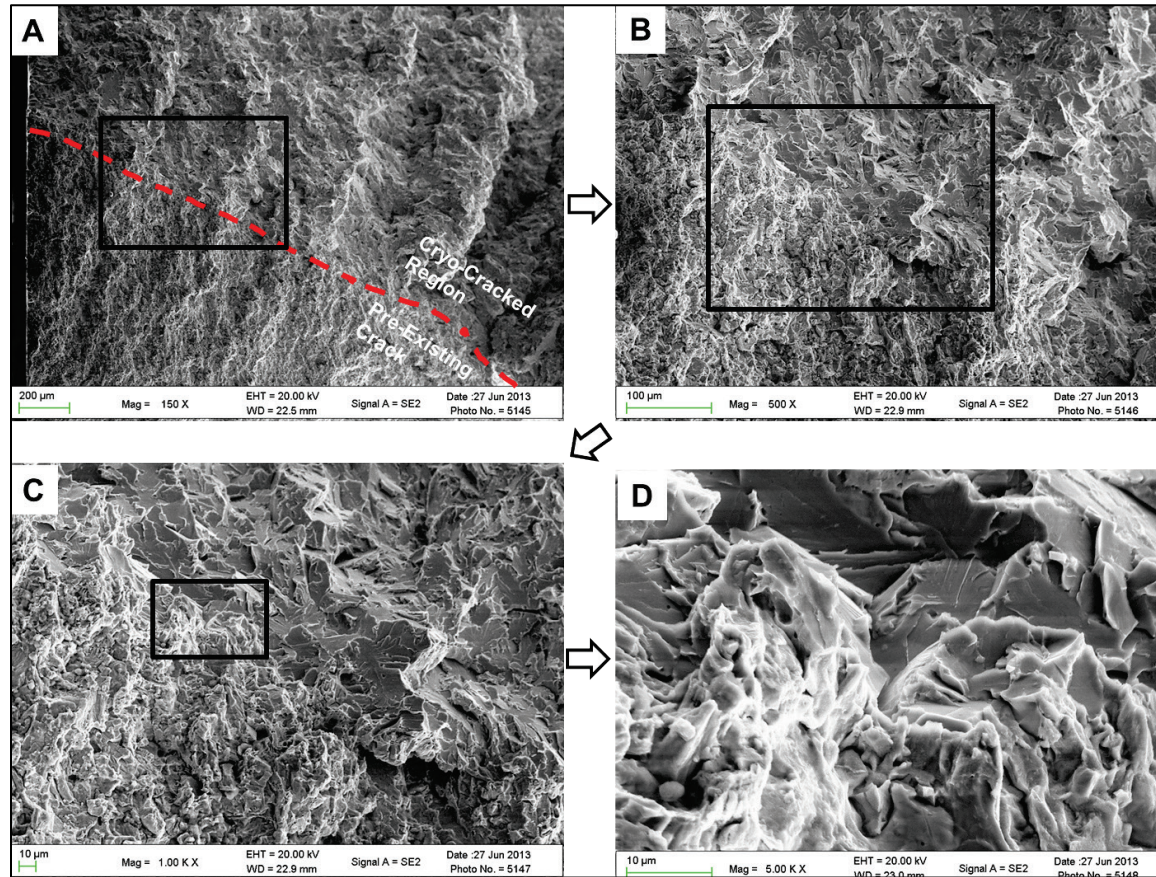


Figure 45. SEM Fractographs of a "Cryo-Cracked" Sample Extracted from Valero Flange #67 showing Partial Oxidation in the Pre-Existing Cracked Surface and Transgranular in the "Cryo-Cracked" Surface.

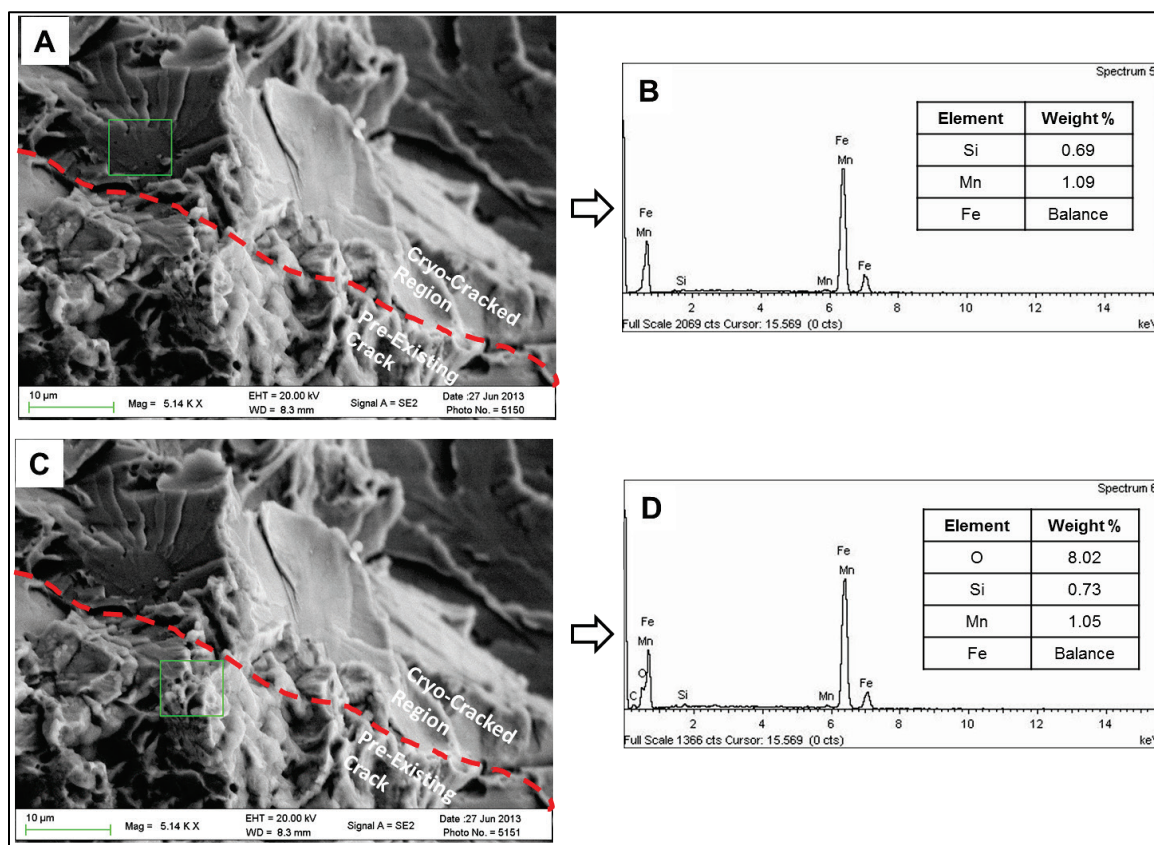


Figure 46. SEM Fractographs of a “Cryo-Cracked” Sample Extracted from Valero Flange #67.
Two Green Boxes in SEM Fractographs A and C correspond to EDS Spectrums
Locations in B and D.

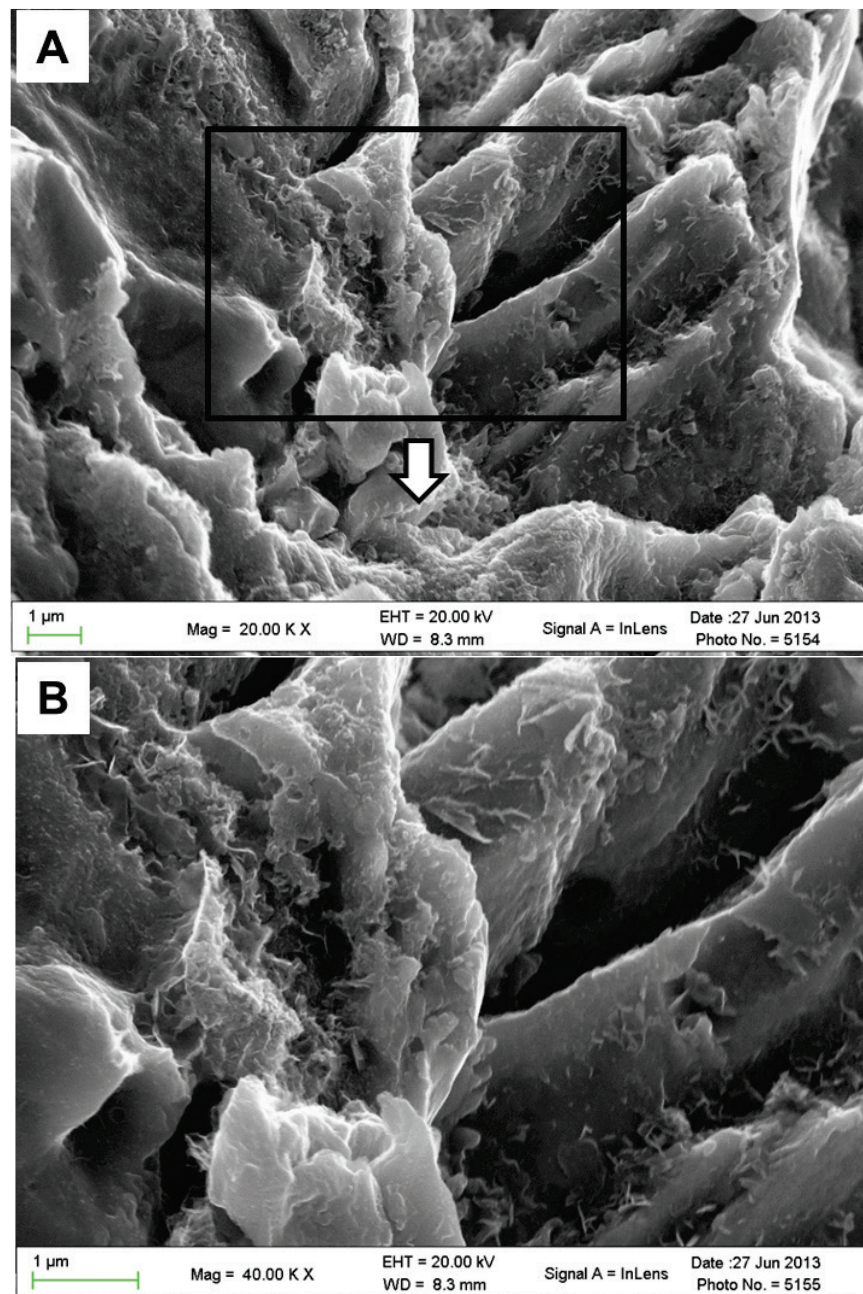


Figure 47. SEM Fractographs of Valero Flange #67 in the Pre-Existing Cracked Region shows Intergranular Cracking Morphology Masked by Partial Oxidation.

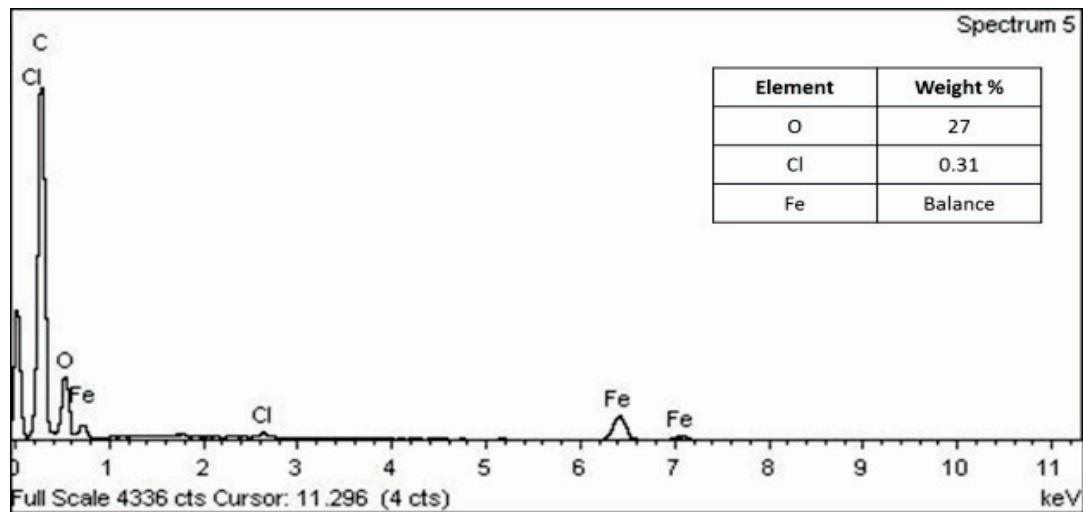


Figure 48. EDS Analysis of the Pre-Existing Cracked Surface at a Location adjacent to the Inside Diameter Surface in Valero Flange #67.

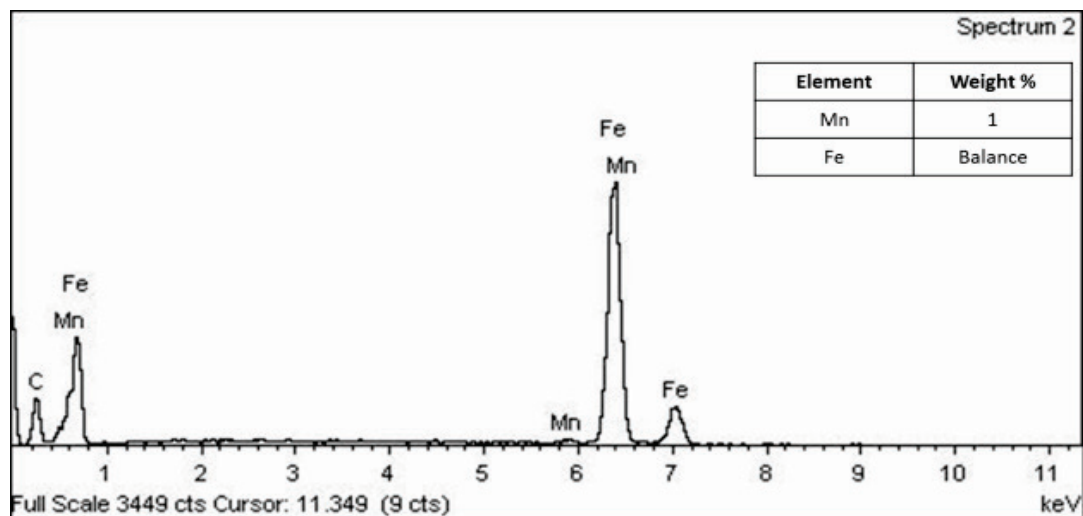


Figure 49. EDS Analysis of the Pre-Existing Cracked Surface at a Location Immediately below the Crack tip in Valero Flange #67. The Spectrum does not show the Presence of the Chlorine as Compared to the Analysis at the Location Adjacent to the Inside Diameter Surface (Figure 48).

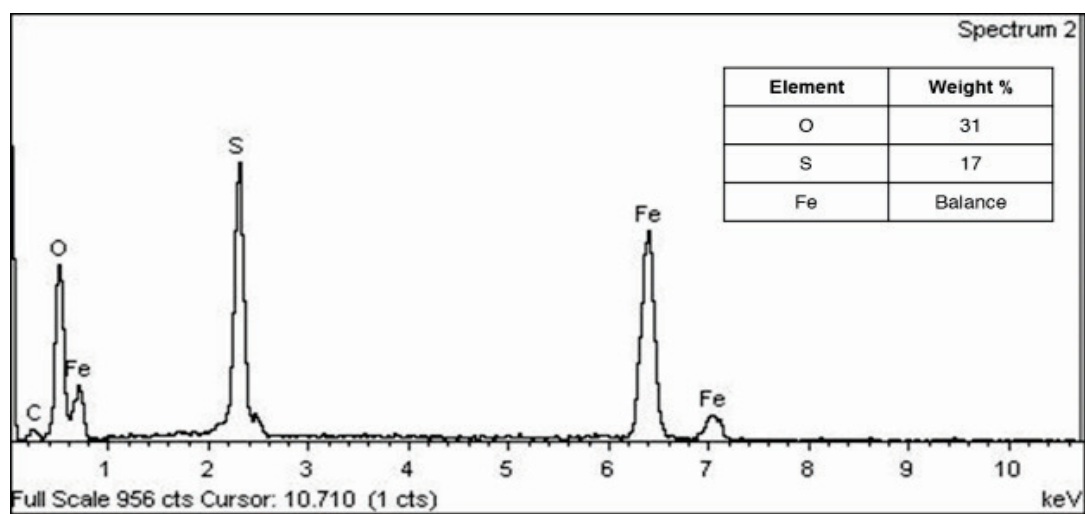


Figure 50. EDS Analysis of the Scale Removed from the Exposed Surface (Inside Diameter Surface) of Valero Flange #67.

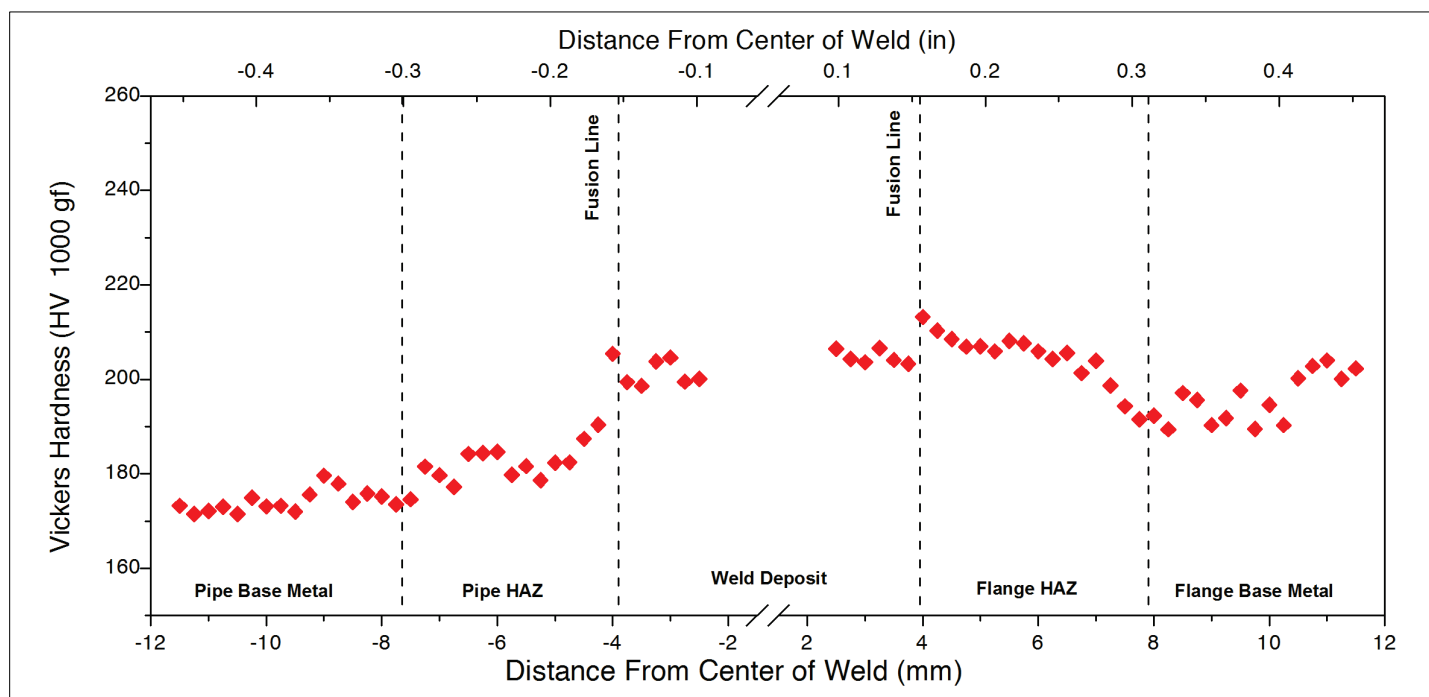


Figure 51. Vickers Micro-hardness Traverse on the Flange-to-Pipe Welded Component #67 across the Flange and Pipe HAZs using 1000 gf load. The Traverses are Similar and Reflect the Starting Hardnesses of Flange and Pipe Material. The Traverse shows no Evidence of Softening or Hardening Behavior just outside of the Flange HAZ (where cracking was observed).

5.2 Irving Oil Refinery (IOR)

5.2.1 Metallography on IOR Component #1110-2

Samples for metallography were extracted from Irving Oil Refinery (IOR) flange-to-pipe welded component #1110-2. Figure 52 shows a photomacrograph of the sample #1110-2-1 extracted from IOR Flange #1110-2. The macrograph shows that the crack (shown by white arrows) is located in the flange base metal just outside of the visible HAZ and extends approximately three-quarters of the flange wall-thickness. The crack is approximately 1/4" (6.4 mm) long in the circumferential direction and 3/8" (9.5 mm) deep from the inside diameter surface in the section extracted from IOR Flange #1110-2. Thus, the section of IOR Flange #1110-2 received at UTK is only a partial crack remaining after the component was evaluated by Wayland Engineering, who observed 15/16" (23.6 mm) long through wall cracking ⁸⁰. The crack initiated at the inside diameter surface (exposed surface) and propagated parallel to the weld fusion line just outside of the visible HAZ in the flange base metal. Figure 53 shows photomicrographs of the cracking in the flange base metal just outside of the visible HAZ in IOR #1110-2. The crack appears to depict both intergranular and transgranular cracking morphology. Internal decarburization was not observed

in the regions adjacent to the crack or at the inside diameter surface (hydrogen exposed) of the IOR Flange #1110-2. Cracking in IOR flange-to-pipe welded component #1110-2 followed the flange forging texture.

Figure 54 and Figure 55 shows the microstructure of the flange and pipe base metals, respectively at (A) 100X and (B) 500X showing a typical forging and rolling texture in IOR Flange #1110-2. The microstructures of the flange and pipe base metal are composed of ferrite and pearlite, which is considered typical for ASTM A105 for the flange material and ASTM A106-Gr.B for the pipe material. The ASTM grain size for the flange and the pipe base metal is approximately 5-6, which is normal for these materials.

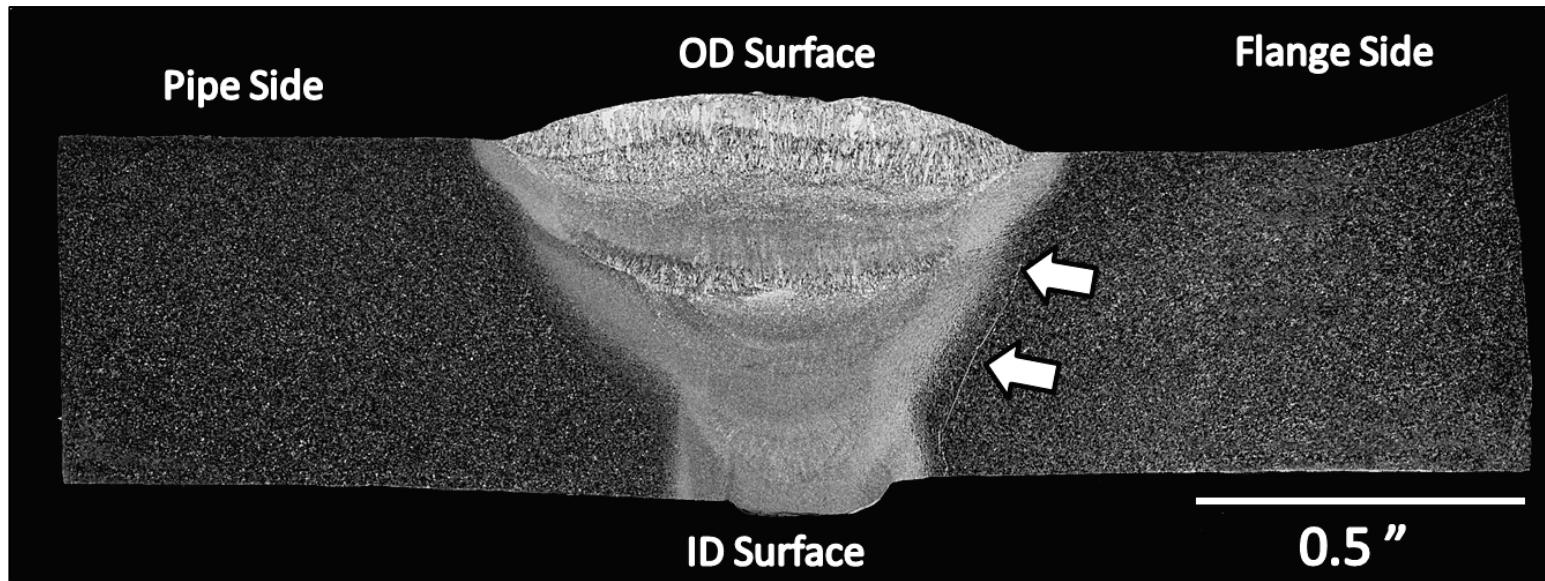


Figure 52. Photomacrograph of the Irving Oil Refinery Flange-to-Pipe Welded Component #1110-2 (section #1110-2-1), White Arrows showing the Crack Location just Outside the Visible HAZ in the Flange Base Metal, 2% Nital Etch. Crack initiated at the Flange ID surface and Propagated $\frac{3}{4}$ of the Flange Wall.

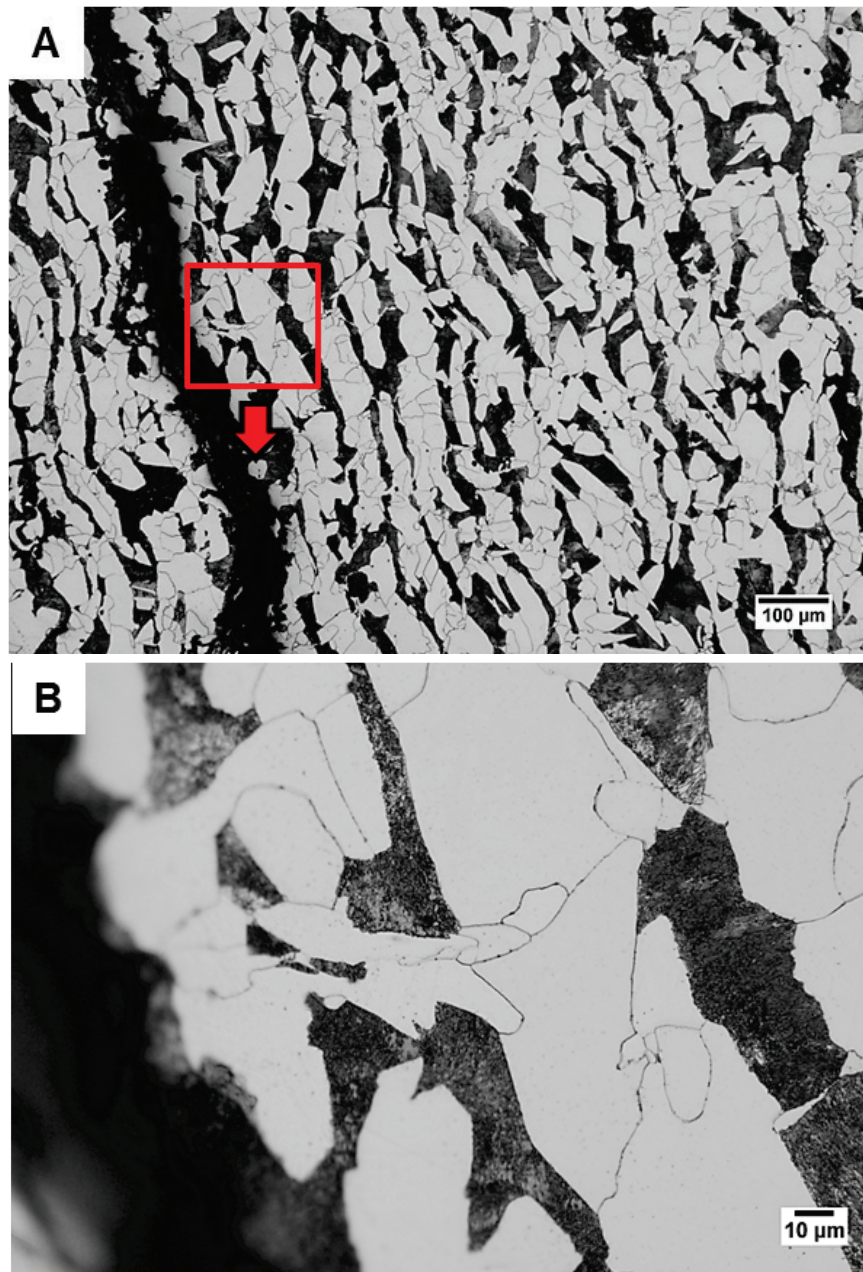


Figure 53. Photomicrographs of the IOR Flange #1110-2 adjacent to ID Surface. Cracking was observed just outside the Visible HAZ in the Flange Base Metal, which Initiated at the Inside Surface and Propagated towards the Outside Surface Parallel to the Weld Fusion Line (~ 5 mm away from weld fusion line), 2% Nital Etch. Decarburization was not observed at any Locations

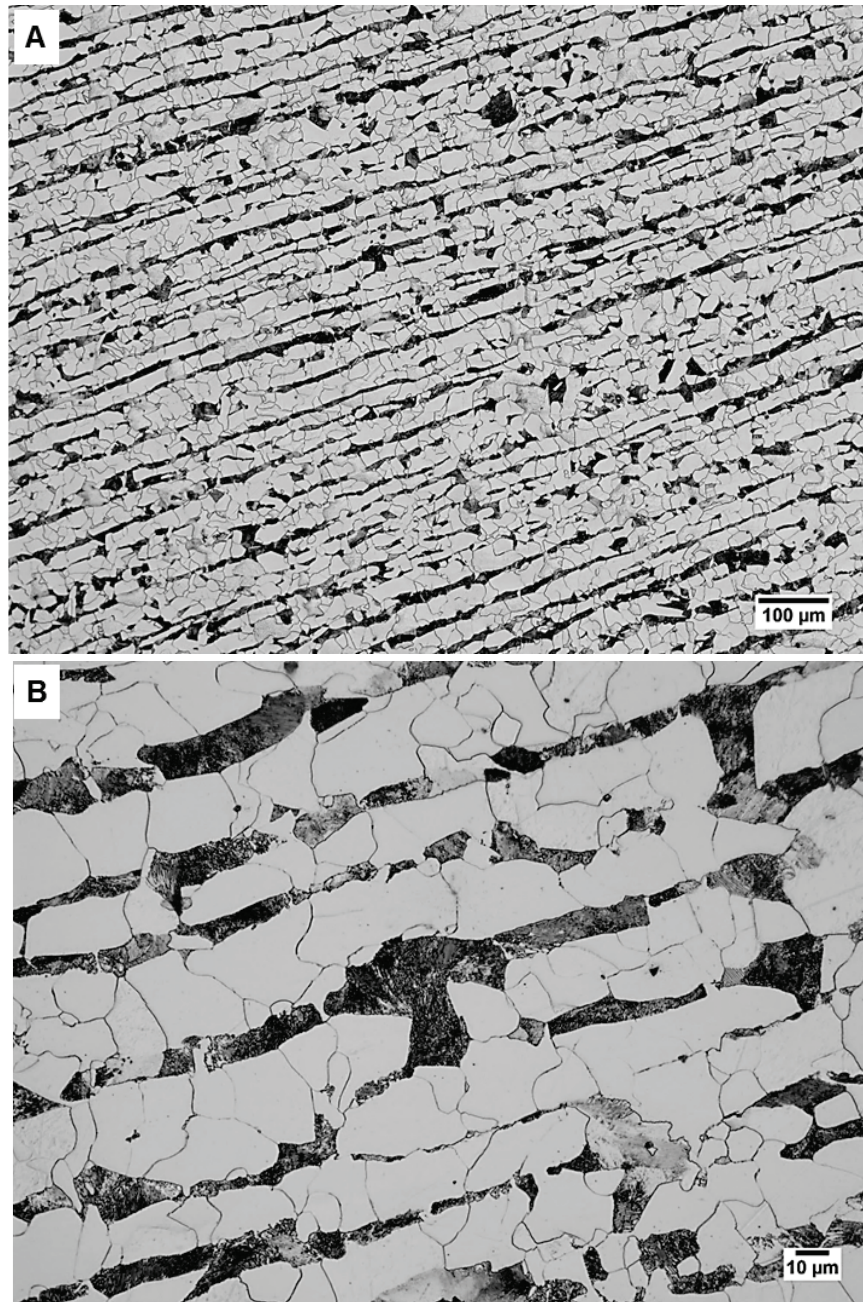


Figure 54. Photomicrographs of the Flange Base Metal showing a Typical Forging Texture in IOR Flange #1110-2, (A) 100X and (B) 500X, 2% Nital Etch. Microstructure consists of Ferrite and Pearlite, ASTM Grain Size #6.

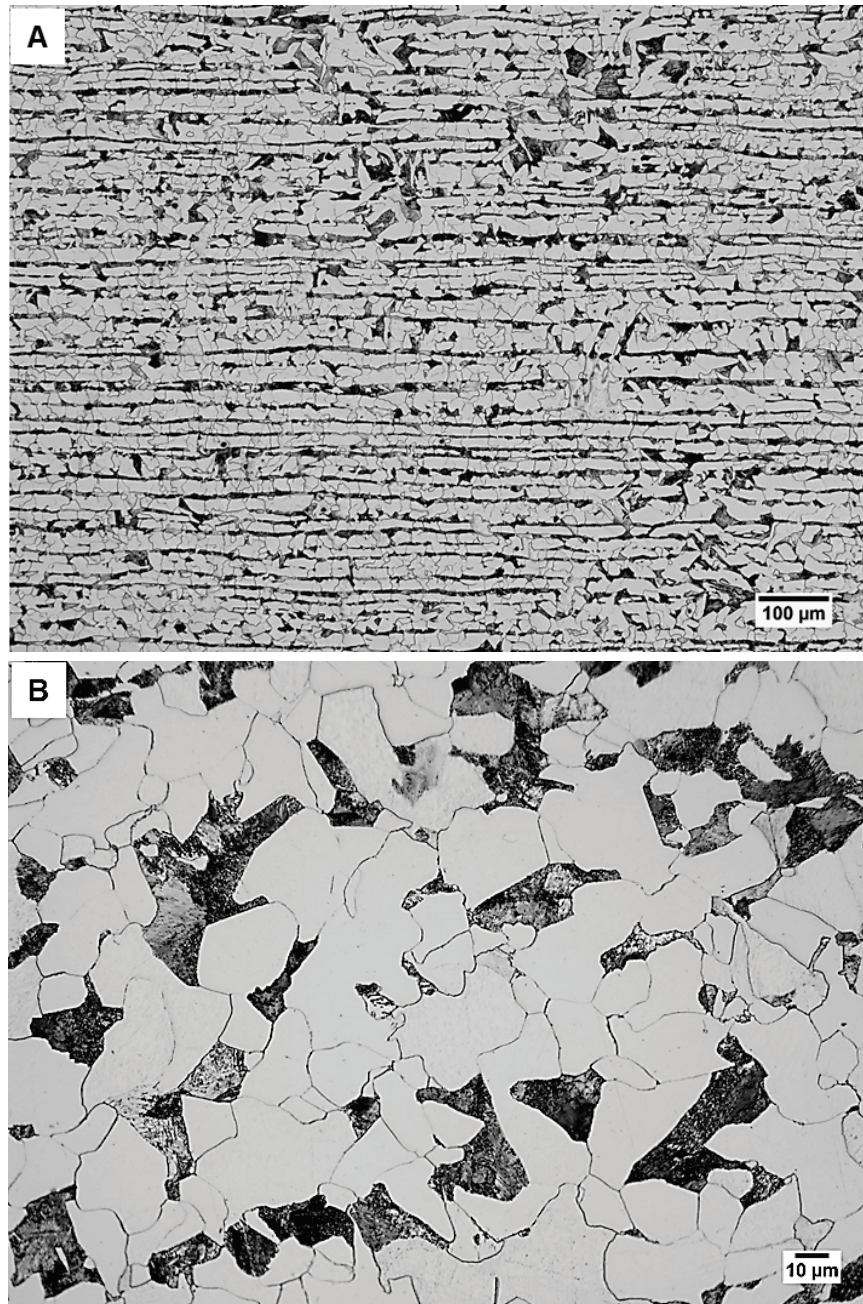


Figure 55. Photomicrographs of the Pipe Base Metal showing the Plate Rolling Texture in the Longitudinal Direction in IOR Flange #1110-2, (A) 100X and (B) 500X, 2% Nital Etch. Microstructure consists of Ferrite and Pearlite, ASTM Grain Size #6.

5.2.2 Hydrogen Measurements on IOR Flange #1110-2

AWS Diffusible Hydrogen Measurement

AWS diffusible hydrogen content was measured on 1/8" thick samples containing pipe base metal, flange base metal and weld deposit which were extracted adjacent to the inside diameter surface from IOR Flange #1110-2 (adjacent to the sample showing cracking). The result showed the presence of less than 1 ppm of AWS diffusible hydrogen in IOR Flange #1110-2. Detailed test results from the AWS diffusible hydrogen tests in IOR Flange #1110-2 are shown in Table 6.

Methane Derived From Measured Hydrogen

Hydrogen content derived from methane was measured on the same sample upon completion of AWS diffusible hydrogen test, and the results showed the presence of 1.04 ppm of hydrogen in IOR Flange #1110-2. The methane measurement was performed by heating the encapsulated sample at 700°C and dissociating methane to hydrogen. The measured hydrogen was used to back calculate the methane levels. Note: If any trapped hydrogen was present in these samples, then that will also be released at 700°C to be combined with any hydrogen dissociated from methane and this will be included in methane

measurement results. A virgin steel sample with no prior hydrogen exposure may contain 1-2 ppm of hydrogen (trapped or diffusible). No methane was detected at the cracked region in IOR #1110-2. Some of the earlier work considers eight ppm of methane a threshold amount for the incubation of HTHA damage in steels^{39, 50}. Thus, the cracking observed in IOR #1110-2 was a result of methane formation. Detailed test results for IOR Flange #1110-2 of the hydrogen measurements after methane dissociation are shown in Table 6.

5.2.3 Charpy Impact Toughness on IOR Flange #1110-2

Exploratory Charpy impact toughness tests were performed at room temperature (74°F) on IOR Flange #1110-2. Charpy samples were prepared such that the notch of the specimen is approximately 5 mm away from the fusion line for both flange and pipe base metal samples. The Charpy impact toughness for IOR Flange #1110-2 for both pipe and flange base metal was 18 ft-lbf and 10 ft-lbf, respectively. Figure 56 shows the photomacrographs of the fracture surfaces of the Charpy bars extracted from (A) flange base metal and (B) pipe base metal. Figure 56 shows SEM fractographs at 500X exhibiting transgranular cleavage fracture morphology on Charpy bars extracted from (C) flange base metal, and (D) pipe base metals.

Wayland Engineering performed a three-point bending test on flange base metal extracted from Flange #1110-2 using dynamic loading rates at ambient temperature. Their results show that the fracture surface exhibited a combination of transgranular cleavage and intergranular separation, which contradicts with the results obtained by UTK, which is 100% transgranular cleavage in flange base metal ⁸⁰.

5.2.4 ASME Section IX Bend Test on IOR Flange #1110-2

An ASME Section IX root bend test on IOR flange-to-pipe welded component #1110-2 sample did not show any cracking or evidence of strain aging, and the material was fully ductile in all regions with 20% outer-fiber strain. The photograph of the specimen after the bend test is shown in Figure 57.

Table 6. Measured Hydrogen Content (ppm) by AWS Diffusible Method and Methane Determination from Hydrogen Measurements using a Methane Dissociation on Irving Oil Refinery Flange-to-Pipe Welded Component #1110-2.

Sample ID	AWS Diffusible Hydrogen at 45°C/72hrs (ppm)	Hydrogen Content Measured during Methane Dissociation (ppm)	Remarks
Irving Oil Refinery Flange-to-Pipe Welded Component #1110-2	< 1 ppm hydrogen	1.04 ppm hydrogen	Methane Level Below the Traditional HTHA Incubation Limit

Methane Dissociation Reaction: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ at 700°C/72hrs. Methane determination was performed by measuring the dissociated hydrogen and back calculating the methane content (4:1 ratio).

Note: The hydrogen content measured by the methane dissociation reaction comply with optical and SEM examinations for this component. (No Methane Present at the Cracked Location)

The hydrogen content measured was 1.04 ppm. A virgin steel sample with no prior hydrogen exposure may contain 1-2 ppm of hydrogen (trapped or diffusible).

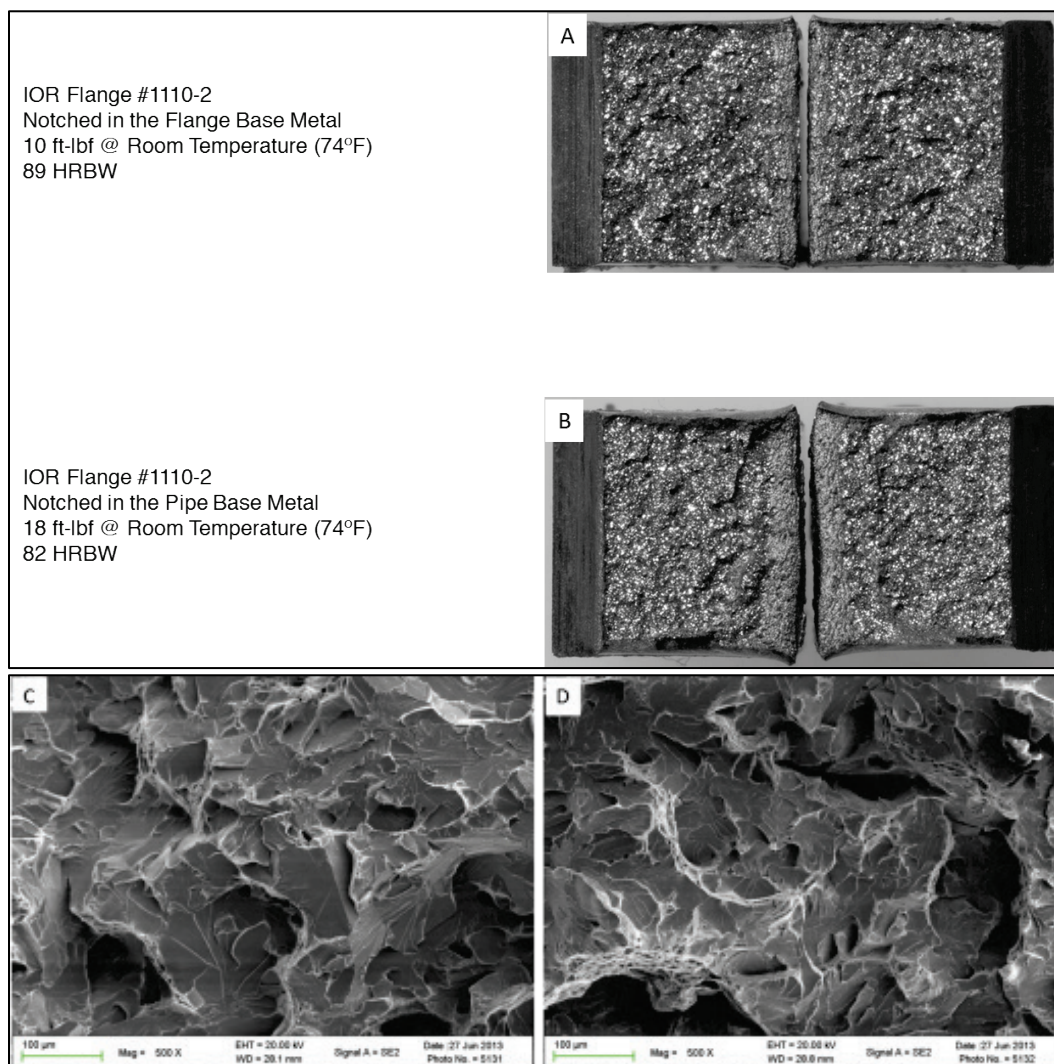


Figure 56. Fractographs of the Charpy Impact Specimens tested at Room Temperature (74°F) for IOR Flange #1110-2, (A) Flange Base Metal (10 ft-lbf), (B) Pipe Base Metal (18 ft-lbf), (C) SEM Fractograph of the Charpy Fracture Surface from Flange Base Metal, 500X and (D) SEM Fractograph of the Charpy Fracture Surface from Pipe Base Metal, 500X.

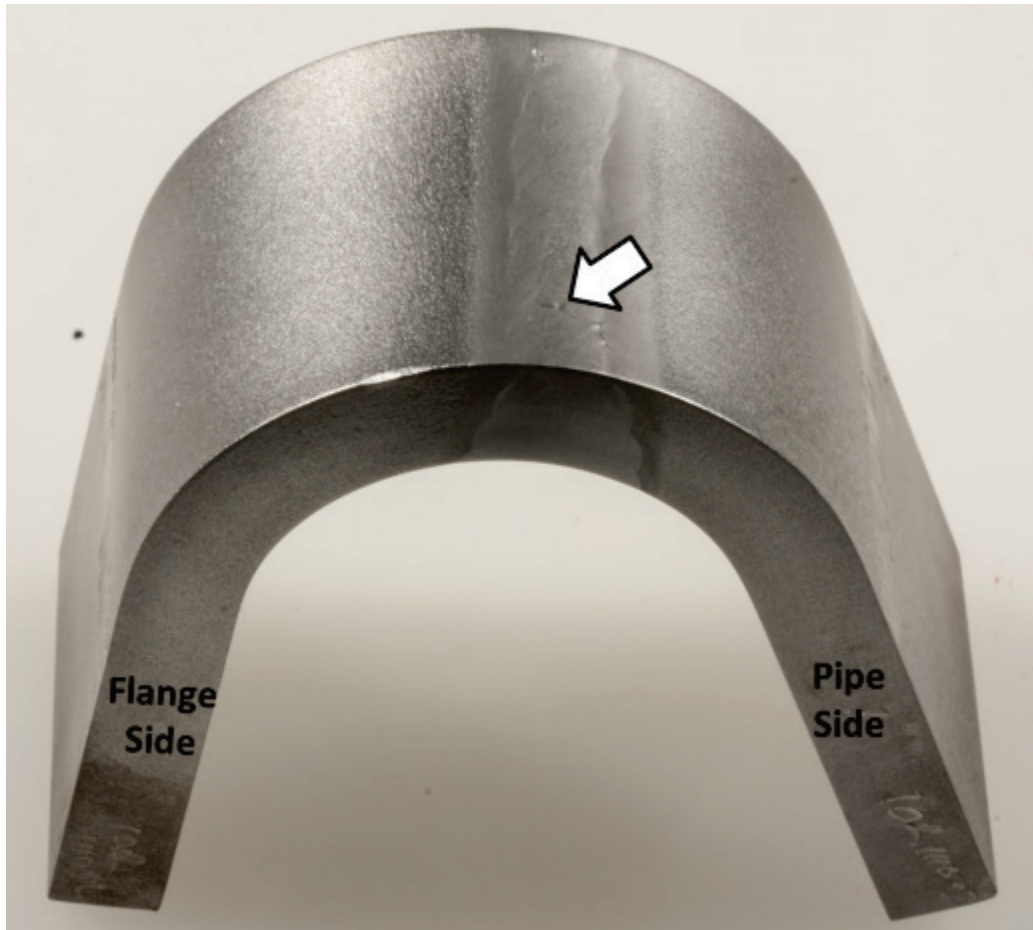


Figure 57. Photograph of ASME IX Bend Specimen extracted from Irving Oil Refinery Flange-to-Pipe Welded Component #1110-2. The Bend Specimen was centered in the Flange Base Metal just outside of the Visible HAZ (~5 mm from the fusion line), and it Exhibited Fully Ductile Behavior with 20% Fiber Strain in all Regions. White Arrow indicates a typical Weld Deposit Slag Inclusion.

5.2.5 “Cryo-Cracking” and SEM Examination on IOR Flange

#1110-2

Figure 58 shows SEM fractographs on the “Cryo-Cracked” sample from IOR flange-to-pipe welded component #1110-2. Figure 58A shows the transition between the pre-existing crack surfaces and the “Cryo-Cracked” region. Higher magnification fractographs of the pre-existing crack surface exhibited an intergranular separation morphology, which was masked by partial oxidation as shown in Figure 58 (B-D). Figure 59 shows SEM fractographs for the “Cryo-Cracked” sample from Flange #1110-2 showing a fractographic appearance with some “lamellar” features (lamellar spacing using SEM ~200 nm) on the cracked surface. The “lamellar” feature is due to the crack propagating through a pearlite colony. Pearlite “lamellar” spacing measured using the polished and etched specimen using image analysis software showed similar results (lamellar spacing using OLM ~250 nm). EDS analysis of the “lamellar” structure showed the presence of oxygen (4%) along with silicon, manganese and iron. The presence of methane bubbles or cavities were not observed in the fracture surface. No evidence of striation or beach marks, which would be recognized as having come from fatigue propagation was found in IOR Flange #1110-2.

EDS analysis of the pre-existing cracked surface adjacent to the inside diameter surface of the IOR Flange #1110-2 showed the presence of sulfur (2 wt.%), but no trace of chlorine was detected compared to the cracked surface in Valero Flange #67 as shown in Figure 60. The presence of oxygen, silicon, and manganese was detected in the “Cryo-Cracked” region (overload region) and in the region immediately below the crack tip. The EDS spectrum of the region immediately below the crack tip in IOR #1110-2 is shown in Figure 61.

5.2.6 Energy Dispersive Spectroscopy (EDS) on IOR Scale

Fragments

Scale fragments 0.019” (0.5 mm) thick were observed in the IOR flange-to-pipe welded component #1110-2. EDS analysis of the scale fragments removed from IOR Flange #1110-2 adjacent to the crack location in the flange base metal showed the presence of 20 wt.% sulfur and 2 wt.% manganese. EDS analysis of IOR Flange #1110-2 is shown in Figure 62.

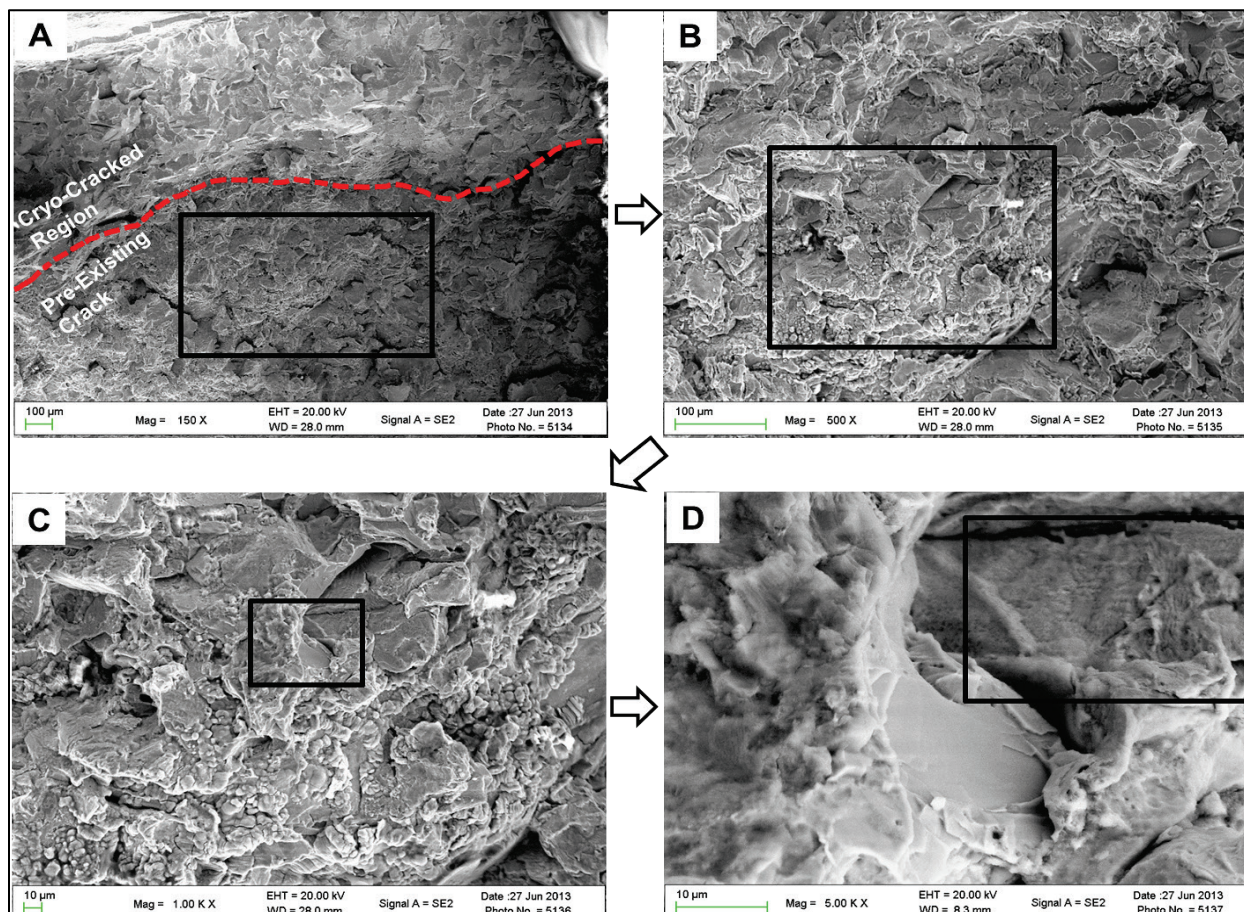


Figure 58. SEM Fractographs of the “Cryo-Cracked” Specimen in IOR Component #1110-2 showing the region immediately below Crack Tip showing Intergranular Morphology with Evidence of Partial Oxidation.

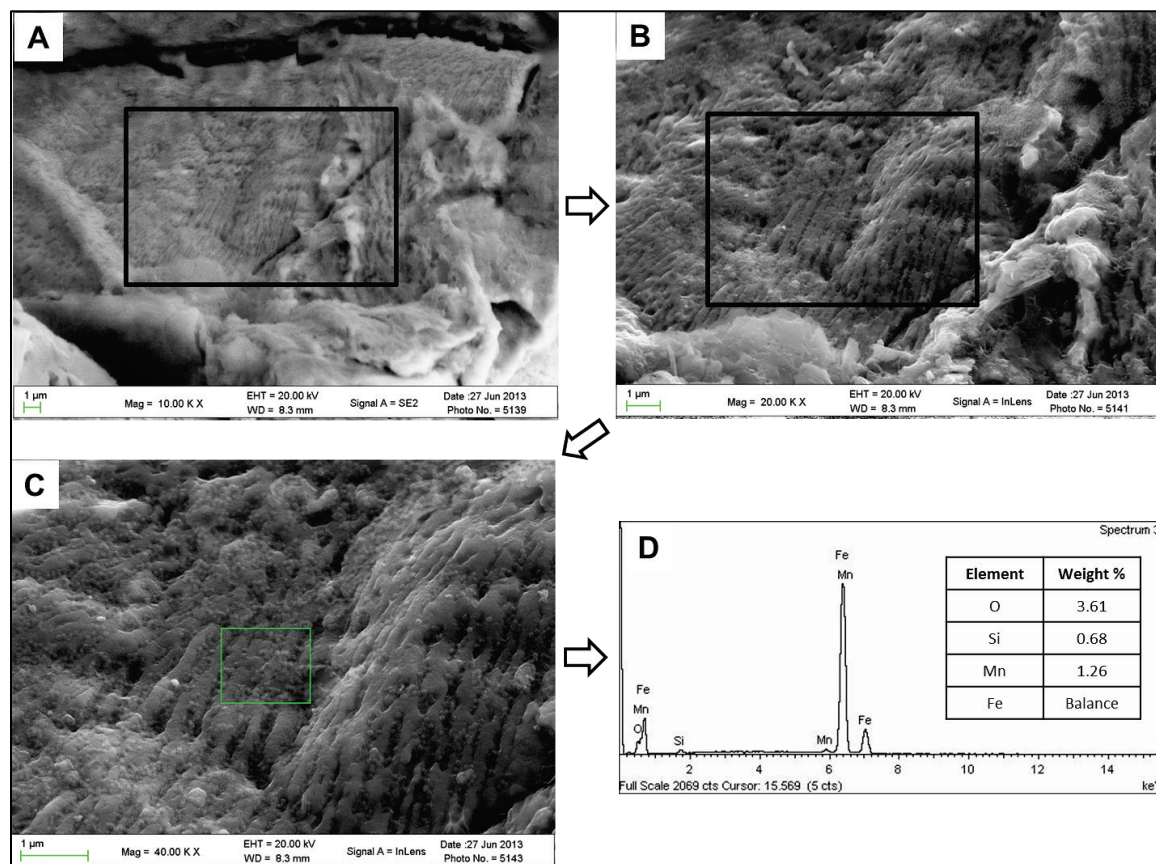


Figure 59. SEM Fractographs of the “Cryo-Cracked” specimen in IOR Flange-to-Pipe Welded Component #1110-2, showing Lamellar Appearance. D) EDS Analysis of the Region inside the Green Box in Figure 59C showing the presence of Oxygen, Manganese, and Silicon. No Evidence of Methane Bubbles or Cavitation was Observed on the Fracture Surface.

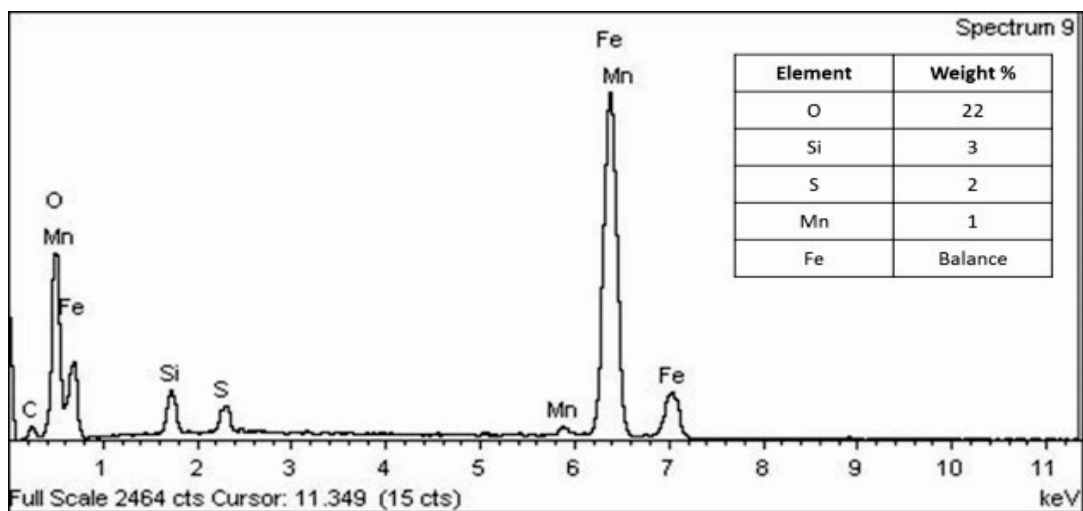


Figure 60. EDS Analysis of the Pre-existing Crack Surface at the Location adjacent to the Inside Diameter Surface in IOR Flange-to-Pipe Welded Component #1110-2. The Analysis showed the presence of 2 wt. % Sulfur and 3 wt. % Silicon.

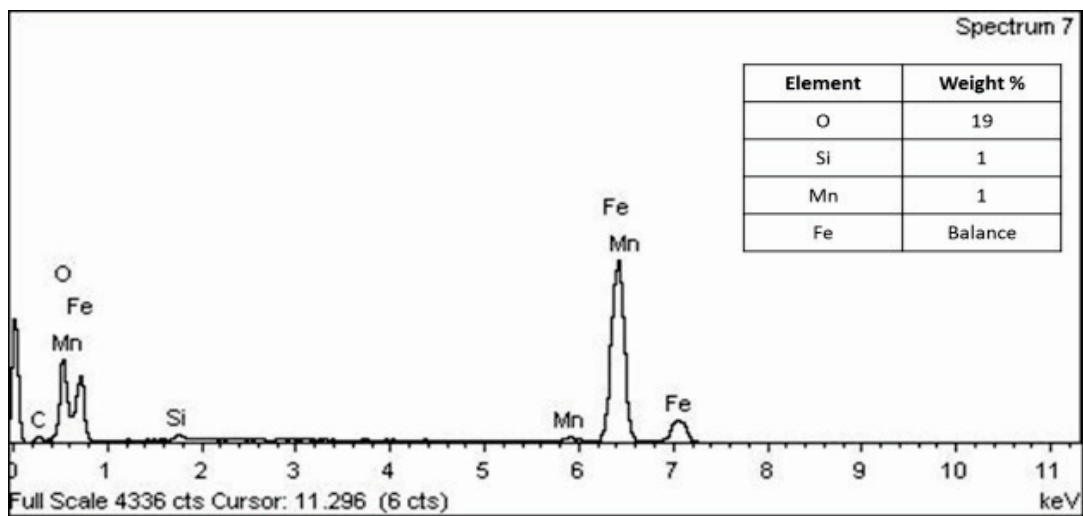


Figure 61. EDS Analysis of the Pre-Existing Crack Surface at the Location immediately below the Crack Tip in IOR Flange-to-Pipe Welded Component #1110-2. No presence of Sulfur was detected compared to the 2 wt. % Sulfur detected at the Location adjacent to the Inside Diameter Surface (Figure 60).

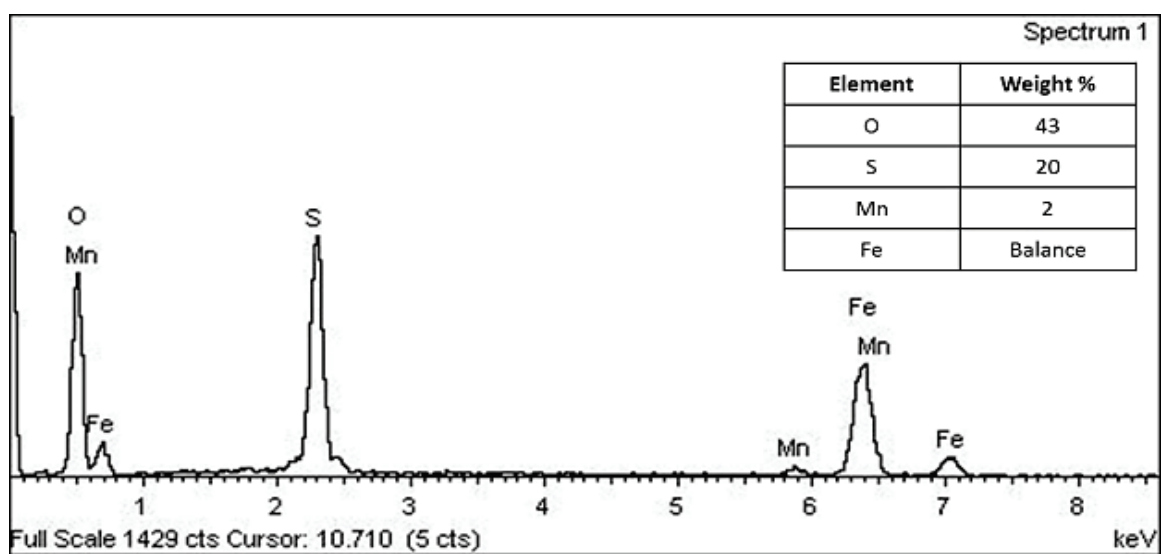


Figure 62. EDS Assessment of the Scale Fragments Removed from the IOR Component #1110-2.

5.2.7 Hardness Assessment of IOR Flange #1110-2

The hardnesses of the pipe base metal, flange base metal, and the weld deposit for IOR Flange #1110-2 are 82 HRBW, 89 HRBW, and 87 HRBW, respectively. The measured hardness were used to estimate the tensile strength (ksi) from the appropriate tables in ASTM E370 ⁸⁵. The strength requirements of ASTM A106-Gr.B for pipe base metal (minimum 60 ksi) and ASTM A105 flange base metal (minimum 60 ksi) were met by conversion ^{86, 87}. Table 9 shows the hardness and tensile strength results for Flange #1110-2.

A Vickers micro-hardness traverse (1000 gf. load) was conducted across the IOR flange-to-pipe welded component #1110-2. The traverse did not show any hardening or softening behavior immediately adjacent to the crack location in the flange base metal just outside the visible HAZ (see Figure 63).

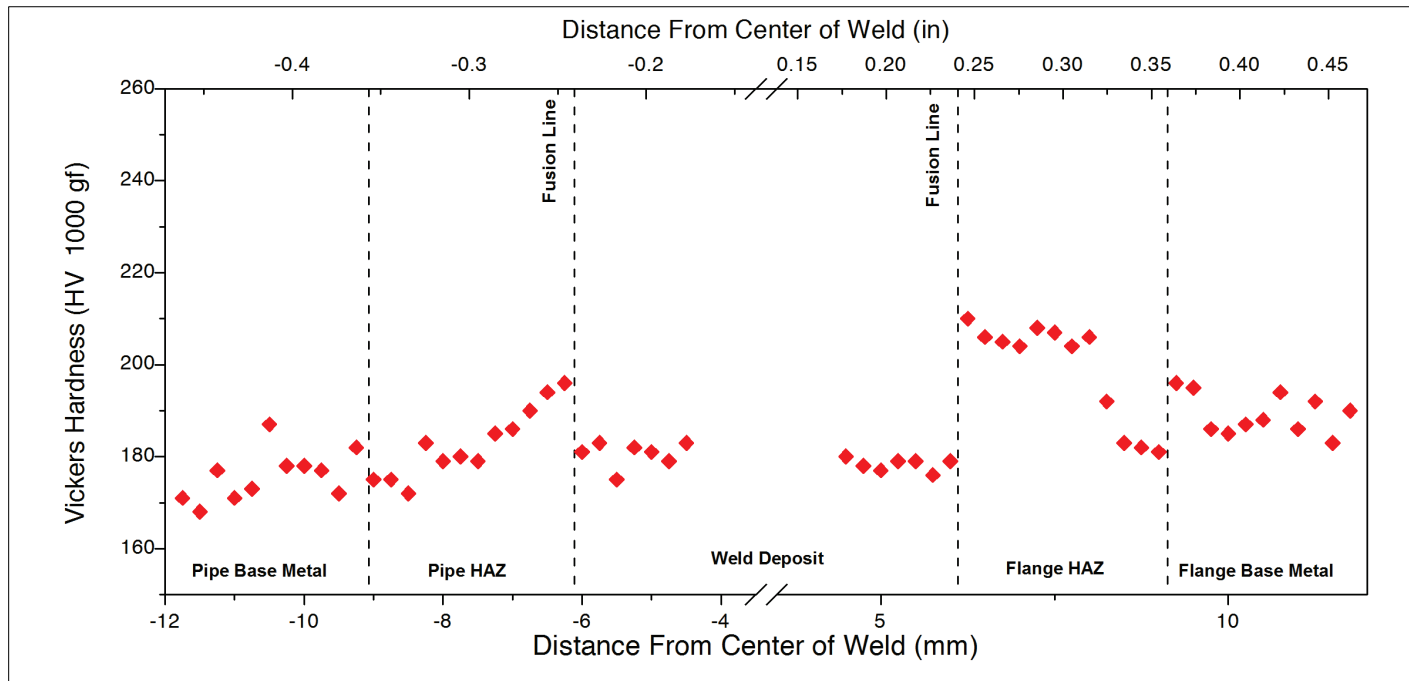


Figure 63. Vickers Micro-hardness Traverse on the IOR Flange-to-Pipe Welded Component #1110-2 across the Flange and Pipe HAZs using 1000 gf load. The Traverses are Similar and Reflect the Starting Hardnesses of Flange and Pipe Material. The Traverse shows no Evidence of Softening or Hardening just outside of the Flange HAZ where cracking was observed using Optical Microscopy.

5.3 Phillips 66 (P66)

Samples for metallography were extracted from the P66 flange-to-pipe welded components #555-S1 and #555-S2. Figure 64 shows a photomacrograph of a sample (#555-S1-1) extracted from flange-to-pipe welded component #555-S1. Microfissures were readily observed in the flange base metal immediately outside of the visible HAZ from the inside diameter surface to half wall-thickness using optical microscopy. Microfissures were observed to a lesser extent (scattered) from the half wall-thickness to the outside diameter surface. The maximum extent of damage was observed adjacent to the inside surface. The approximate location of the damage is shown by the boxed region in the photomacrograph in Figure 64.

Figure 65 shows the photomacrograph of a sample (#555-S2-1) extracted from flange-to-pipe welded component #555-S2. No evidence of decarburization or fissuring was observed in the weld deposit, pipe HAZ, flange HAZ, or in the pipe or flange base metals. The outside surface of the flange-to-pipe welded component #555-S2 had been ground smooth to contour the weld, and the inside surface had been ground flush by P66 prior to the receipt of the component by the University of Tennessee. From the appearance of the inside and outside

surface of flange-to-pipe welded component #555-S2, it appears that the inside and outside surfaces were ground prior to the service installation.

The P66 flange-to-pipe welded components #555-S1 and #555-2 were both operating under the same conditions (time, temperature and hydrogen partial pressure). However, the component #555-S1 showed the presence of microfissures and #555-S2 was free of any fissuring or internal decarburization. The macroscopic examination of both flange-to-pipe weld components show differences in the etching characteristics (see macrographs in Figure 64 and Figure 65), and reflects a potential difference in the use of the welding processes/parameters. The undamaged flange-to-pipe welded component (#555-S2) exhibits smaller size weld beads and has higher number of weld passes (number of passes #11) compared to the damaged component (#555-S1) which exhibit larger size weld beads and fewer number of weld passes (number of passes #9). The use of different heat-input is also evident in the width of two heat-affected zones between #555-S1 (damaged component = 3 mm) and #555-S2 (undamaged component = 2 mm). Information on welding parameters is unavailable for both P66 flange-to-pipe welded components #555-S1 and #555-S2.

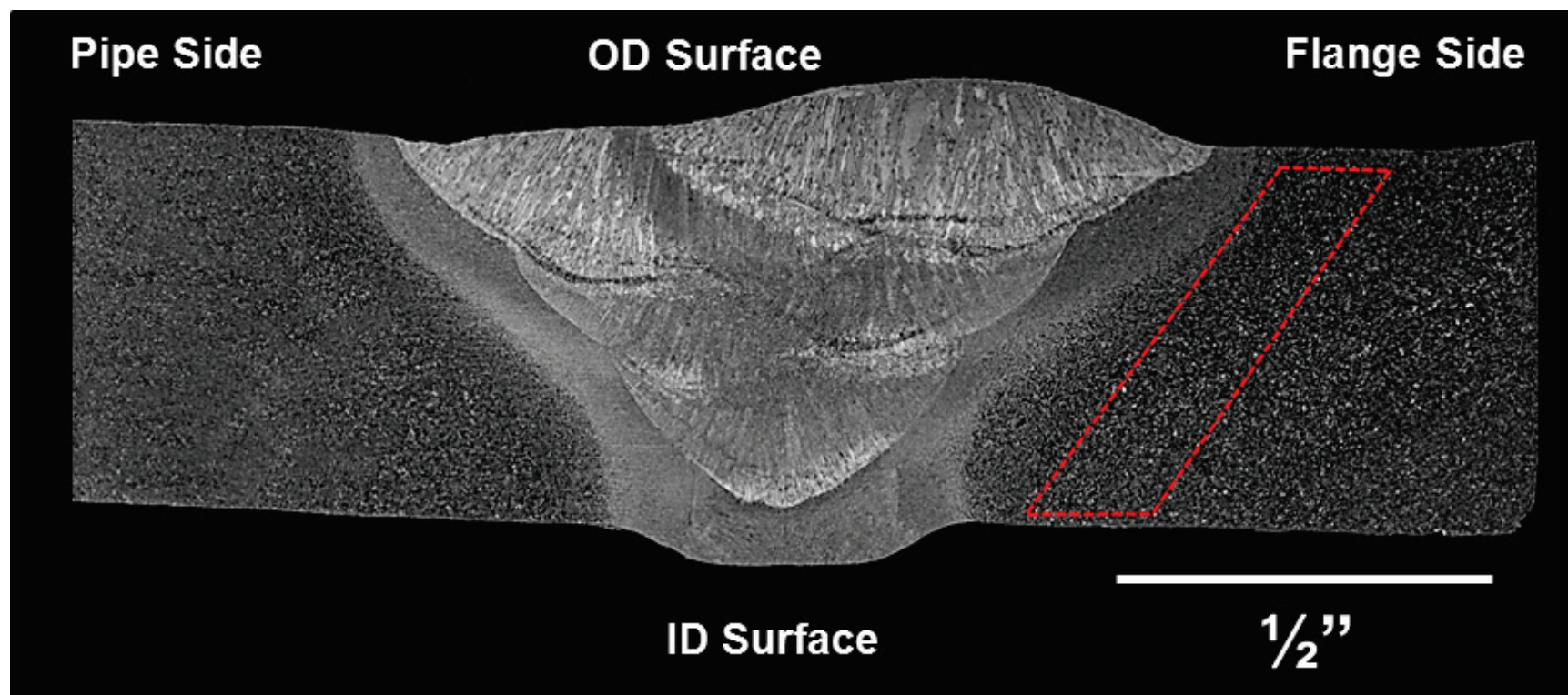


Figure 64. Photomacrograph of P66 Component #555-S1. Microfissures were readily observed (at 100X magnification using optical microscopy in the as-polished condition) outside of the Visible HAZ in the Flange Base Metal from the ID Surface to $\frac{1}{2}$ the Wall-Thickness. Microfissures were observed to a Lesser Extent (scattered) from the $\frac{1}{2}$ Wall-Thickness to the OD Surface. Maximum Extent of Damage was observed adjacent to the ID Surface. Approximate Location of fissuring is shown by the Red Boxed Region in the above Macrograph. No Damage was observed in the Weld Deposit, Pipe or Flange HAZs or in the Pipe Base Metal, 2% Nital Etch.

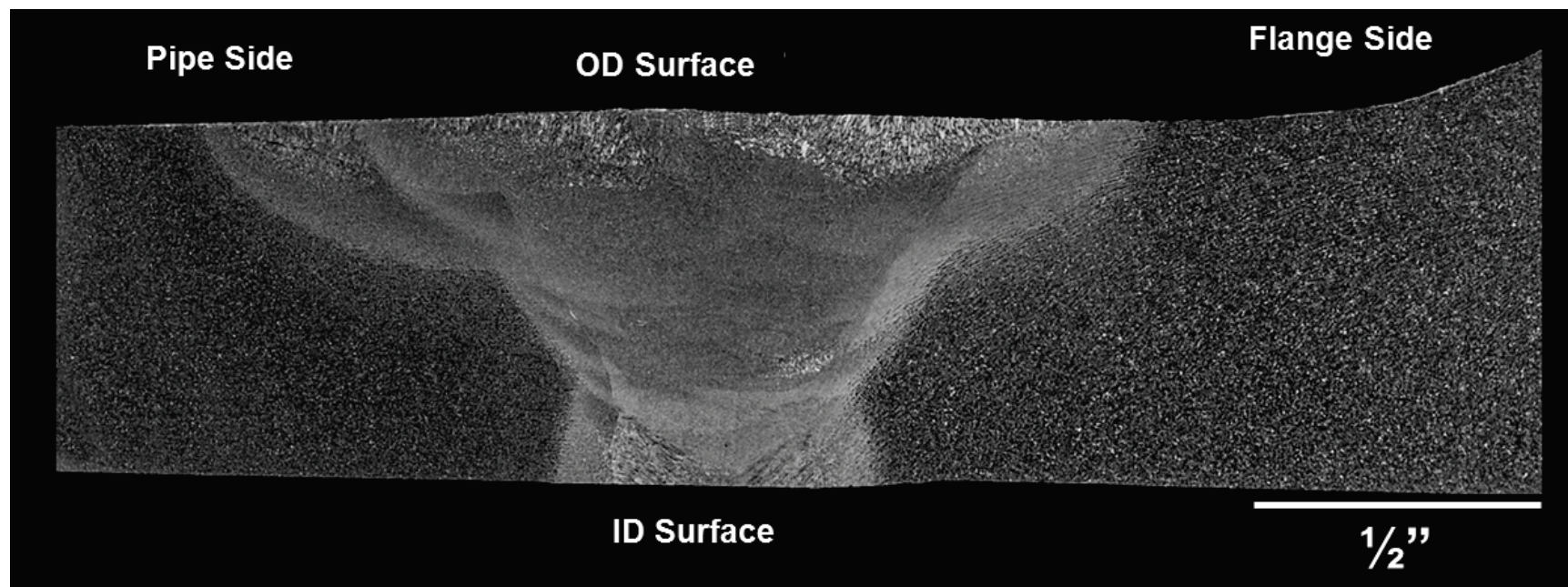


Figure 65. Photomacrograph of P66 Component #555-S2. No evidence of Decarburization or Fissuring was observed in the Weld Deposit, Pipe or Flange HAZs or in the Pipe or Flange Base Metals, 2% Nital Etch. (Note: OD Surface had been Ground Smooth to Contour the Weld, and the ID Surface had been Ground Flush by P66 prior to the receipt of Component by UTK.

5.3.1 Metallography on P66 Flange #555-S1

Microfissures were observed in the flange base metal just outside of the visible HAZ. Optical micrographs at 100X adjacent to the ID surface in the flange base metal in as polished condition and after etching show the presence of microfissures along grain boundaries in Figure 66. Fissures were readily visible at 100X in as-polished condition (see Figure 66A), but were difficult to depict when etched with 2% Nital (see Figure 66B) (note: micrographs were obtained at the same location before and after etching, Vickers indent was used as a marker). Figure 67 shows the higher magnification optical micrograph of the flange base metal just outside of the visible HAZ revealing microfissures at 600X along ferrite-ferrite (red arrows) and ferrite-pearlite boundaries (green arrows).

The SEM was utilized to further characterize the nature of the microfissures observed in the flange base metal just outside of the visible HAZ adjacent to the ID surface using high magnification microscopy in Flange #555-S1. Cavitation and fissuring was observed along ferrite-ferrite and ferrite-pearlite boundaries. Figure 68 shows the SEM micrographs at (A) 1000X, and (B) 2500X. Figure 69 shows the SEM micrographs at (A) 5000X, and (B) 10000X, which show the evidence of microfissures along ferrite-pearlite (shown by green

arrow) and ferrite-ferrite boundaries (shown by red arrow). Also, note the formation of voids/cavities ahead of the tip of micro-fissure (as shown by green arrows Figure 68 and Figure 69). Figure 69 show voids/cavities linked-up to form microfissures at a (A) ferrite-pearlite boundary (shown by green arrow) and B) a ferrite-ferrite triple point separation (shown by red arrow). The voids/cavities sizes ranged from $\frac{1}{4} \mu\text{m}$ to $\frac{1}{2} \mu\text{m}$.

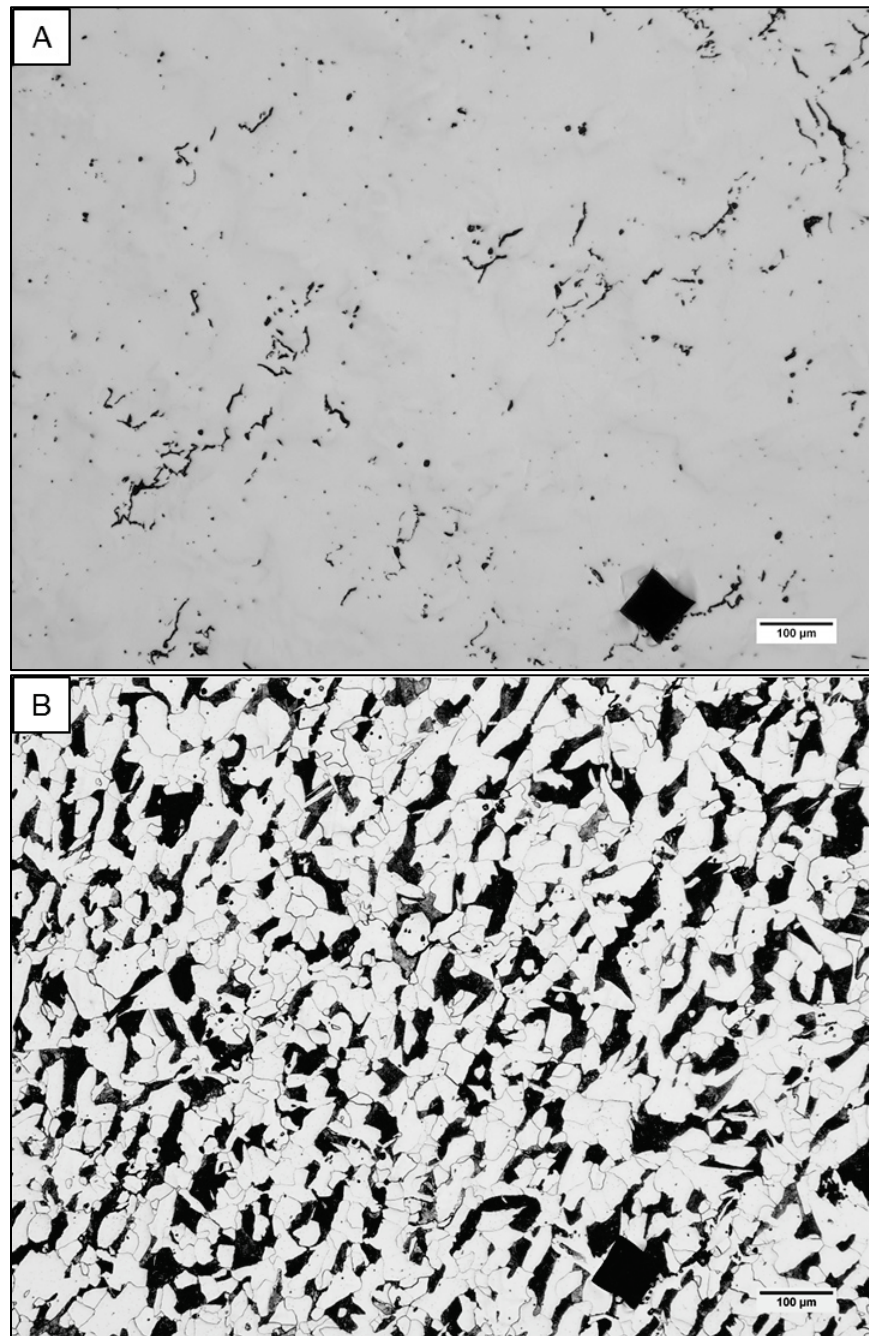


Figure 66. Photomicrographs of the Flange Base Metal (at 100X) just outside of the visible HAZ adjacent to the ID surface, (A) As-Polished and (B) 2% Nital Etch. ASTM G.S. #7, 70% Ferrite, and 30% Pearlite.

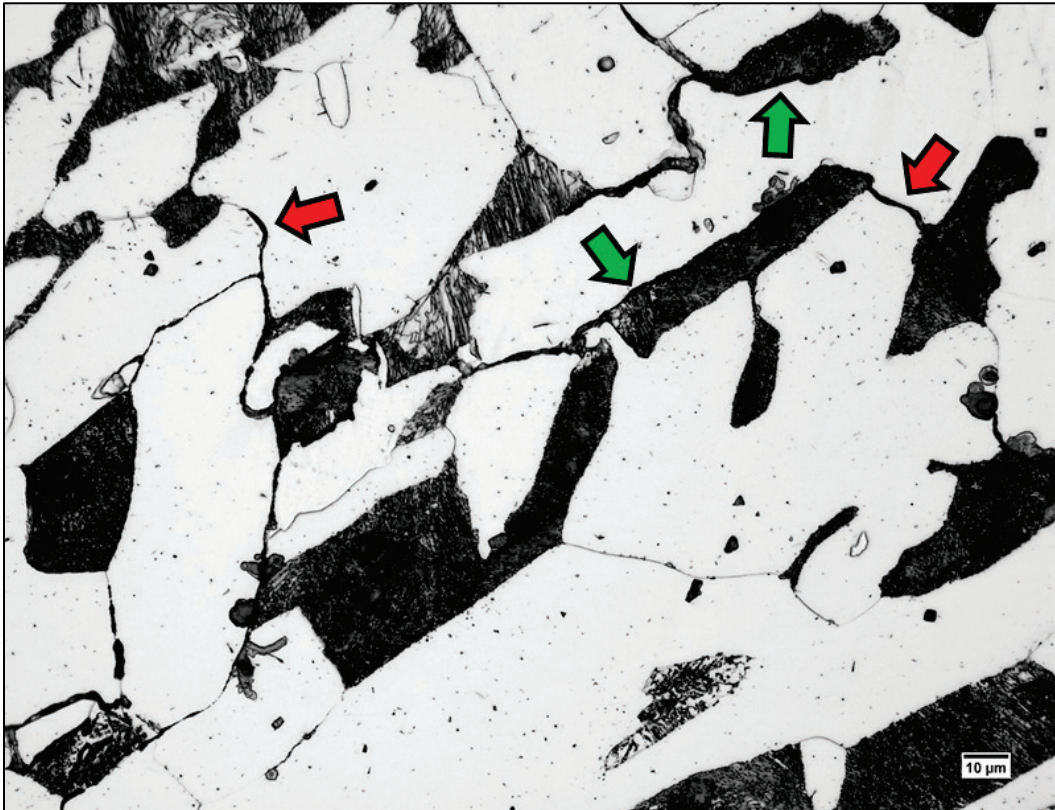


Figure 67. Photomicrograph of the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S1 showing the Evidence of Microfissures along the Ferrite-Ferrite (red arrows) and Ferrite-Pearlite Boundaries (green arrows), 600X, 2% Nital Etch.

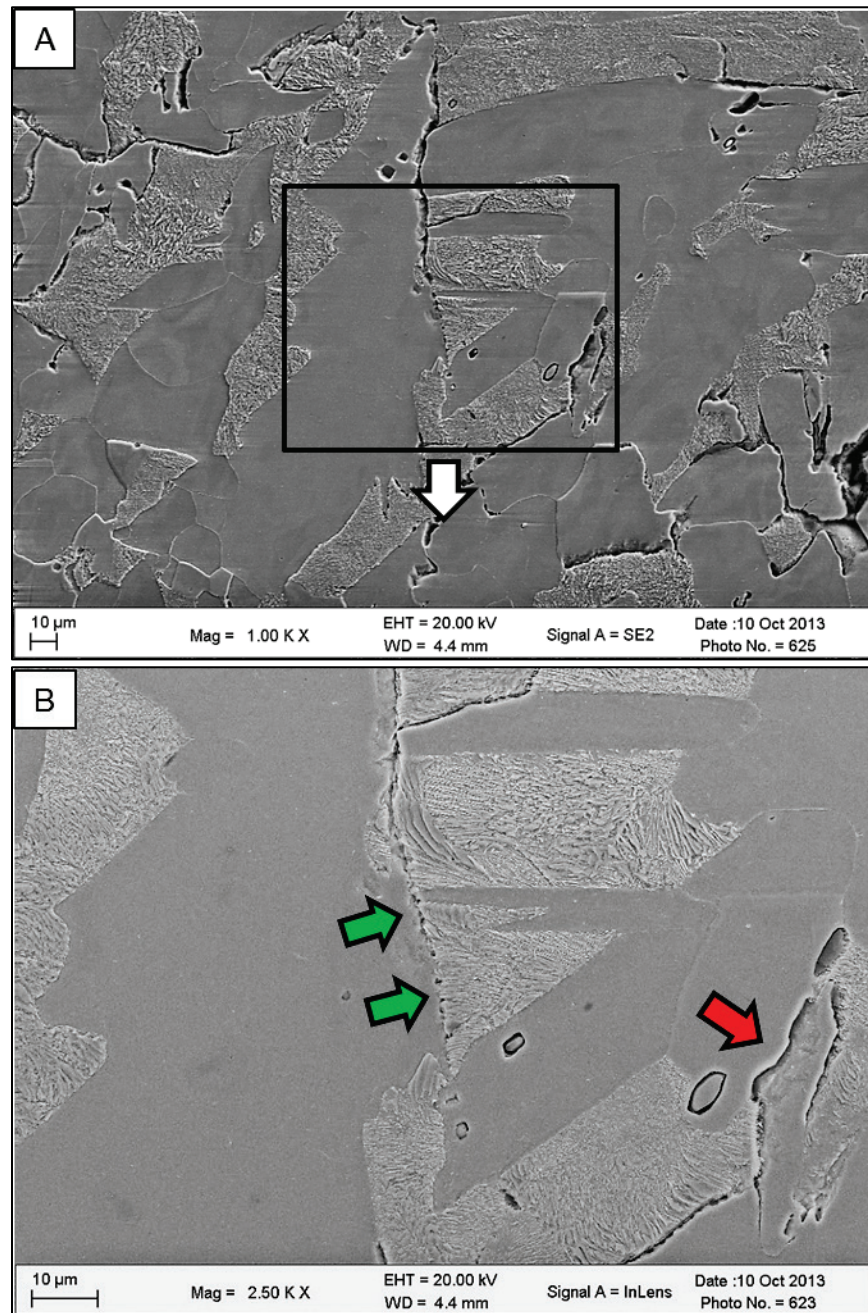


Figure 68. SEM Micrographs Showing Fissuring/Cavities along a Ferrite-Ferrite (red arrow) and Ferrite-Pearlite Boundaries (green arrows) in the Flange Base Metal just outside of the Visible HAZ adjacent to the ID surface in #555-S1, 2% Nital Etch.

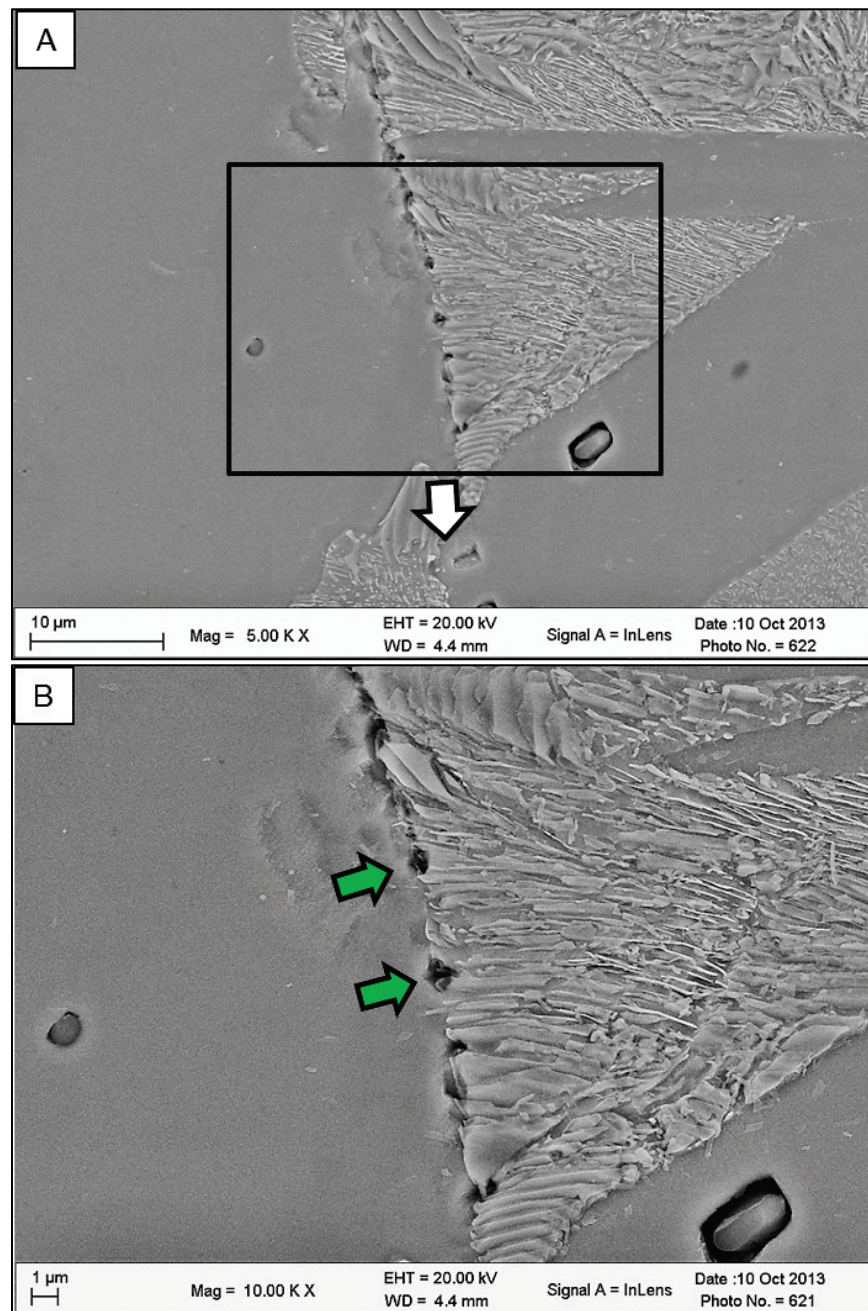


Figure 69. SEM Micrographs Showing Voids/Cavities along a Ferrite-Pearlite Boundary (green arrows) in the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface (Location 1 in Figure 64) in #555-S1-1, 2% Nital Etch.

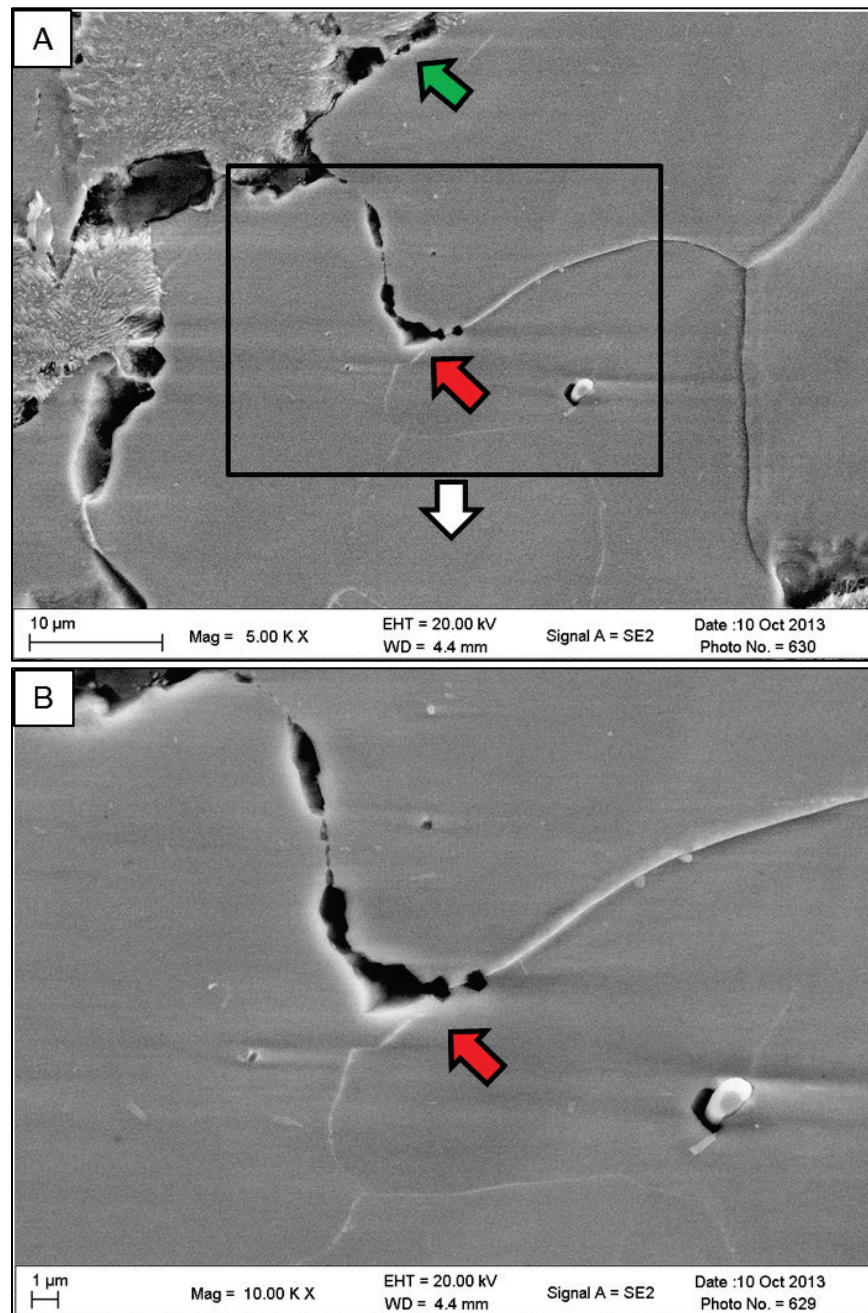


Figure 70. SEM Micrographs Showing Voids/Cavitation Linked-up to form Microfissures at a Ferrite-Pearlite Boundary (green arrow) and a Ferrite-Ferrite Triple Point Separation (red arrow) in the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in #555-S1-1, 2% Nital Etch.

5.3.2 “Cryo-Cracking” and SEM Examination of P66 Flange #555-S1

The SEM fractographs of the “Cryo-Cracked” specimen extracted from the damaged region of the flange base metal (just outside of the visible HAZ) adjacent to the ID surface of flange-to-pipe welded component #555-S1 show the formation of voids/cavities and intergranular separation. SEM fractographs in Figure 71 at (A) 10,000X and (B) 20,000X show the formation of voids/cavities along the ferrite-pearlite boundary (see green arrows). SEM fractographs in Figure 72 at (A) 20,000X and (B) 40,000X show voids/cavities along ferrite-pearlite boundaries (see green arrows). Figure 74 at (A) 20,000X and (B) 40,000X show the evidence of intergranular separation and the formation of voids/cavities along ferrite-ferrite grain boundary (see red arrows). The voids/cavities size ranged from $\frac{1}{4}$ μm to $\frac{1}{2}$ μm . Note that the size and shape of the voids/cavities is similar to those observed in polished and etched samples by SEM examination in Figure 69.

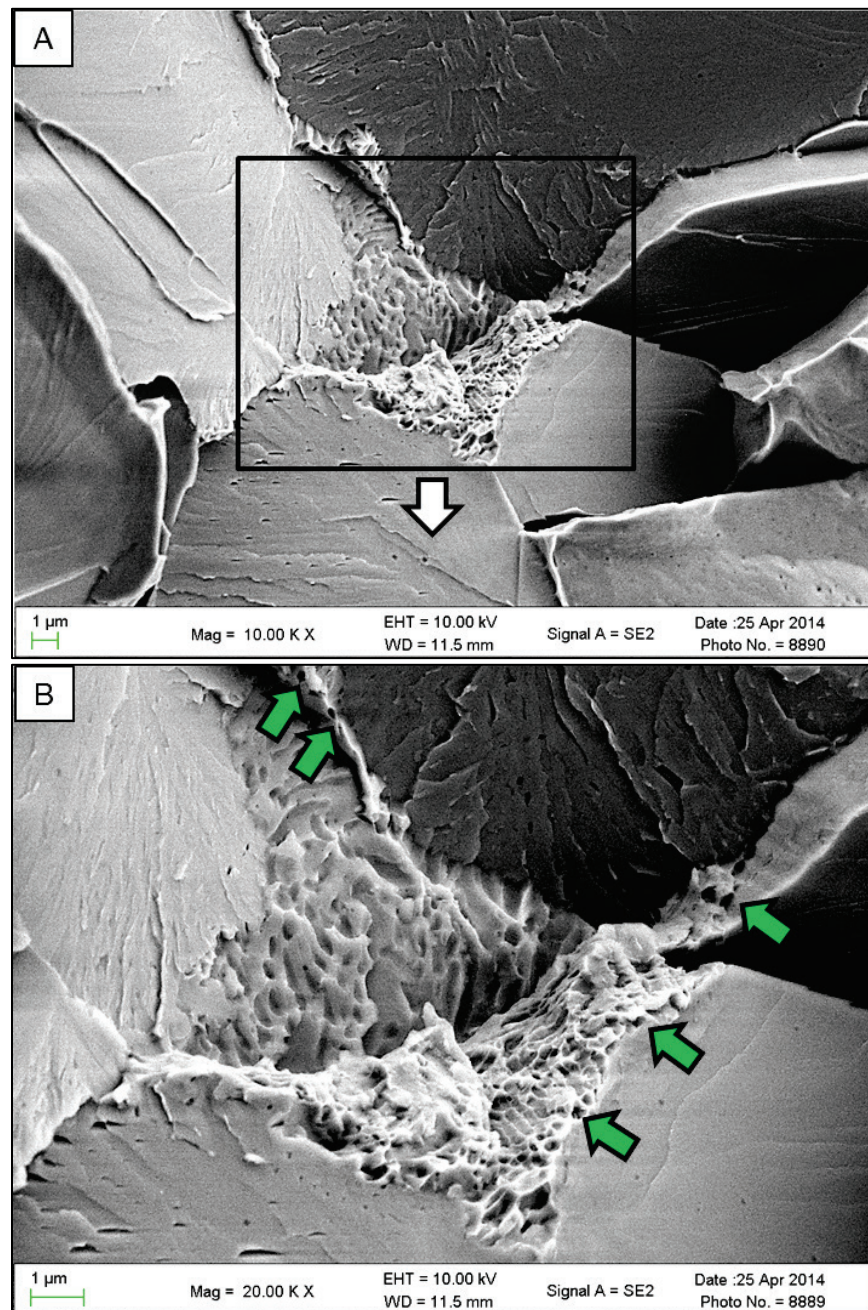


Figure 71. SEM Fractographs of the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S1 showing formation of Voids/Cavities along the Ferrite-Pearlite Boundary (shown by green arrows). Voids/Cavities sizes ranged from $\frac{1}{4}$ µm to $\frac{1}{2}$ µm.

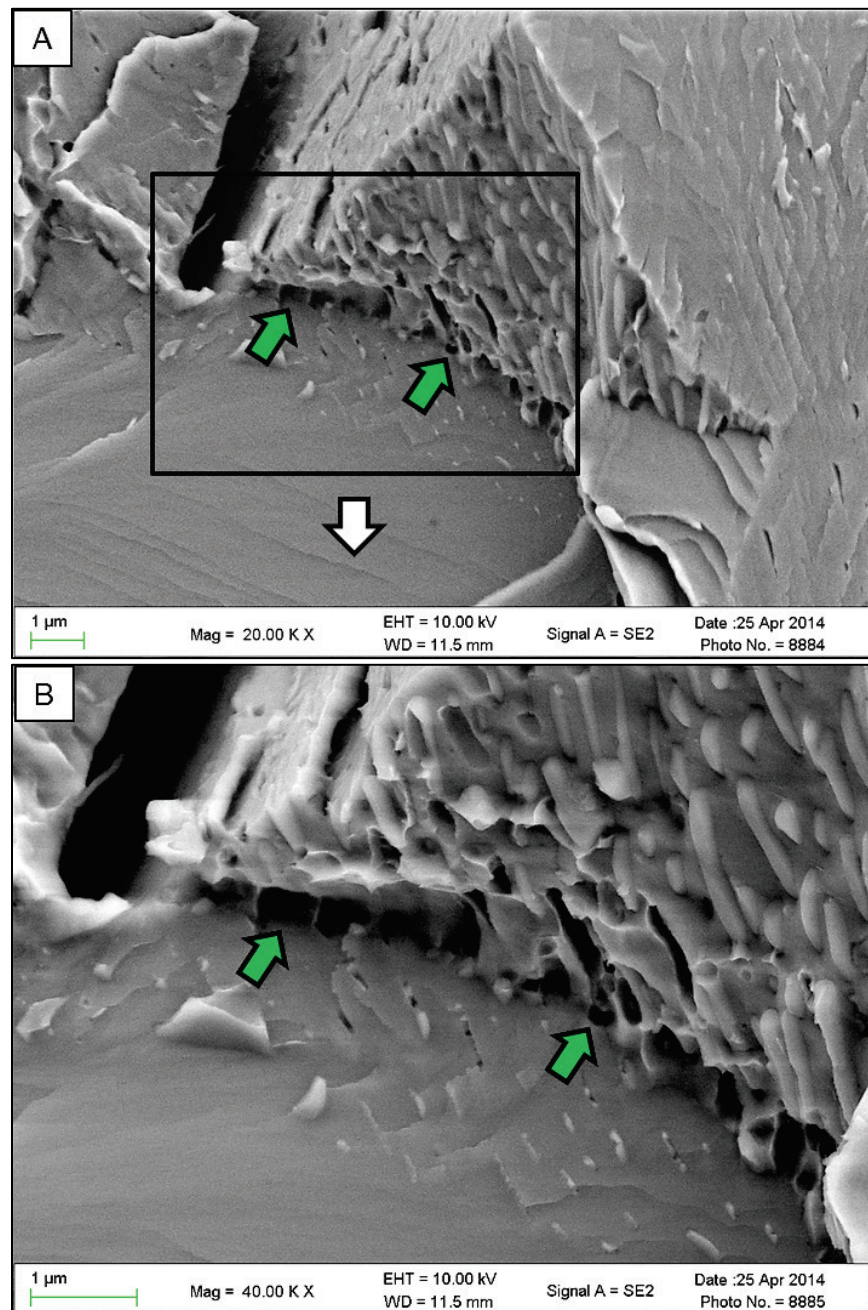


Figure 72. SEM Fractographs in the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S1 showing Voids/Cavities along the Ferrite-Pearlite Boundary (shown by green arrows).

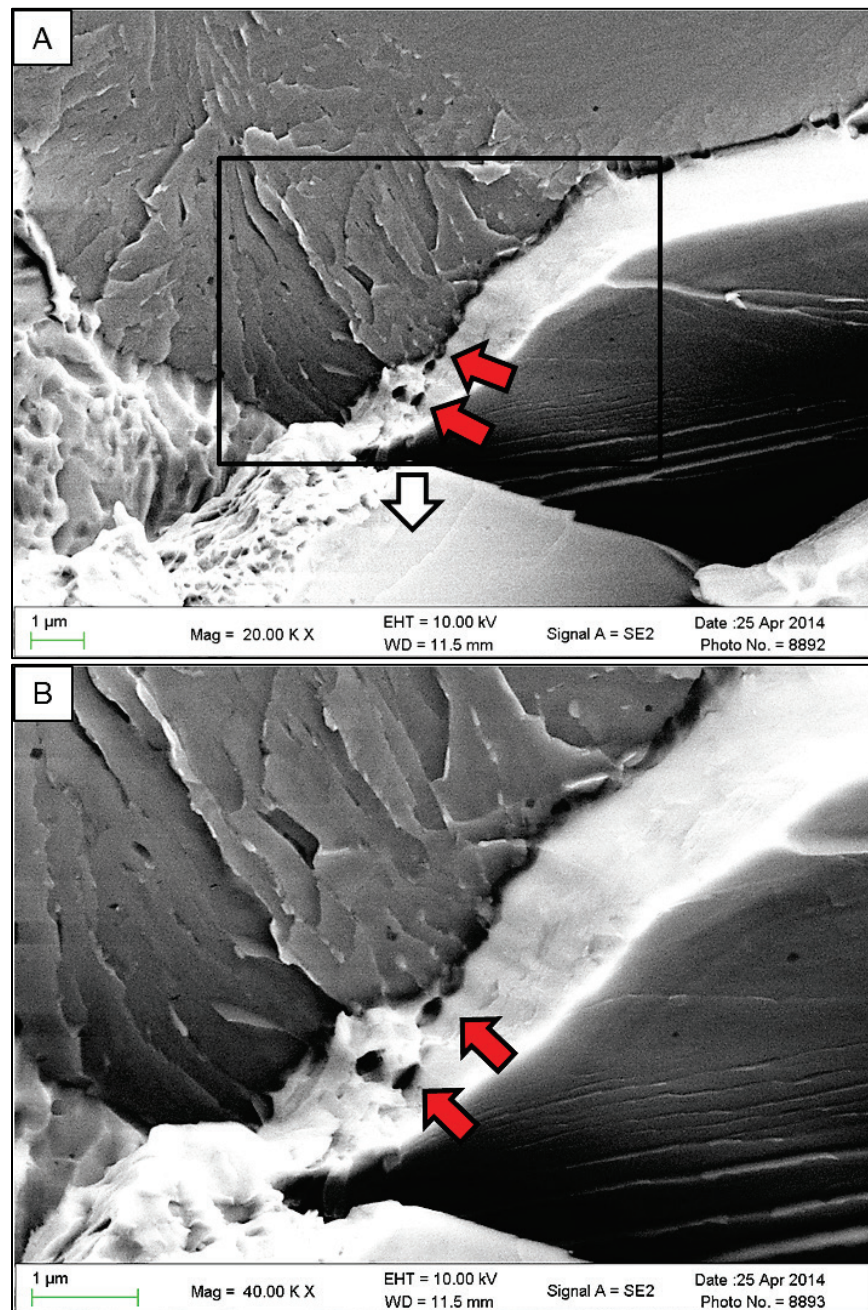


Figure 73. SEM Fractographs of the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S1 showing Intergranular Separation and formation of Cavities along the Ferrite-Ferrite Grain Boundary (shown by red arrows). Cavities sizes ranged from $\frac{1}{4}$ µm to $\frac{1}{2}$ µm.

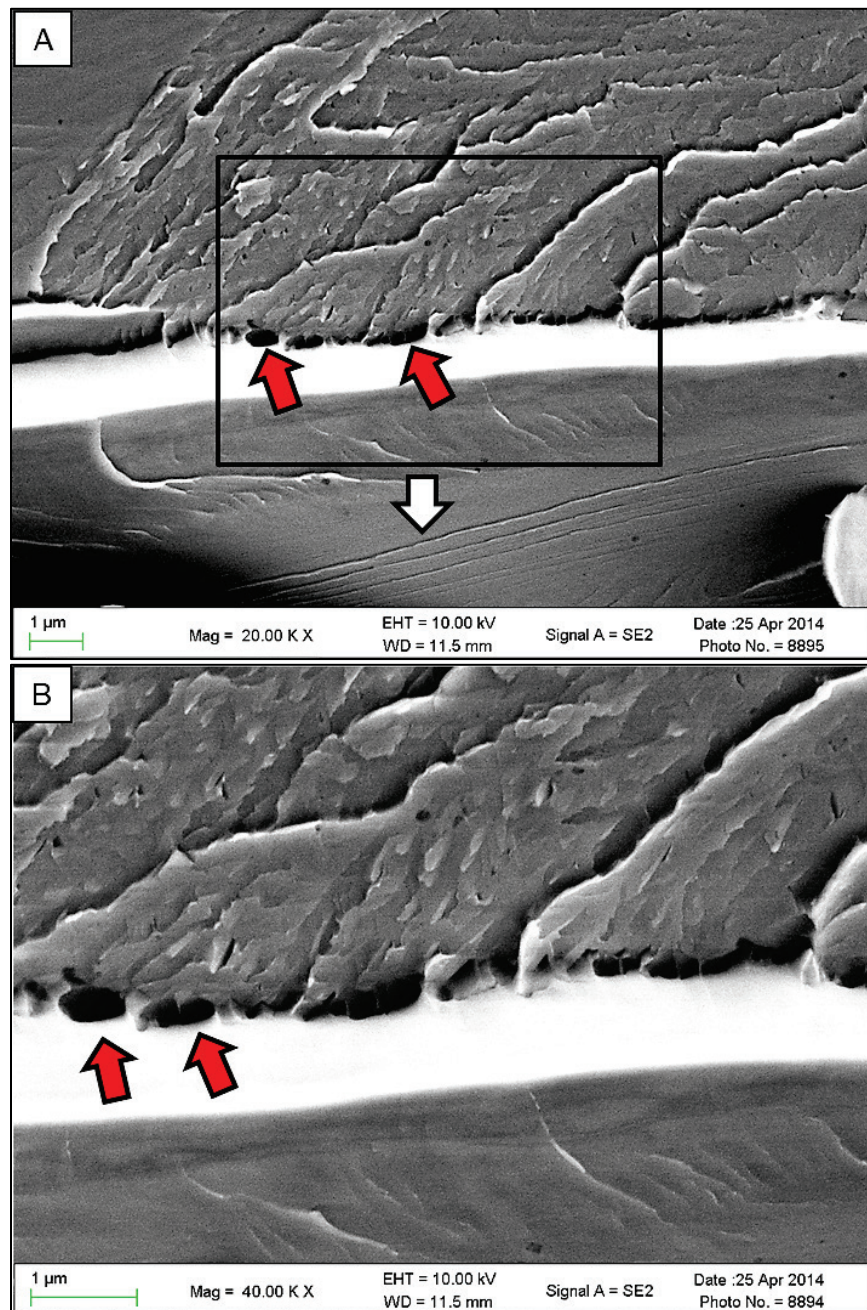


Figure 74. SEM Fractographs of the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S1 showing Intergranular Separation and formation of Cavities along the Ferrite-Ferrite Grain Boundary (shown by red arrows). Cavities sizes ranged from $\frac{1}{4}$ μm to $\frac{1}{2}$ μm.

5.3.3 Metallography of the Pipe Base Metal on P66 Flange #555-S1

Figure 75 show photomicrographs of the pipe base metal at (A) 100X and (B) 500X respectively; the microstructure consists of 75% ferrite and 25% pearlite with an ASTM grain size #6. The microstructure exhibits directional features resulting from segregation and rolling, which is typical of piping products. No evidence of decarburization or fissuring, which is a common feature of traditional high temperature hydrogen attack (HTHA), was observed in the pipe base metal, pipe and flange HAZs or in the weld deposit in flange-to-pipe welded component #555-S1.

5.3.4 Metallography on P66 Flange #555-S2

The microstructure of Flange #555-S2 was composed of ferrite and pearlite for both pipe and flange base metals. Figure 76 show photomicrographs of the flange base metal at (A) 100X and (B) 500X, respectively showing a typical forging pattern. Microstructure consists of 75% ferrite and 25% pearlite with an ASTM grain size #6. Figure 77 shows photomicrographs of the pipe base metal at (A) 100X and (B) 500X, respectively, showing typical pipe rolling/forming texture. Microstructure consists of 80% ferrite and 20% pearlite with an ASTM grain size #6. Two samples were extracted 180 degrees apart circumferentially

from Flange #555-S2 for a microstructural examination. No evidence of decarburization or fissuring/cracking which are common features of traditional high temperature hydrogen attack (HTHA) was observed in the pipe base metal, flange base metal, pipe and flange HAZs or in the weld deposit in Flange #555-S2.

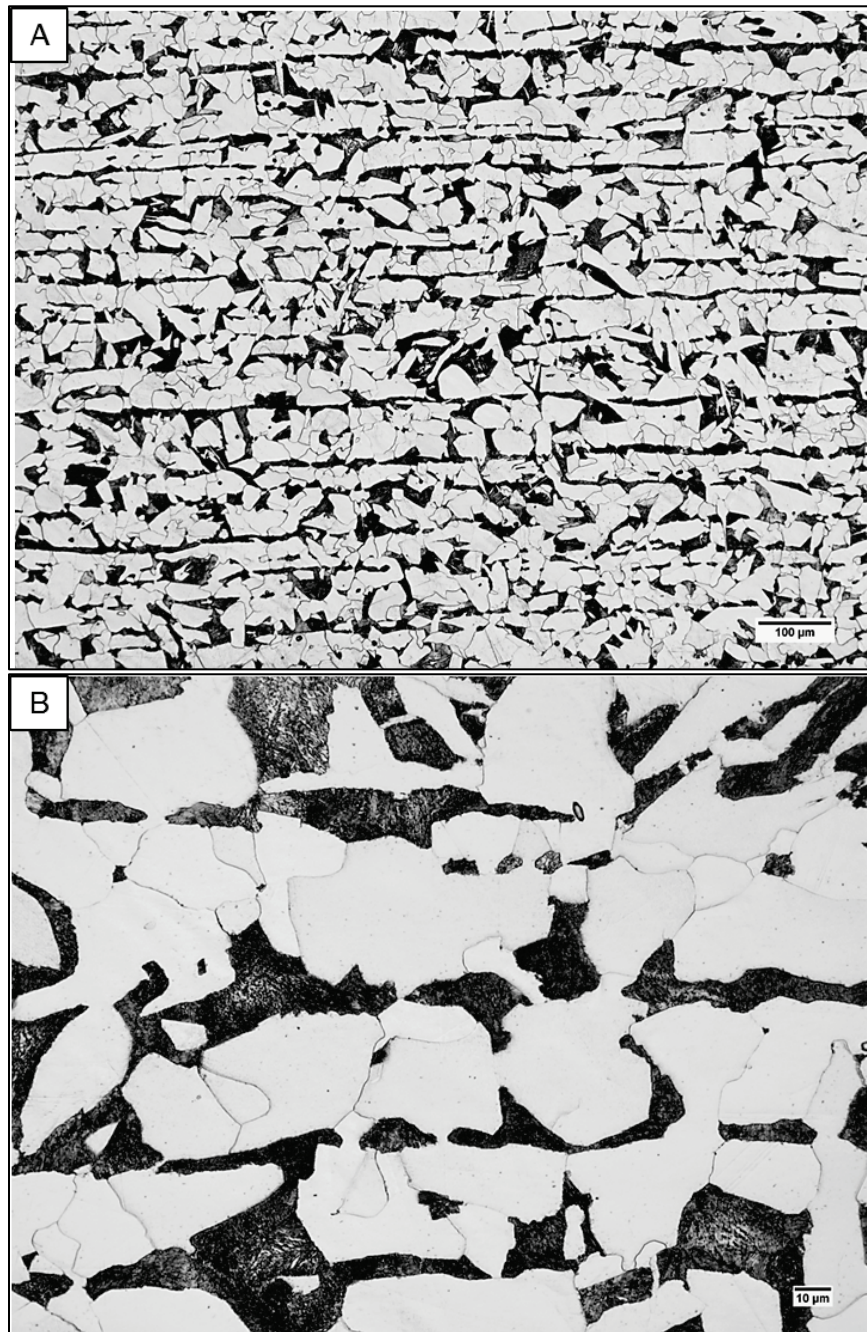


Figure 75. Photomicrographs of the Pipe Base Metal in #555-S1 with No evidence of Decarburization or Cracking. Ferritic and Pearlitic Microstructure with typical Directional Features resulting from Segregation and Rolling, ASTM G.S. #6, 75 % Pearlite and 25 % Ferrite. 2% Nital Etch.

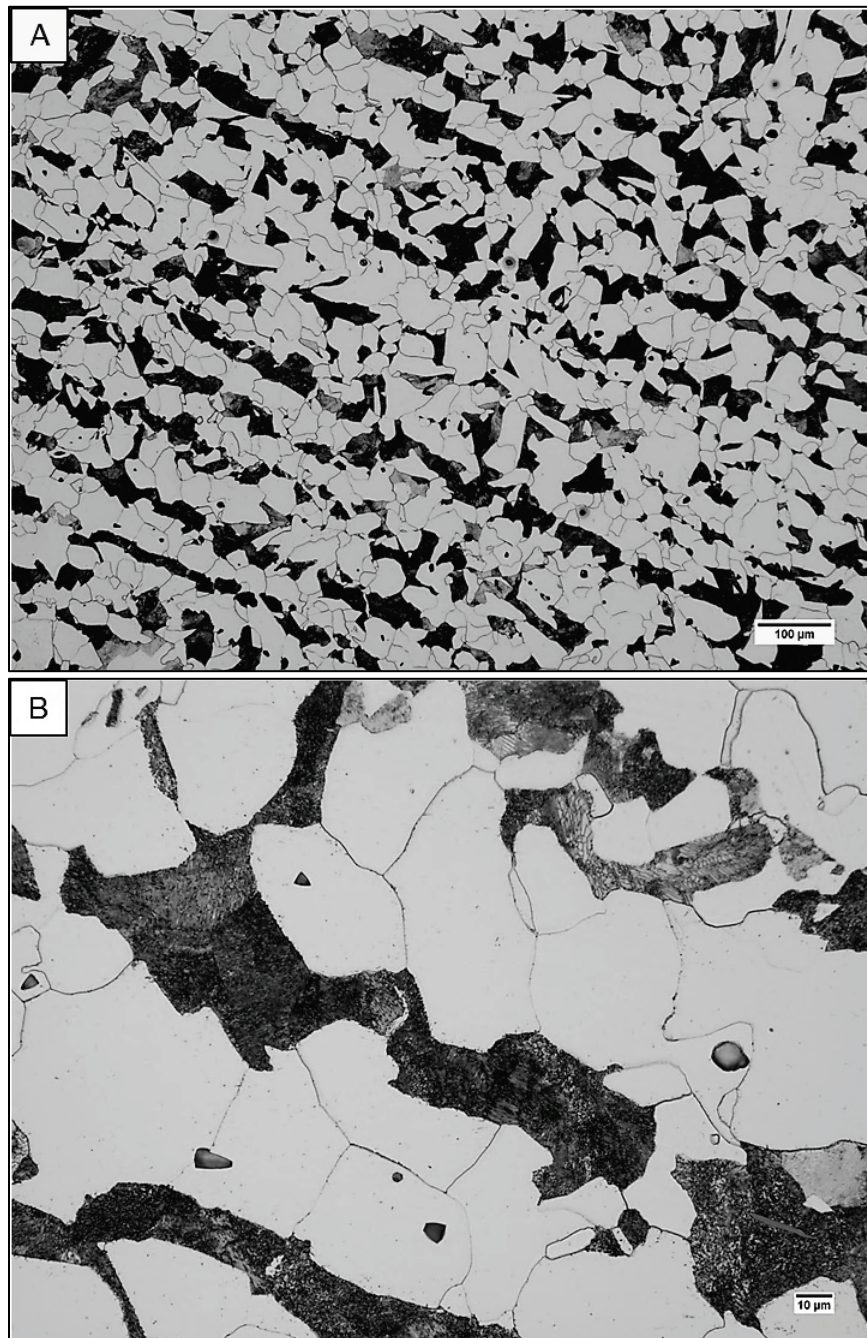


Figure 76. Photomicrographs of the Flange Base Metal just outside of the Visible HAZ adjacent to the ID Surface in P66 #555-S2. Ferritic and Pearlitic Microstructure with typical Forging Texture. ASTM G.S. #6, 75% Ferrite, 25% Pearlite, 2% Nital Etch.

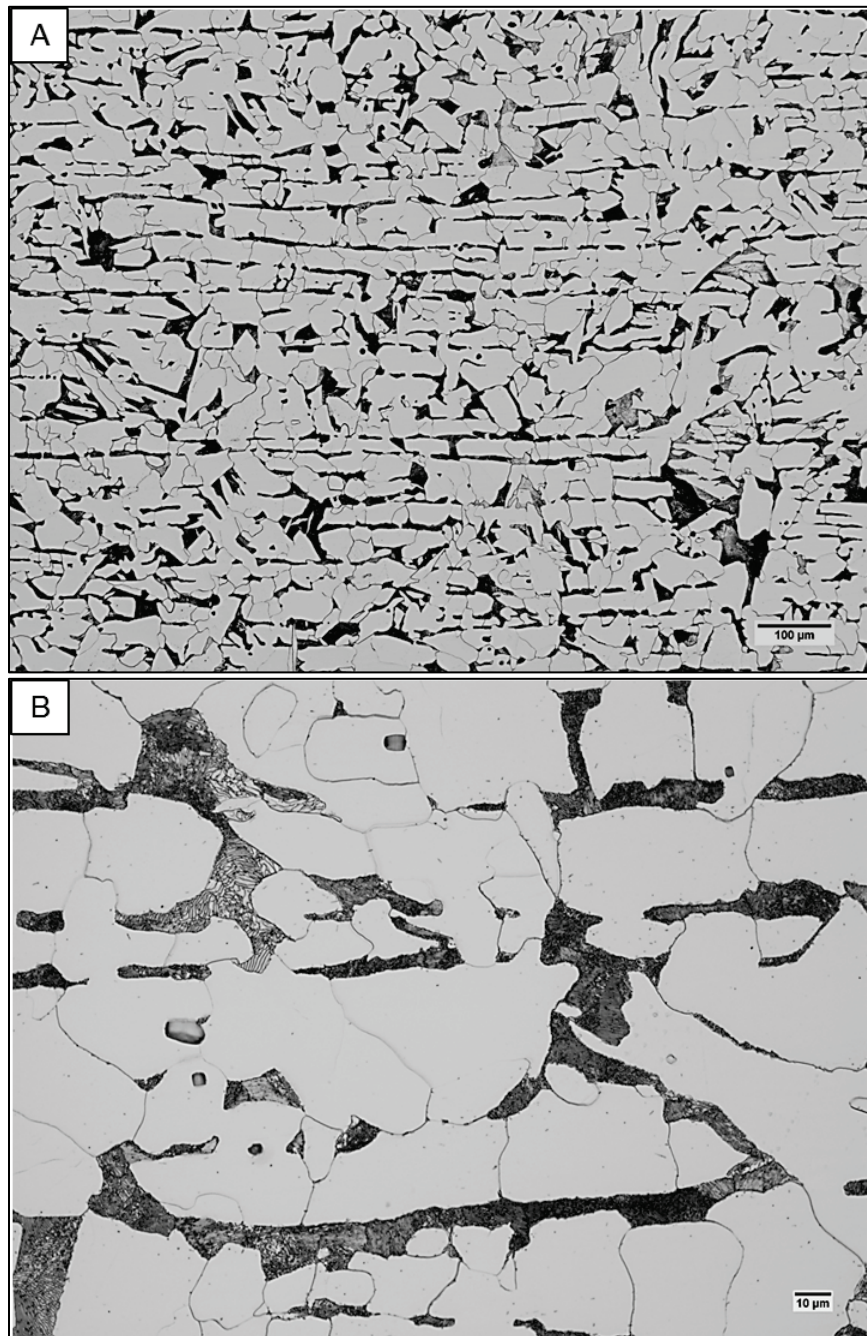


Figure 77. Photomicrographs of the Pipe Base Metal adjacent to the ID Surface in P66 #555-S2,. Ferritic and Pearlitic Microstructure with typical Directional Features Resulting from Segregation and Rolling. ASTM G.S. #6, 80% Ferrite, 20% Pearlite, 2% Nital Etch.

5.3.5 Hardness Assessment of P66 Flanges #555-S1 and #555-S2

Table 8 shows the measured hardness values and estimated tensile strengths for both P66 flange-to-pipe components #555-S1 and #555-S2. The hardnesses of the pipe, flange, and the weld deposit are considered normal at 82-87 HRBW for #555-S1 (damaged). The hardness of the pipe, flange and weld deposit for #555-S2 (undamaged) are slightly lower at 70-81 HRBW. Measured hardness (HRBW) was used to estimate tensile strength (ksi) from the appropriate tables in ASTM A370 (see Table 8 for detailed hardness/strength results). The strength requirements of ASTM A106-Gr.B (60 ksi) for pipe base metal and ASTM A105 (70 ksi) for flange base metal were met by conversion⁸⁵⁻⁸⁷. The differences in the hardness/strength are reflective of the difference in carbon content in flange and pipe components. Vickers micro-hardness on the damaged flange #555-S1 across the pipe and flange HAZs is shown in Figure 78. The hardness traverse on the damaged flange across the pipe and flange HAZs is shown in Figure 79. The traverses for both components #555-S1 and #555-S2 are similar, and reflect the starting hardnesses of the flange and pipe material. The hardness of the flange base metal immediately outside of the visible HAZ (adjacent to the microfissures) is 82 HRB (154 HV). Thus, there is no significant

difference in the hardness of the flange base metal between the area adjacent to the microfissures and the unaffected base metal (within +/- 5 HV).

The hardness and strength (by conversion) results of P66 flange-to-pipe welded component #555-S1 show that at the early stages of HTHA these properties are not significantly impaired. The earlier studies on C-1/2 Mo steel at UTK also showed similar results at this level of methane (28 ppm). Figure 80A shows the co-relation between the strength (ksi) as a function of methane content (ppm) and Figure 80B shows the co-relation between the impact toughness (ft-lbf) as a function of methane content (ppm) ³⁹. The strength and toughness results are not significantly impaired on C-1/2 Mo when the methane content is less than 30-35 ppm ³⁹.

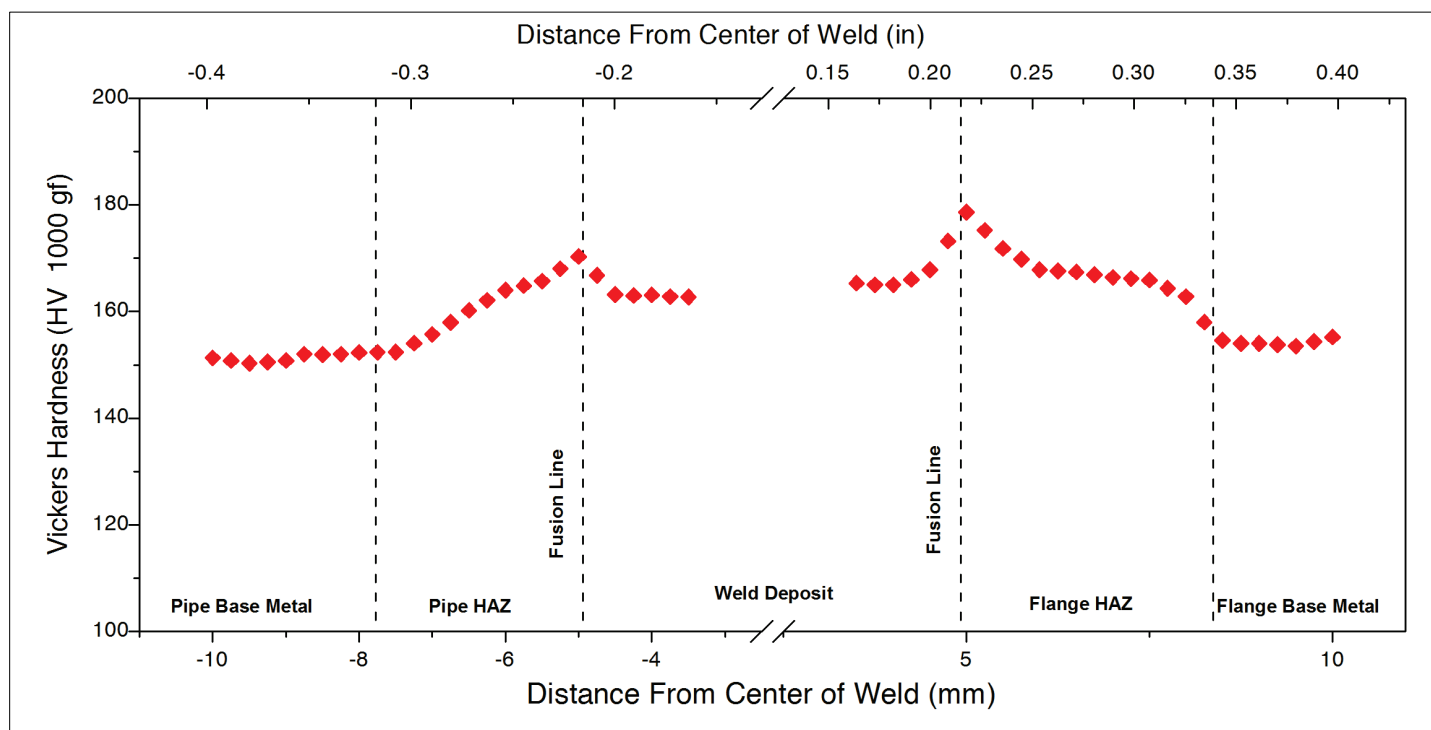


Figure 78. Vickers Micro-hardness Traverse on the P66 Flange-to-Pipe Welded Component #555-S1 across the Flange and Pipe HAZs using 1000 gf load. The Traverses are Similar and Reflect the Starting Hardnesses of Flange and Pipe Material. Hardnesses in the area adjacent to the Microfissures (flange base metal just outside of the visible HAZ) and the Unaffected Flange Base Metal show no Significant Difference in Hardness Results (within ± 5 HV).

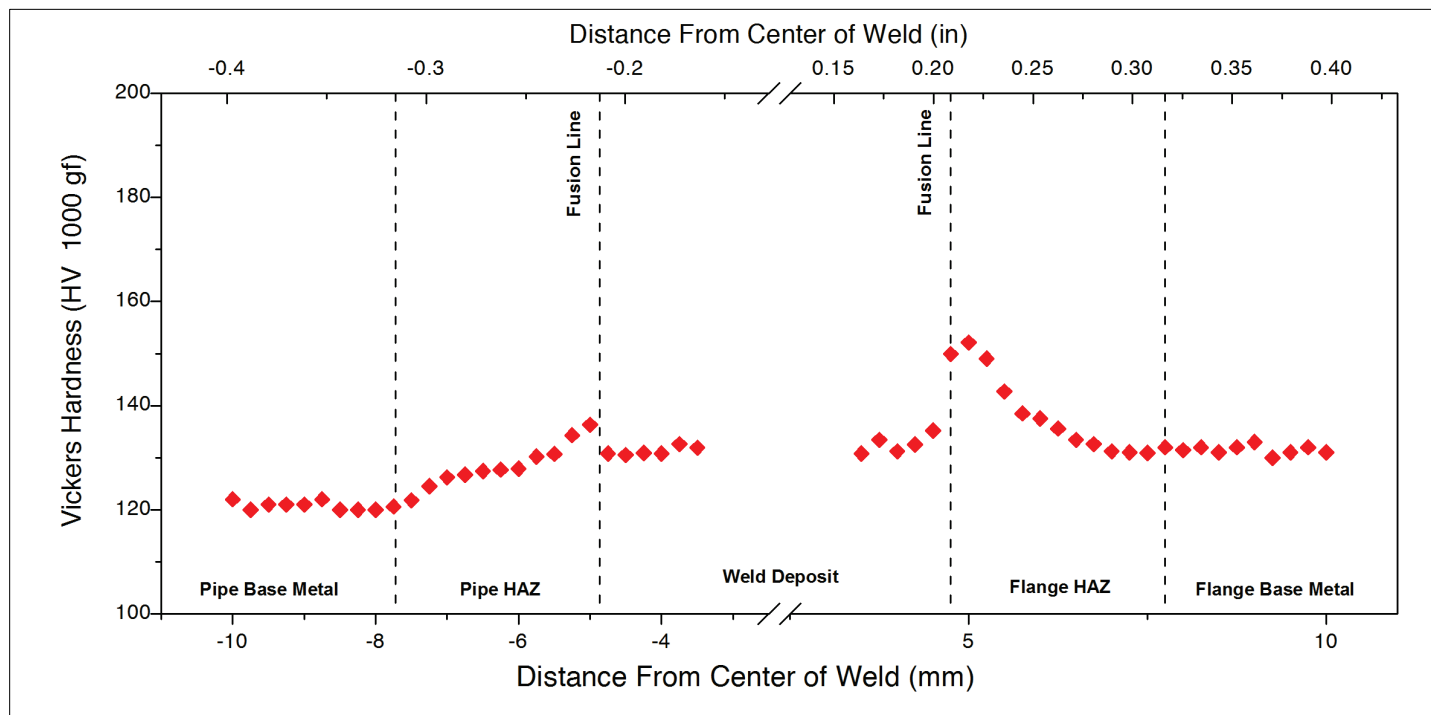


Figure 79. Vickers Micro-hardness Traverse on the P66 Flange-to-pipe Weld Component #555-S2 across the Flange and Pipe HAZs using 1000 gf load. The Traverses are Similar and Reflect the Starting Hardnesses of Flange and Pipe Material.

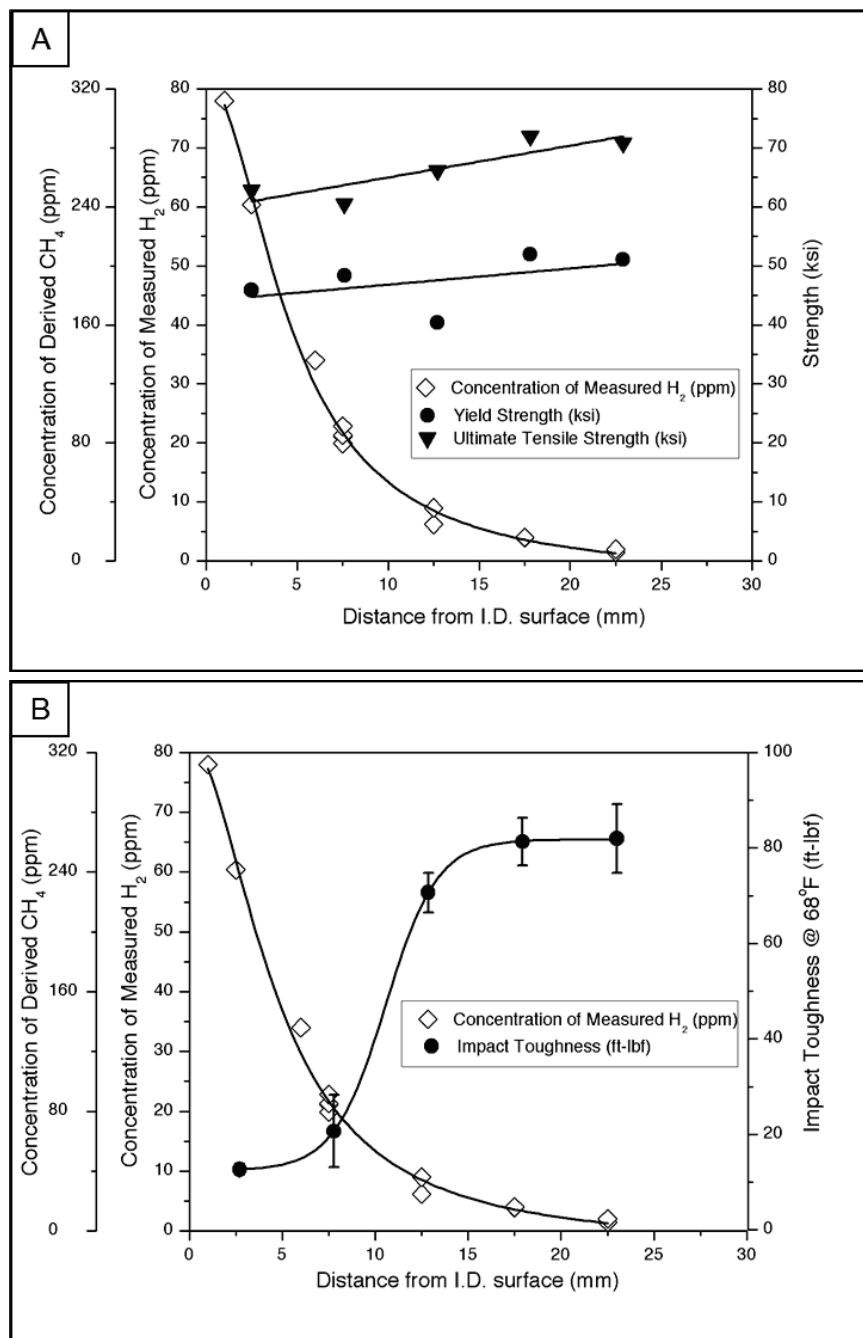


Figure 80. Concentration of Methane, CH_4 (ppm) content vs. Change in Mechanical Properties (Strength and Toughness) on C-1/2 Mo Steel as a Function of Wall-thickness ³⁹.

5.3.6 Hydrogen and Methane Content Determination on P66 #555-

S1

AWS Diffusible Hydrogen Measurement

AWS diffusible hydrogen content was measured on samples extracted from P66 flange-to-weld component #555-S1 (#555-S1-5 - ~1/2 wall sample containing flange base metal and the weld deposit and #555-S1-6 – a slug sample extracted from the flange base metal just outside of the visible HAZ from the maximum damage location). The results showed that the diffusible hydrogen content present in both the samples was less than 1 ppm, which is a nominal amount for steel components with no hydrogen damage. Detailed results of the AWS diffusible hydrogen tests for each sample are shown in Table 7.

Hydrogen Content Derived from Methane Dissociation

Hydrogen content derived from methane was measured on same samples upon completion of AWS diffusible hydrogen test Hydrogen. Hydrogen contents measured on two samples P66 #555-S1-5 and #555-S1-6 extracted from the maximum damage location in the flange base metal was 6.5 ppm and 7.1 ppm, respectively (thus approximately 25 ppm and 28 ppm methane, respectively). The methane measurement was performed by heating the

encapsulated sample at 700°C and dissociating methane to hydrogen. The measured hydrogen was used to back calculate the methane levels. Note: If any trapped hydrogen was present in these samples, then that will also be released at 700°C to be combined with any hydrogen dissociated from methane and this will be included in methane measurement results. Detailed test results for hydrogen measurements by methane dissociation on flange-to-pipe welded component #555-S1 are shown in Table 7. These results suggest that the methane level is indicative of the early stages of HTHA in flange-to-pipe welded component #555-S1. Thus, it can be concluded that the void/cavities observed on the fracture surface of the “Cryo-Cracked” specimen extracted from the damaged region of the flange-to-pipe weld component (#555-S1) was a result of the formation of methane bubbles.

Table 7. Measured Hydrogen Content (ppm) by AWS Diffusible Method and Methane Determination from Hydrogen Measurements using Methane Dissociation on Phillips 66 Flange-to-Pipe Welded Component #555-S1.

Sample ID	AWS Diffusible Hydrogen at 45°C/72hrs (ppm)	Methane Content Determined from Hydrogen Measurements using Methane Dissociation (ppm)	Remarks
Phillips 66 Flange-to-Pipe Welded Component #555-S1	< 1 ppm hydrogen	28 methane (7 ppm of measured hydrogen)	Initial Stage of HTHA Damage

Methane Dissociation Reaction: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ at 700°C/72hrs. Methane Determination was Performed by Measuring the Dissociated Hydrogen and Back Calculating the Methane Content (4:1 ratio)

Note: The methane level determined (28 ppm) are a result of HTHA damage and these results comply with optical and SEM examinations at these two locations.

Note: Hydrogen Measurement on P66 Flange-to-Pipe Welded Component #555-S2 was not Performed based on Metallography and Hardness Results.

Contributor Sample ID	Average Measured Rockwell B (HRBW)			Estimated Tensile Strength (ksi) ^(a)		
	Pipe Base Metal	Flange Base Metal	Weld Deposit	Pipe Base Metal	Flange Base Metal	Weld Deposit
Valero Energy Flange #67	82	85	84	75	79	77
Valero Energy Flange #1252134	72	87	83	62	84	76
Irving Oil Refinery Flange #1110-2	82	89	87	75	86	84
Phillips 66 Flange #555-S1	82	83	87	77	80	84
Phillips 66 Flange #555-S2	70	77	81	61	68	73

- Tensile Strength was Estimated from Measured HRBW using ASTM E370. Estimated Tensile Strength Meets the Minimum ASTM Strength Requirements of ASTM A106-Gr B, ASTM A105, and ASTM A516-70.
- Minimum Tensile Requirement for Pipe Base Metal (ASTM A106-Gr B) and Flange Base Metal (ASTM A105) are 60 ksi and 70 ksi respectively.

Chapter 6 – Conclusions

Five in-service flange-to-pipe welded components were submitted for metallurgical assessment by three refineries and the detailed conclusions based on this extensive evaluation are discussed separately for each refinery. The individual component conclusions are also summarized highlighting the potential reasons for damage occurrence in terms of the mechanisms responsible for various discontinuity occurrences and for the need for removal of damaged components from service. No PWHT of any of the welded components was conducted and the flange-to-pipe welds employed the SMAW process.

6.1 Valero Energy Submissions

Valero Energy submitted flange-to-pipe-components, #67 (cracked) and #1252134 (Undamaged) which were exposed to a hydrogen partial pressure of 71 psia in service at 650 °F for ~8 years. ASTM A105 & ASTM A106-Gr. B was used for the flange and pipe base metals, respectively, in both components.

1. The ferritic/pearlitic microstructure for each component exhibited an ASTM grain size of 6-7 that is considered normal for these material forms.

2. The hardnesses for all regions of the weldment are in the 82-87 HRBW range save for the #125213 pipe base metal that exhibits a hardness of 72 HRBW.

Thus, the weldment strength requirements (derived from hardness) meet the ASTM A106-Gr. B and ASTM A105 Ultimate Tensile Strength requirements of 60 and 70 ksi, respectively.
3. The crack found by Valero's UT-NDE in "Quadrant 270°" of the component (#67) was 5/8" long parallel to the weld. The crack initiated at the ID surface outside of the visible HAZ and propagated to within 0.15" of the OD surface (wall-thickness at this location is 0.55") terminating in the outer region of the weld HAZ.
4. Microstructural assessment did not reveal any decarburization at the ID surface or adjacent to the crack. No cavities/voids/bubbles were present adjacent to the ID surface or along the crack as revealed from SEM examinations at magnifications to 10,000X.
5. The diffusible hydrogen content determined using the AWS/ISO methodology, in the crack region, revealed that the diffusible hydrogen content is less than 2 ppm. The methane content, derived by dissociation, was also revealed to be less than 2 ppm. These measurements indicate that

neither content was above the level corresponding to the occurrence of hydrogen damage by any traditional service related HTHA mechanism.

6. "Cryo-Cracking" and SEM assessment of the crack surface morphology did not reveal any characteristics other than a mixture of intergranular separation and transgranular cleavage at magnifications to 40,000X. No evidence of striations or beach marks, which would be recognized as originating from fatigue propagation, was found. EDS analysis of the crack surface (only a very thin layer of oxide which did not interfere with fractography was present) revealed only oxygen, silicon, manganese and iron with no sulfur contamination to indicate environmentally related crack initiation or propagation.
7. There were no notches or discontinuities on/at the ID surface where the crack initiated and thus notch effects can be discounted.
8. Toughness was evaluated by limited Charpy testing adjacent to the ID surface at ambient temperature (74°F) on the flange side (cracked side) of the weld region and a level of 27-31 ft-lbf was determined. While this level is less than the pipe side toughness of 125 ft-lbf adjacent to the ID surface, this does

not appear to show that toughness alone is responsible, in any way, for the crack to have occurred on the flange side of the weld.

9. The flange side microstructure in terms of the forging pattern did not appear to be a major consideration in the crack propagation path.
10. Thus, for Valero flange #67 the crack occurrence is not considered to be related to any recognized HTHA mechanism. However, to assign another definitive mechanism to the crack occurrence is hampered by lack of knowledge of the secondary stresses and the operational characteristics together with weld residual stresses. Furthermore, one would not expect to have ID surface crack initiation by service-related bending stresses as these would be prone to cause OD surface crack initiation. In addition, it is well known that hydrogen can reduce the surface energy for crack propagation, but in this instance it appears that for this to be a major contributor to crack extension there would have to have been a pre-existing crack, from welding, but this is only a remote possibility as the material is not very hardenable (CE < 0.43) and the crack initiation and propagation occurred outside of the HAZ in the base metal. Furthermore, there is no information on post weld NDE to indicate a crack before the component-entered service.

11. Flange-to-pipe welded component #1252134, proactively extracted by Valero, was not cracked and it exhibited virtually the same range of mechanical properties as Flange #67 and the hydrogen and methane contents were at the same low level as well. This would further indicate that the cracking in Flange #67 is not related to any form of HTHA.

6.2 Irving Oil Refinery Submissions

Irving Oil Refinery submitted a flange-to-pipe component (#1110-2) that exhibited a through wall crack on the flange side of the weld very similar to the Valero #67 submission. The IOR component operated at 640°F and a hydrogen partial pressure of 85 psia for approximately 8 years. Wayland Engineering previously examined this component and thus not all of the component segments from the Wayland examination were available for this assessment. The portion of the crack received at UTK for this examination was only ¼" long and did not reach the OD surface of the component.

1. All of the microstructural and property characteristics met ASTM A106-Gr. B for the pipe material and ASTM A105 for the flange forging, with the microstructure being typical ferritic/pearlitic for carbon steel (similar to the Valero components).

2. The IOR component was removed from service due to leakage from a circumferentially oriented through-wall crack approximately 15/16" long on the flange side of the weld at the ID surface. The crack initiated at the ID surface outside of the optically visible HAZ and propagated toward the OD surface remaining outside of the HAZ for its full extent.
3. There was normally appearing scale on the ID surface, which revealed oxygen, sulfur, silicon, manganese, and iron by EDS analysis, as anticipated.
4. In addition to the hardness and Charpy toughness evaluations an ASME Section IX bend test was conducted to assess if any unusual low ductility in the region adjacent to the crack would be revealed. This testing revealed no unexpected ductility response (20% outer-fiber strain) and thus the potential for strain-age cracking was not evident. Hardness traverses across the cracked region did not reveal any local hardening.
5. "Cryo-Cracking" to expose the crack surface and subsequent SEM examination did not reveal any unusual fracture surface features. The crack propagation was shown to be transgranular cleavage and intergranular separation. No evidence for fatigue influencing the crack propagation was evident.

6. No ID surface decarburization was found and no decarburization in the vicinity of the crack was found.
7. AWS/ISO diffusible hydrogen measurements, adjacent to the crack, revealed less than 2 ppm hydrogen. Hydrogen measured, in the same region, but from dissociated methane revealed that the methane content was less than 5 ppm. This result is in conjunction with the fact that SEM examination did not reveal cavities or voids indicating methane bubbles on the grain boundaries along the crack path.
8. EDS analysis on the crack surfaces revealed presence of oxygen, silicon, sulfur, manganese, iron with a level of sulfur (2 wt. %).
9. The above determinations indicate that the IOR flange cracking morphology does not fit any of the traditional HTHA characteristics. This cracking is virtually identical to that shown for the Valero flange-to-pipe component (#67) cracking and the same factors described for the Valero incident would be operative for the IOR cracking incident.

6.3 Phillips 66 (P66) Alliance Highway Submissions

The Phillips components were in operation for 6 years at 670°F with a hydrogen partial pressure of 83 psia. Phillips 66 submitted flange-to-pipe

welded components (#555-S1 and #555-S2) after inspection by Phillips using AUBT, Spectrum Analysis, Velocity Ratio, and Phase Array techniques that did not detect any discontinuities in the weld regions. Like-wise, a similar ultrasonic inspection at Tennessee also did not reveal any recordable indications.

1. The measured chemistry of both components showed that they fall within the ranges required by ASTM A106 Gr.B and ASTM A105 respectively for the pipe and flange base metals. The hardness measurements showed that the components conform (by conversion) to the tensile strength required of the respective pipe and flange materials. The grain size of both components is within the normal ASTM size range (6-7) for the pipe and forging material used.
2. Metallographic examination of the region on the flange, adjacent to the weld, revealed grain boundary microfissures in component #555-S1 but no discontinuities were found in component #555-S2. Thus, the majority of the measurements and examinations were conducted on component S1 since this was the only flange-to-pipe weld component to exhibit any discontinuities. The microfissures were readily visible in the as-polished condition for S1 but were difficult to define after etching except at high magnifications. The

maximum microfissure damaged region was adjacent to the ID surface. The microfissure damaged region extended to mid-wall.

3. No evidence for decarburization was found at the ID surface or in the vicinity of the microfissures.
4. SEM evaluation found grain boundary bubbles coupled with the microfissures. The bubbles/cavities were on the order of $\frac{1}{4}$ to $\frac{1}{2}$ μm in diameter and located on both ferrite-ferrite boundaries as well as along ferrite-pearlite colony boundaries. The link-up of the cavities along some boundaries indicates that definitive HTHA damage was in the early stages.
5. AWS/ISO diffusible hydrogen measurements revealed only 1 ppm of hydrogen and thus the hydrogen present as atomic hydrogen had escaped after the removal of the component from service. However, the hydrogen derived from the dissociation of methane yielded the result that the methane content was on the order of 28 ppm. This measurement is in line with the observation of bubbles along the boundaries coincident with the microfissuring.
6. The above-described attributes of the pipe-to-flange components indicate that they conform to the required specifications. Furthermore, the damage

sustained in terms of microfissures and the level of methane reveals that the ex-service condition of the S1 component fits the normal definition for HTHA. Subtle differences in the environment, stress, and/or temperature in the vicinity of component S2 may explain the lack of damage in S2.

7. The Ultrasonic NDE results, which did not show any damage or recordable indications in either component, reflects the current difficulty in finding HTHA damage at low levels or at the initiation stage of HTHA.

6.4 General Conclusions

1. Of the five Non-PWHT'ed carbon steel flange-to-pipe components critically examined, 2 were undamaged, 1 contained traditional HTHA damage and 2 revealed singular cracks originating in the flange base metal outside of the HAZ which propagated toward the OD surface resulting in leakage.
2. The HTHA damaged components exhibited the well-known characteristics of fissuring and the linking of the microfissures to form cracks in the HAZ adjacent to welds. General decarburization at the OD surface was not present in all cases of HTHA, but internal decarburization adjacent to fissures and cracks was observed. Methane bubble formation along the grain boundaries preceded the fissuring and linking of fissures to form microcracks. This

occurred under the operating conditions, which placed the carbon steel material in the region of the Nelson Diagram where API RP 941 can be interpreted to indicate no HTHA is to be expected.

3. For the two components (out of five) which developed singular cracks emanating from the flange side of the welded pipe-to-flange component, the cracks formed and propagated just outside of the visible HAZ, directly toward the OD surface. The specific reason for the formation and propagation of these cracks is difficult to ascertain, but the rationale is quite different than any form of traditional HTHA (not at all found related to these cracks). Absent the precise nature of the cracks, it is to be recognized that singular and straight discontinuities of this type should be easily detected by normal Ultrasonic NDE techniques. Furthermore, in the cases shown herein, the cracks are “short” (< 1” long) and they did not propagate circumferentially around the periphery of the component. They resulted in through-wall leakage, but did not propagate in a way so as to result in guillotine type of rupture (pipe break). At this juncture it would be with some speculation to assume that the cracks are in some way related only to the forging process as they did not follow the forging pattern in the

microstructure and they appeared to be free of corrosion products at the crack tip. Hydrogen may have been associated with the propagation of these types of cracks since hydrogen lowers the energy for crack formation, but a further driving force must be present. This driving force may or may not be the residual stress state of the Non-PWHT'd welds. Therefore, this type of cracking requires greater study. However, this type of crack should be recognized for carbon steels in high temperature hydrogen service and the API RP 941 committee should consider defining this occurrence in addition to traditional HTHA.

Chapter 7 – Future Studies

The damage in all the three components was observed in the base metal just outside of the visible heat-affected zone. The susceptibility of the region just outside of the visible HAZ is an area that should be pursued. Gleeble may be utilized to simulate the weld thermal cycle of the susceptible region just outside of the visible for further fine scale microstructural examination.

The earlier studies at the University of Tennessee by Lundin et. al on C-1/2 Mo steel showed the degradation of toughness behavior during service. The studied showed that the toughness decreased with the increase in the hydrogen damage ³⁹. Toughness is an important material parameter to be taken into consideration for service performance to evaluate resistance against brittle/low ductility fracture. Toughness is an important material property for a hydrogen environment. Toughness is an ability of material to absorb energy and deform without fracture. Upper shelf temperature and ductile to brittle temperature (DBTT) are affected by composition, microstructure, and possible degradation in service. During startup and shut down, the DBTT is of key importance in avoiding any failures of pressure vessel steels. Thus, the further understanding

toughness characteristics of materials used in hot hydrogen environment will be of great assistance in fitness-for-service evaluation to make run, repair and replace decisions for carbon and C-1/2 Mo steels used in pressure vessel and piping.

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Appendices

Appendix A – ASTM A105 “Standard Specification for Carbon Steel Forgings for Piping Applications”⁸⁶



Designation: A105/A105M – 11a

Endorsed by
Manufacturers Standardization Society
of the Valve and Fittings Industry
Used in USDOE-NE Standards

Standard Specification for Carbon Steel Forgings for Piping Applications¹

This standard is issued under the fixed designation A105/A105M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This specification² covers forged carbon steel piping components for ambient- and higher-temperature service in pressure systems. Included are flanges, fittings, valves, and similar parts ordered either to dimensions specified by the purchaser or to dimensional standards such as the MSS, ASME, and API specifications referenced in Section 2. Forgings made to this specification are limited to a maximum weight of 10 000 lb [4540 kg]. Larger forgings may be ordered to Specification A266/A266M. Tubesheets and hollow cylindrical forgings for pressure vessel shells are not included within the scope of this specification. Although this specification covers some piping components machined from rolled bar and seamless tubular products (see 4.2), it does not cover raw material produced in these product forms.

1.2 Supplementary requirements are provided for use when additional testing or inspection is desired. These shall apply only when specified individually by the purchaser in the order.

1.3 Specification A266/A266M covers other steel forgings and Specifications A675/A675M and A696 cover other steel bars.

1.4 This specification is expressed in both inch-pound units and SI units. However, unless the order specifies the applicable “M” specification designation (SI units), the material shall be furnished to inch-pound units.

The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.5 The values stated in either SI units or inch-pound units are to be regarded separately as standard. Within the text, the SI units are shown in brackets. The values stated in each

system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

NOTE 1—The dimensionless designator NPS (nominal pipe size) has been substituted in this standard for such traditional terms as “nominal diameter,” “size,” and “nominal size.”

2. Referenced Documents

2.1 In addition to those reference documents listed in Specification A961/A961M, the following list of standards apply to this specification:

2.2 ASTM Standards:³

A266/A266M Specification for Carbon Steel Forgings for Pressure Vessel Components

A675/A675M Specification for Steel Bars, Carbon, Hot-Wrought, Special Quality, Mechanical Properties

A696 Specification for Steel Bars, Carbon, Hot-Wrought or Cold-Finished, Special Quality, for Pressure Piping Components

A788/A788M Specification for Steel Forgings, General Requirements

A961/A961M Specification for Common Requirements for Steel Flanges, Forged Fittings, Valves, and Parts for Piping Applications

2.3 MSS Standards:

SP 44 Standard for Steel Pipe Line Flanges⁴

2.4 ASME Standards:

B16.5 Dimensional Standards for Steel Pipe Flanges and Flanged Fittings⁵

B16.9 Wrought Steel Buttwelding Fittings⁵

B16.10 Face-to-Face and End-to-End Dimensions of Ferrous Valves⁵

¹ This specification is under the jurisdiction of ASTM Committee A01 on Steel, Stainless Steel and Related Alloys and is the direct responsibility of Subcommittee A01.22 on Steel Forgings and Wrought Fittings for Piping Applications and Bolting Materials for Piping and Special Purpose Applications.

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² For ASME Boiler and Pressure Vessel Code applications see related Specification SA-105 in Section II of that Code.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Available from Manufacturers Standardization Society of the Valve and Fittings Industry (MSS), 127 Park St., NE, Vienna, VA 22180-4602, <http://www.mss-hq.com>.

⁵ Available from American Society of Mechanical Engineers (ASME), ASME International Headquarters, Three Park Ave., New York, NY 10016-5990, <http://www.asme.org>.

*A Summary of Changes section appears at the end of this standard.

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 A105/A105M – 11a

B16.11 Forged Steel Fittings, Socket Weld, and Threaded⁵
B16.34 Valves-Flanged, Threaded and Welding End⁵
 B16.47 Large Diameter Steel Flanges⁵
 2.5 *ASME Boiler and Pressure Vessel Code*:
 Section IX Welding Qualifications⁵
 2.6 *API Standards*:
 API-600 Flanged and Butt-Welding-End Steel Gate Valves⁶
 API-602 Compact Design Carbon Steel Gate Valves for
 Refinery Use⁶

3. Ordering Information

3.1 See Specification **A961/A961M**.
 3.1.1 Additional requirements (see 12.2).

4. General Requirements

4.1 Product furnished to this specification shall conform to the requirements of Specification **A961/A961M**, including any supplementary requirements that are indicated in the purchase order. Failure to comply with the requirements of Specification **A961/A961M** constitutes nonconformance with this specification. In case of a conflict between the requirements of this specification and Specification **A961/A961M**, this specification shall prevail.

4.2 Except as permitted by Section 6 in Specification **A961/A961M**, the finished product shall be a forging as defined in the Terminology Section of Specification **A788/A788M**.

5. Heat Treatment

5.1 Heat treatment is not a mandatory requirement of this specification except for the following piping components:

5.1.1 Flanges above Class 300,⁷

5.1.2 Flanges of special design where the design pressure at the design temperature exceeds the pressure-temperature ratings of Class 300, Group 1.1,

5.1.3 Flanges of special design where the design pressure or design temperature are not known,

5.1.4 Piping components other than flanges which meet both of the following criteria: (1) over NPS 4 and (2) above Class 300, and

5.1.5 Piping components of Special Class⁸ other than flanges which meet both of the following criteria: (1) over NPS 4 and (2) when the working pressure at the operating temperature exceeds the tabulated values for Special Class 300, Group 1.1.

5.2 Heat treatment, when required by 5.1 shall be annealing, normalizing, or normalizing and tempering or quenching and tempering in accordance with Specification **A961/A961M**.

6. Chemical Composition

6.1 The steel shall conform to the chemical requirements specified in Table 1.

6.2 Steels to which lead has been added shall not be used.

TABLE 1 Chemical Requirements

NOTE—For each reduction of 0.01 % below the specified carbon maximum (0.35 %), an increase of 0.06 % manganese above the specified maximum (1.05 %) will be permitted up to a maximum of 1.65 %.

Element	Composition, %
Carbon	0.35 max
Manganese	0.60–1.05
Phosphorus	0.035 max
Sulfur	0.040 max
Silicon	0.10–0.35
Copper	0.40 max ^A
Nickel	0.40 max ^A
Chromium	0.30 max ^{A,B}
Molybdenum	0.12 max ^{A,B}
Vanadium	0.08 max

^A The sum of copper, nickel, chromium, molybdenum and vanadium shall not exceed 1.00 %.

^B The sum of chromium and molybdenum shall not exceed 0.32 %.

7. Mechanical Properties

7.1 The material shall conform to the mechanical property requirements prescribed in Table 2 and Table 3.

7.2 For normalized, normalized and tempered, or quenched and tempered forgings, the central axis of the test specimen shall correspond to the $\frac{1}{4} T$ plane or deeper position, where T is the maximum heat-treated thickness of the represented forging. In addition, for quenched and tempered forgings, the midlength of the test specimen shall be at least T from any second heat-treated surface. When section thickness does not permit this positioning, the test specimen shall be positioned as near as possible to the prescribed location.

7.3 *Tension Tests*:

7.3.1 One tension test shall be made for each heat of as-forged components.

7.3.2 One tension test shall be made from each heat-treating charge. If more than one heat is included in such a charge, each heat shall be tested.

7.3.2.1 When the heat-treating temperatures are the same and the furnaces (either batch or continuous type), are controlled within $\pm 25^\circ\text{F}$ [$\pm 14^\circ\text{C}$] and equipped with recording pyrometers so that complete records of heat treatment are available, then one tension test from each heat is required

TABLE 2 Mechanical Requirements^A

Tensile strength, min, psi [MPa]	70 000 [485]
Yield strength, min, psi [MPa] ^B	36 000 [250]
Elongation in 2 in. or 50 mm, min, %	
Basic minimum elongation for walls $\frac{1}{16}$ in. [7.9 mm] and over in thickness, strip tests	30
When standard round 2-in. or 50-mm gage length or smaller proportionally sized specimen with the gage length equal to 4D is used	22
For strip tests, a deduction for each $\frac{1}{16}$ -in. [0.8-mm] decrease in wall thickness below $\frac{1}{16}$ in. [7.9 mm] from the basic minimum elongation of the percentage points of Table 3	1.50 ^C
Reduction of area, min, % ^D	30
Hardness, HBW, max	187

^A For small forgings, see 7.3.4.

^B Determined by either the 0.2 % offset method or the 0.5 % extension-under-load method.

^C See Table 3 for computed minimum values.

^D For round specimens only.



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TABLE 3 Computed Minimum Values

Wall Thickness		Elongation in 2 in. or 50
in.	mm	mm, min, %
5/16 (0.312)	7.9	30.00
3/8 (0.281)	7.1	28.50
1/4 (0.250)	6.4	27.00
7/32 (0.219)	5.6	25.50
3/16 (0.188)	4.8	24.00
5/32 (0.156)	4.0	22.50
1/8 (0.125)	3.2	21.00
3/32 (0.094)	2.4	19.50
1/16 (0.062)	1.6	18.00

Note—The above table gives the computed minimum elongation values for each 1/2-in. [0.8-mm] decrease in wall thickness. Where the wall thickness lies between two values shown above, the minimum elongation value is determined by the following equation:

$$E = 48T + 15.00$$

where:

E = elongation in 2 in. or 50 mm, %, and
 T = actual thickness of specimen, in. [mm].

instead of one test from each heat in each heat-treatment charge. The test specimen material shall be included with a furnace charge.

7.3.3 Testing shall be performed as specified in Specification A961/A961M. The largest feasible round specimen shall be used except when hollow cylindrically shaped parts are machined from seamless tubulars. When hollow cylindrically shaped parts are machined from seamless tubular materials, strip tests may be used.

7.3.4 Forgings too small to permit obtaining a subsized specimen of 0.250 in. [6.35 mm] diameter or larger parallel to the dimension of maximum working, and produced in equipment unsuitable for the production of a separately forged test bar such as an automatic or semi-automatic press, may be accepted on the basis of hardness only. One percent of the forgings per lot (see Note 2), or ten forgings, whichever is the lesser number, shall be selected at random, prepared, and tested using the standard Brinell test. The locations of the indentations shall be at the option of the manufacturer but shall be selected to be representative of the forging as a whole. One indentation per forging shall be required but additional indentations may be made to establish the representative hardness. The hardness of all forgings so tested shall be 137 to 187 HBW inclusive.

NOTE 2—A lot is defined as the product from a mill heat or if heat treated, the product of a mill heat per furnace charge.

7.4 Hardness Tests:

7.4.1 Two hardness tests shall be made for each heat of as-forged components. When more than one forging is produced from each heat, a minimum of two forgings shall be tested with one reading from each forging. When only one forging is produced, it shall be tested in two locations.

7.4.2 Except when only one forging is produced, a minimum of two forgings shall be hardness tested per batch or continuous run as defined in 7.3.2.1 to ensure that forgings are within the hardness limits given in Table 2. When only one forging is produced, it shall be hardness tested in two locations to ensure it is within the hardness limits given in Table 2.

7.4.3 Testing shall be as specified in Specification A961/A961M. The purchaser may verify that the requirement has been met by testing at any location on the forging, provided such testing does not render the forging useless.

8. Hydrostatic Tests

8.1 Such tests shall be conducted by the forging manufacturer only when Supplementary Requirement S57 in Specification A961/A961M is specified.

9. Retreatment

9.1 If the results of the mechanical tests do not conform to the requirement specified, the manufacturer may heat treat or reheat treat the forgings as applicable and repeat the test specified in Section 7.

10. Repair by Welding

10.1 Repair of defects by the manufacturer is permissible for forgings made to dimensional standards such as those of ASME or for other parts made for stock by the manufacturer. Prior approval of the purchaser is required to repair-weld special forgings made to the purchaser's requirements.

10.2 Weld repairs shall be made by a process that does not produce undesirably high levels of hydrogen in the welded areas.

10.3 All forgings repaired by welding shall be post-weld heat treated between 1100 °F [593 °C] and the lower transformation temperature for a minimum of 1/2 h/in. [1/2 h/25.4 mm] of maximum section thickness, or alternatively annealed, normalized and tempered, or quenched and tempered. If the forging was not previously heat treated, the original tempering temperature was exceeded, or the forging was fully heat treated in the post weld cycle, then the forging shall be tested in accordance with Section 7 on completion of the cycle.

10.4 The mechanical properties of the procedure-qualification weldment shall, when tested in accordance with Section IX of the ASME Boiler and Pressure Vessel Code, conform with the requirements listed in Table 2 for the thermal condition of repair-welded forgings.

11. Rejection and Reheating

11.1 Each forging that develops injurious defects during shop working or application shall be rejected and the manufacturer notified.

12. Certification

12.1 *Identification Marking*—For forgings made to specified dimensions, when agreed upon by the purchaser, and for forgings made to dimensional standards, application of identification marks as required in Specification A961/A961M shall be the certification that the forgings have been furnished in accordance with the requirements of this specification. The specification designation included on test reports shall include year date and revision letter, if any.

12.2 *Test Reports*—When test reports are required, the manufacturer shall also provide the following, where applicable:

12.2.1 Type heat treatment, Section 5,


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12.2.2 Tensile property results, Section 7 (Table 2), report the yield strength and ultimate strength, in ksi [MPa], elongation and reduction in area, in percent; and, if longitudinal strip tension specimens are used, report the width of the gage length,

12.2.3 Chemical analysis results, Section 6 (Table 1). Reported results shall be to the same number of significant figures as the limits specified in Table 1 for that element.

12.2.4 Hardness results, Section 7 (Table 2), a minimum of two readings, and

12.2.5 Any supplementary testing required by the purchase order.

13. Product Marking

13.1 If the forgings have been quenched and tempered, the letters “QT” shall be stamped on the forgings following this specification number.

13.2 Forgings repaired by welding shall be marked with the letter “W” following this specification number.

13.3 When test reports are required for larger products, the markings shall consist of the manufacturer’s symbol or name,

this specification number, and such other markings as necessary to identify the part with the test report (13.1 and 13.2 shall apply). The specification number marked on the forgings need not include specification year date and revision letter.

13.4 *Bar Coding*—In addition to the requirements in Specification A961/A961M and 13.3, bar coding is acceptable as a supplemental identification method. The purchaser may specify in the order a specific bar coding system to be used. The bar coding system, if applied at the discretion of the supplier, should be consistent with one of the published industry standards for bar coding. If used on small parts, the bar code may be applied to the box or a substantially applied tag.

14. Keywords

14.1 pipe fittings, steel; piping applications; pressure containing parts; steel flanges; steel forgings, carbon; steel valves; temperature service applications, elevated; temperature service applications, high

SUPPLEMENTARY REQUIREMENTS

The following supplementary requirements shall apply only when specified by the purchaser in the inquiry, contract, and order.

S1. Hardness

S1.1 The purchaser may check the hardness of any or all forgings supplied at any location on the forging and the hardness shall be 137 to 187 HBW. All forgings not within the specified hardness range shall be rejected.

S2. Heat Treatment

S2.1 All forgings shall be heat treated as specified by the purchaser.

S2.2 When forgings not requiring heat treatment by 5.1 are supplied heat treated by purchaser request, the basis for determining conformance with Table 2 and Table 3 shall be hardness testing per 7.4 and either (1) tensile testing of heat treated forgings per 7.2, or (2) tensile tests from as-forged forgings or separately forged test blanks, as agreed upon between the supplier and purchaser.

S2.3 When test reports are required, and tensile test results were obtained from as-forged forgings or as-forged test blanks, it shall be so indicated on the test report.

S2.4 In addition to the marking required by Section 13, this specification shall be followed by the letter: A for annealed, N for normalized, NT for normalized and tempered, or QT for quenched and tempered, as appropriate.

S3. Marking Small Forgings

S3.1 For small products where the space for marking is less than 1 in. [25 mm] in any direction, test reports are mandatory and marking may be restricted to only such symbols or codes as are necessary to identify the parts with test reports.

S3.2 When the configuration or size does not permit marking directly on the forging, the marking method shall be a matter of agreement between the manufacturer and the purchaser.

S4. Carbon Equivalent

S4.1 The maximum carbon equivalent, based on heat analysis, shall be 0.47 for forgings with a maximum section thickness of 2 in. or less, and 0.48 for forgings with a maximum section thickness of greater than 2 in.

S4.2 Determine the carbon equivalent (CE) as follows:

$$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$$

S4.3 A lower maximum carbon equivalent may be agreed upon between the supplier and the purchaser.

Appendix B - ASTM A106 “Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service”⁸⁷



Designation: A106/A106M – 11

Used in USDOE-NE standards

Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service¹

This standard is issued under the fixed designation A106/A106M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This specification² covers seamless carbon steel pipe for high-temperature service (Note 1) in NPS ½ to NPS 48 [DN 6 to DN 1200] (Note 2) inclusive, with nominal (average) wall thickness as given in ASME B 36.10M. It shall be permissible to furnish pipe having other dimensions provided such pipe complies with all other requirements of this specification. Pipe ordered under this specification shall be suitable for bending, flanging, and similar forming operations, and for welding. When the steel is to be welded, it is presupposed that a welding procedure suitable to the grade of steel and intended use or service will be utilized.

NOTE 1—It is suggested, consideration be given to possible graphitization.

NOTE 2—The dimensionless designator NPS (nominal pipe size) [DN (diameter nominal)] has been substituted in this standard for such traditional terms as “nominal diameter,” “size,” and “nominal size.”

1.2 Supplementary requirements of an optional nature are provided for seamless pipe intended for use in applications where a superior grade of pipe is required. These supplementary requirements call for additional tests to be made and when desired shall be so stated in the order.

1.3 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.4 The following precautionary caveat pertains only to the test method portion, Sections 11, 12, and 13 of this specification: *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

¹ This specification is under the jurisdiction of Committee A01 on Steel, Stainless Steel and Related Alloys and is the direct responsibility of Subcommittee A01.09 on Carbon Steel Tubular Products.

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² For ASME Boiler and Pressure Vessel Code applications see related Specifications SA-106 in Section II of that Code.

2. Referenced Documents

2.1 ASTM Standards:³

A530/A530M Specification for General Requirements for Specialized Carbon and Alloy Steel Pipe

E213 Practice for Ultrasonic Testing of Metal Pipe and Tubing

E309 Practice for Eddy-Current Examination of Steel Tubular Products Using Magnetic Saturation

E381 Method of Macroetch Testing Steel Bars, Billets, Blooms, and Forgings

E570 Practice for Flux Leakage Examination of Ferromagnetic Steel Tubular Products

2.2 ASME Standard:

ASME B 36.10M Welded and Seamless Wrought Steel Pipe⁴

2.3 Military Standards:

MIL-STD-129 Marking for Shipment and Storage⁵

MIL-STD-163 Steel Mill Products, Preparation for Shipment and Storage⁵

2.4 Federal Standard:

Fed. Std. No. 123 Marking for Shipments (Civil Agencies)⁵

Fed. Std. No. 183 Continuous Identification Marking of Iron and Steel Products⁵

2.5 Other Standards:

SSPC-SP 6 Surface Preparation Specification No. 6⁶

3. Ordering Information

3.1 The inclusion of the following, as required will describe the desired material adequately, when ordered under this specification:

3.1.1 Quantity (feet, metres, or number of lengths),

3.1.2 Name of material (seamless carbon steel pipe),

3.1.3 Grade (Table 1),

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Available from American Society of Mechanical Engineers (ASME), ASME International Headquarters, Three Park Ave., New York, NY 10016-5990, http://www.asme.org.

⁵ Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098.

⁶ Available from Society for Protective Coatings (SSPC), 40 24th St., 6th Floor, Pittsburgh, PA 15222-4656, http://www.sspc.org.

*A Summary of Changes section appears at the end of this standard.

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TABLE 1 Chemical Requirements

	Composition, %		
	Grade A	Grade B	Grade C
Carbon, max	0.25 ^A	0.30 ^B	0.35 ^B
Manganese	0.27–0.93	0.29–1.06	0.29–1.06
Phosphorus, max	0.035	0.035	0.035
Sulfur, max	0.035	0.035	0.035
Silicon, min	0.10	0.10	0.10
Chrome, max ^C	0.40	0.40	0.40
Copper, max ^C	0.40	0.40	0.40
Molybdenum, max ^C	0.15	0.15	0.15
Nickel, max ^C	0.40	0.40	0.40
Vanadium, max ^C	0.08	0.08	0.08

^A For each reduction of 0.01 % below the specified carbon maximum, an increase of 0.06 % manganese above the specified maximum will be permitted up to a maximum of 1.35 %.

^B Unless otherwise specified by the purchaser, for each reduction of 0.01 % below the specified carbon maximum, an increase of 0.06 % manganese above the specified maximum will be permitted up to a maximum of 1.65 %.

^C These five elements combined shall not exceed 1 %.

3.1.4 Manufacture (hot-finished or cold-drawn),

3.1.5 Size (NPS [DN] and weight class or schedule number, or both; outside diameter and nominal wall thickness; or inside diameter and nominal wall thickness),

3.1.6 Special outside diameter tolerance pipe (16.2.2),

3.1.7 Inside diameter tolerance pipe, over 10 in. [250 mm] ID (16.2.3),

3.1.8 Length (specific or random, Section 17),

3.1.9 Optional requirements (Section 9 and S1 to S8),

3.1.10 Test report required (Section on Certification of Specification A530/A530M),

3.1.11 Specification designation (A106 or A106M, including year-date),

3.1.12 End use of material,

3.1.13 Hydrostatic test in accordance with Specification A530/A530M or 13.3 of this specification, or NDE in accordance with Section 14 of this specification.

3.1.14 Special requirements.

4. Process

4.1 The steel shall be killed steel, with the primary melting process being open-hearth, basic-oxygen, or electric-furnace, possibly combined with separate degassing or refining. If secondary melting, using electroslag remelting or vacuum-arc remelting is subsequently employed, the heat shall be defined as all of the ingots remelted from a single primary heat.

4.2 Steel cast in ingots or strand cast is permissible. When steels of different grades are sequentially strand cast, identification of the resultant transition material is required. The producer shall remove the transition material by any established procedure that positively separates the grades.

4.3 For pipe NPS 1½ [DN 40] and under, it shall be permissible to furnish hot finished or cold drawn.

4.4 Unless otherwise specified, pipe NPS 2 [DN 50] and over shall be furnished hot finished. When agreed upon between the manufacturer and the purchaser, it is permissible to furnish cold-drawn pipe.

5. Heat Treatment

5.1 Hot-finished pipe need not be heat treated. When hot-finished pipe is heat treated, it shall be heat treated at a temperature of 1200 °F (650 °C) or higher.

5.2 Cold-drawn pipe shall be heat treated after the final cold draw pass at a temperature of 1200 °F (650 °C) or higher.

6. General Requirements

6.1 Material furnished to this specification shall conform to the applicable requirements of the current edition of Specification A530/A530M unless otherwise provided herein.

7. Chemical Composition

7.1 The steel shall conform to the requirements as to chemical composition prescribed in Table 1.

8. Heat Analysis

8.1 An analysis of each heat of steel shall be made by the steel manufacturer to determine the percentages of the elements specified in Section 7. If the secondary melting processes of 5.1 are employed, the heat analysis shall be obtained from one remelted ingot or the product of one remelted ingot of each primary melt. The chemical composition thus determined, or that determined from a product analysis made by the manufacturer, if the latter has not manufactured the steel, shall be reported to the purchaser or the purchaser's representative, and shall conform to the requirements specified in Section 7.

9. Product Analysis

9.1 At the request of the purchaser, analyses of two pipes from each lot (see 20.1) shall be made by the manufacturer from the finished pipe. The results of these analyses shall be reported to the purchaser or the purchaser's representative and shall conform to the requirements specified in Section 7.

9.2 If the analysis of one of the tests specified in 9.1 does not conform to the requirements specified in Section 7, analyses shall be made on additional pipes of double the original number from the same lot, each of which shall conform to requirements specified.

10. Tensile Requirements

10.1 The material shall conform to the requirements as to tensile properties given in Table 2.

11. Bending Requirements

11.1 For pipe NPS 2 [DN 50] and under, a sufficient length of pipe shall stand being bent cold through 90° around a cylindrical mandrel, the diameter of which is twelve times the outside diameter (as shown in ASME B 36.10M) of the pipe, without developing cracks. When ordered for close coiling, the pipe shall stand being bent cold through 180° around a cylindrical mandrel, the diameter of which is eight times the outside diameter (as shown in ASME B 36.10M) of the pipe, without failure.

11.2 For pipe whose diameter exceeds 25 in. [635 mm] and whose diameter to wall thickness ratio, where the diameter to wall thickness ratio is the specified outside diameter divided by the nominal wall thickness, is 7.0 or less, the bend test shall be conducted. The bend test specimens shall be bent at room temperature through 180° with the inside diameter of the bend being 1 in. [25 mm] without cracking on the outside portion of the bent portion.

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TABLE 2 Tensile Requirements

	Grade A		Grade B		Grade C	
Tensile strength, min, psi [MPa]	48 000 [330]		60 000 [415]		70 000 [485]	
Yield strength, min, psi [MPa]	30 000 [205]		35 000 [240]		40 000 [275]	
	Longitu- dinal	Transverse	Longitu- dinal	Transverse	Longitu- dinal	Transverse
Elongation in 2 in. [50 mm], min, %:						
Basic minimum elongation transverse strip tests, and for all small sizes tested in full section	35	25	30	16.5	30	16.5
When standard round 2-in. [50-mm] gage length test specimen is used	28	20	22	12	20	12
For longitudinal strip tests	A		A		A	
For transverse strip tests, a deduction for each ½-in. [0.8-mm] decrease in wall thickness below ¼ in. [7.9 mm] from the basic minimum elongation of the following percentage shall be made		1.25		1.00		1.00

^A The minimum elongation in 2 in. [50 mm] shall be determined by the following equation:

$$e = 625\ 000A^{0.2} / U^{0.9}$$

for inch-pound units, and

$$e = 1\ 940A^{0.2} / U^{0.9}$$

for SI units,

where:

e = minimum elongation in 2 in. [50 mm], %, rounded to the nearest 0.5 %,

A = cross-sectional area of the tension test specimen, in.² [mm²], based upon specified outside diameter or nominal specimen width and specified wall thickness, rounded to the nearest 0.01 in.² [1 mm²]. (If the area thus calculated is equal to or greater than 0.75 in.² [500 mm²], then the value 0.75 in.² [500 mm²] shall be used), and

U = specified tensile strength, psi [MPa].

Example: For 28 in. [711 mm] diameter 5.000 in. [127 mm] thick pipe the diameter to wall thickness ratio = 28/5 = 5.6 [711/127 = 5.6].

12. Flattening Tests

12.1 Although testing is not required, pipe shall be capable of meeting the flattening test requirements of Supplementary Requirement S3, if tested.

13. Hydrostatic Test

13.1 Except as allowed by 13.2, 13.3, and 13.4, each length of pipe shall be subjected to the hydrostatic test without leakage through the pipe wall.

13.2 As an alternative to the hydrostatic test at the option of the manufacturer or where specified in the purchase order, it shall be permissible for the full body of each pipe to be tested with a nondestructive electric test described in Section 14.

13.3 Where specified in the purchase order, it shall be permissible for pipe to be furnished without the hydrostatic test and without the nondestructive electric test in Section 14; in this case, each length so furnished shall include the mandatory marking of the letters “NH.” It shall be permissible for pipe meeting the requirements of 13.1 or 13.2 to be furnished where pipe without either the hydrostatic or nondestructive electric test has been specified in the purchase order; in this case, such pipe need not be marked with the letters “NH.” Pipe that has failed either the hydrostatic test of 13.1 or the nondestructive electric test of 13.2 shall not be furnished as “NH” pipe.

13.4 Where the hydrostatic test and the nondestructive electric test are omitted and the lengths marked with the letters “NH,” the certification, where required, shall clearly state “Not Hydrostatically Tested,” and the letters “NH” shall be ap-

pended to the product specification number and material grade shown on the certification.

14. Nondestructive Electric Test

14.1 As an alternative to the hydrostatic test at the option of the manufacturer or where specified in the purchase order as an alternative or addition to the hydrostatic test, the full body of each pipe shall be tested with a nondestructive electric test in accordance with Practice E213, E309, or E570. In such cases, the marking of each length of pipe so furnished shall include the letters “NDE.” It is the intent of this nondestructive electric test to reject pipe with imperfections that produce test signals equal to or greater than that produced by the applicable calibration standard.

14.2 Where the nondestructive electric test is performed, the lengths shall be marked with the letters “NDE.” The certification, where required, shall state “Nondestructive Electric Tested” and shall indicate which of the tests was applied. Also, the letters “NDE” shall be appended to the product specification number and material grade shown on the certification.

14.3 The following information is for the benefit of the user of this specification:

14.3.1 The reference standards defined in 14.4 through 14.6 are convenient standards for calibration of nondestructive testing equipment. The dimensions of such standards are not to be construed as the minimum sizes of imperfections detectable by such equipment.

14.3.2 The ultrasonic testing referred to in this specification is capable of detecting the presence and location of significant longitudinally or circumferentially oriented imperfections; however, different techniques need to be employed for the

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detection of such differently oriented imperfections. Ultrasonic testing is not necessarily capable of detecting short, deep imperfections.

14.3.3 The eddy current examination referenced in this specification has the capability of detecting significant imperfections, especially of the short abrupt type.

14.3.4 The flux leakage examination referred to in this specification is capable of detecting the presence and location of significant longitudinally or transversely oriented imperfections; however, different techniques need to be employed for the detection of such differently oriented imperfections.

14.3.5 The hydrostatic test referred to in Section 13 has the capability of finding defects of a size permitting the test fluid to leak through the tube wall and may be either visually seen or detected by a loss of pressure. Hydrostatic testing is not necessarily capable of detecting very tight, through-the-wall imperfections or imperfections that extend an appreciable distance into the wall without complete penetration.

14.3.6 A purchaser interested in ascertaining the nature (type, size, location, and orientation) of discontinuities that can be detected in the specific applications of these examinations is directed to discuss this with the manufacturer of the tubular product.

14.4 For ultrasonic testing, the calibration reference notches shall be, at the option of the producer, any one of the three common notch shapes shown in Practice E213. The depth of notch shall not exceed $12\frac{1}{2}\%$ of the specified wall thickness of the pipe or 0.004 in. [0.1 mm], whichever is greater.

14.5 For eddy current testing, the calibration pipe shall contain, at the option of the producer, any one of the following discontinuities to establish a minimum sensitivity level for rejection:

14.5.1 *Drilled Hole*—The calibration pipe shall contain depending upon the pipe diameter three holes spaced 120° apart or four holes spaced 90° apart and sufficiently separated longitudinally to ensure separately distinguishable responses. The holes shall be drilled radially and completely through the pipe wall, care being taken to avoid distortion of the pipe while drilling. Depending upon the pipe diameter the calibration pipe shall contain the following hole:

NPS	DN	Diameter of Drilled Hole
$\leq \frac{1}{8}$	≤ 15	0.039 in. [1 mm]
$> \frac{1}{8} \leq 1\frac{1}{4}$	$> 15 \leq 32$	0.055 in. [1.4 mm]
$> 1\frac{1}{4} \leq 2$	$> 32 \leq 50$	0.071 in. [1.8 mm]
$> 2 \leq 5$	$> 50 \leq 125$	0.087 in. [2.2 mm]
> 5	> 125	0.106 in. [2.7 mm]

14.5.2 *Transverse Tangential Notch*—Using a round tool or file with a $\frac{1}{4}$ -in. [6-mm] diameter, a notch shall be filed or milled tangential to the surface and transverse to the longitudinal axis of the pipe. The notch shall have a depth not exceeding $12\frac{1}{2}\%$ of the specified wall thickness of the pipe or 0.004 in. [0.1 mm], whichever is greater.

14.5.3 *Longitudinal Notch*—A notch 0.031 in. [0.8 mm] or less in width shall be machined in a radial plane parallel to the tube axis on the outside surface of the pipe, to have a depth not exceeding $12\frac{1}{2}\%$ of the specified wall thickness of the tube or 0.004 in. [0.1 mm], whichever is greater. The length of the notch shall be compatible with the testing method.

14.5.4 *Compatibility*—The discontinuity in the calibration pipe shall be compatible with the testing equipment and the method being used.

14.6 For flux leakage testing, the longitudinal calibration reference notches shall be straight-sided notches machined in a radial plane parallel to the pipe axis. For wall thicknesses under $\frac{1}{2}$ in. [12.7 mm], outside and inside notches shall be used; for wall thicknesses equal to and above $\frac{1}{2}$ in. [12.7 mm], only an outside notch shall be used. Notch depth shall not exceed $12\frac{1}{2}\%$ of the specified wall thickness, or 0.004 in. [0.1 mm], whichever is greater. Notch length shall not exceed 1 in. [25 mm], and the width shall not exceed the depth. Outside diameter and inside diameter notches shall be located sufficiently apart to allow separation and identification of the signals.

14.7 Pipe containing one or more imperfections that produce a signal equal to or greater than the signal produced by the calibration standard shall be rejected or the area producing the signal shall be reexamined.

14.7.1 Test signals produced by imperfections which cannot be identified, or produced by cracks or crack-like imperfections

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shall result in rejection of the pipe, unless it is repaired and retested. To be accepted, the pipe must pass the same specification test to which it was originally subjected, provided that the remaining wall thickness is not decreased below that permitted by this specification. The OD at the point of grinding may be reduced by the amount so reduced.

14.7.2 Test signals produced by visual imperfections such as those listed below may be evaluated in accordance with the provisions of Section 18:

- 14.7.2.1 Dinges,
- 14.7.2.2 Straightener marks,
- 14.7.2.3 Cutting chips,
- 14.7.2.4 Scratches,
- 14.7.2.5 Steel die stamps,
- 14.7.2.6 Stop marks, or
- 14.7.2.7 Pipe reducer ripple.

14.8 The test methods described in this section are not necessarily capable of inspecting the end portion of pipes, a condition referred to as “end effect.” The length of such end effect shall be determined by the manufacturer and, when specified in the purchase order, reported to the purchaser.

15. Nipples

15.1 Nipples shall be cut from pipe of the same dimensions and quality described in this specification.

16. Dimensions, Mass, and Permissible Variations

16.1 *Mass*—The mass of any length of pipe shall not vary more than 10 % over and 3.5 % under that specified. Unless otherwise agreed upon between the manufacturer and the purchaser, pipe in NPS 4 [DN 100] and smaller may be weighed in convenient lots; pipe larger than NPS 4 [DN 100] shall be weighed separately.

16.2 *Diameter*—Except as provided for thin-wall pipe in paragraph 11.2 of Specification A530/A530M, the tolerances for diameter shall be in accordance with the following:

16.2.1 Except for pipe ordered as special outside diameter tolerance pipe or as inside diameter tolerance pipe, variations in outside diameter shall not exceed those given in Table 3.

TABLE 3 Variations in Outside Diameter

NPS [DN Designator]	Permissible Variations in Outside Diameter			
	Over		Under	
	in.	mm	in.	mm
½ to 1½ [6 to 40], incl	⅛ ₆₄ (0.015)	0.4	⅛ ₆₄ (0.015)	0.4
Over 1½ to 4 [40 to 100], incl	⅛ ₃₂ (0.031)	0.8	⅛ ₃₂ (0.031)	0.8
Over 4 to 8 [100 to 200], incl	⅛ ₁₆ (0.062)	1.6	⅛ ₃₂ (0.031)	0.8
Over 8 to 18 [200 to 450], incl	⅜ ₃₂ (0.093)	2.4	⅛ ₃₂ (0.031)	0.8
Over 18 to 26 [450 to 650], incl	⅛ (0.125)	3.2	⅛ ₃₂ (0.031)	0.8
Over 26 to 34 [650 to 850], incl	⅜ ₃₂ (0.156)	4.0	⅛ ₃₂ (0.031)	0.8
Over 34 to 48 [850 to 1200], incl	⅜ ₁₆ (0.187)	4.8	⅛ ₃₂ (0.031)	0.8

16.2.2 For pipe over 10 in. [250 mm] OD ordered as special outside diameter tolerance pipe, the outside diameter shall not vary more than 1 % over or 1 % under the specified outside diameter.

16.2.3 For pipe over 10 in. [250 mm] ID ordered as inside diameter tolerance pipe, the inside diameter shall not vary more than 1 % over or 1 % under the specified inside diameter.

16.3 *Thickness*—The minimum wall thickness at any point shall not be more than 12.5 % under the specified wall thickness.

17. Lengths

17.1 Pipe lengths shall be in accordance with the following regular practice:

17.1.1 The lengths required shall be specified in the order, and

17.1.2 No jointers are permitted unless otherwise specified.

17.1.3 If definite lengths are not required, pipe may be ordered in single random lengths of 16 to 22 ft [4.8 to 6.7 m] with 5 % 12 to 16 ft [3.7 to 4.8 m], or in double random lengths with a minimum average of 35 ft [10.7 m] and a minimum length of 22 ft [6.7 m] with 5 % 16 to 22 ft [4.8 to 6.7 m].

18. Workmanship, Finish and Appearance

18.1 The pipe manufacturer shall explore a sufficient number of visual surface imperfections to provide reasonable assurance that they have been properly evaluated with respect to depth. Exploration of all surface imperfections is not required but consideration should be given to the necessity of exploring all surface imperfections to assure compliance with 18.2.

18.2 Surface imperfections that penetrate more than 12½ % of the nominal wall thickness or encroach on the minimum wall thickness shall be considered defects. Pipe with such defects shall be given one of the following dispositions:

18.2.1 The defect shall be removed by grinding, provided that the remaining wall thickness is within the limits specified in 16.3.

18.2.2 Repaired in accordance with the repair welding provisions of 18.6.

18.2.3 The section of pipe containing the defect may be cut off within the limits of requirements on length.

18.2.4 Rejected.

18.3 To provide a workmanlike finish and basis for evaluating conformance with 18.2 the pipe manufacturer shall remove by grinding the following noninjurious imperfections:

18.3.1 Mechanical marks and abrasions—such as cable marks, dinges, guide marks, roll marks, ball scratches, scores, and die marks—and pits, any of which imperfections are deeper than ⅛ in. [1.6 mm].

18.3.2 Visual imperfections commonly referred to as scabs, seams, laps, tears, or slivers found by exploration in accordance with 18.1 to be deeper than 5 % of the nominal wall thickness.

18.4 At the purchaser's discretion, pipe shall be subjected to rejection if surface imperfections acceptable under 18.2 are not scattered, but appear over a large area in excess of what is

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considered a workmanlike finish. Disposition of such pipe shall be a matter of agreement between the manufacturer and the purchaser.

18.5 When imperfections or defects are removed by grinding, a smooth curved surface shall be maintained, and the wall thickness shall not be decreased below that permitted by this specification. The outside diameter at the point of grinding is permitted to be reduced by the amount so removed.

18.5.1 Wall thickness measurements shall be made with a mechanical caliper or with a properly calibrated nondestructive testing device of appropriate accuracy. In case of dispute, the measurement determined by use of the mechanical caliper shall govern.

18.6 Weld repair shall be permitted only subject to the approval of the purchaser and in accordance with Specification A530/A530M.

18.7 The finished pipe shall be reasonably straight.

19. End Finish

19.1 The Pipe shall be furnished to the following practice, unless otherwise specified.

19.1.1 *NPS 1½ [DN 40] and Smaller*—All walls shall be either plain-end square cut, or plain-end beveled at the option of the manufacturer.

19.1.2 *NPS 2 [DN 50] and Larger*—Walls through extra strong weights, shall be plain-end beveled.

19.1.3 *NPS 2 [DN 50] and Larger*—Walls over extra strong weights, shall be plain-end square cut.

19.2 Plain-end beveled pipe shall be plain-end pipe having a bevel angle of 30°, + 5° or - 0°, as measured from a line drawn perpendicular to the axis of the pipe with a root face of ⅛ ± ½ in. [1.6 ± 0.8 mm]. Other bevel angles may be specified by agreement between the purchaser and the manufacturer.

20. Sampling

20.1 For product analysis (see 9.1) and tensile tests (see 21.1), a lot is the number of lengths of the same size and wall thickness from any one heat of steel; of 400 lengths or fraction thereof, of each size up to, but not including, NPS 6 [DN 150]; and of 200 lengths or fraction thereof of each size NPS 6 [DN 150] and over.

20.2 For bend tests (see 21.2), a lot is the number of lengths of the same size and wall thickness from any one heat of steel, of 400 lengths or fraction thereof, of each size.

20.3 For flattening tests, a lot is the number of lengths of the same size and wall thickness from any one heat of steel, of 400 lengths or fraction thereof of each size over NPS 2 [DN 50], up to but not including NPS 6 [DN 150], and of 200 lengths or fraction thereof, of each size NPS 6 [DN 150] and over.

21. Number of Tests

21.1 The tensile requirements specified in Section 10 shall be determined on one length of pipe from each lot (see 20.1).

21.2 For pipe NPS 2 [DN 50] and under, the bend test specified in 11.1 shall be made on one pipe from each lot (see 20.2). The bend test, where used as required by 11.2, shall be made on one end of 5 % of the pipe from each lot. For small lots, at least one pipe shall be tested.

21.3 If any test specimen shows flaws or defective machining, it shall be permissible to discard it and substitute another test specimen.

22. Retests

22.1 If the percentage of elongation of any tension test specimen is less than that given in Table 1 and any part of the fracture is more than ¾ in. [19 mm] from the center of the gage length of a 2-in. [50-mm] specimen as indicated by scribe scratches marked on the specimen before testing, a retest shall be allowed. If a specimen breaks in an inside or outside surface flaw, a retest shall be allowed.

23. Test Specimens and Test Methods

23.1 On NPS 8 [DN 200] and larger, specimens cut either longitudinally or transversely shall be acceptable for the tension test. On sizes smaller than NPS 8 [DN 200], the longitudinal test only shall be used.

23.2 When round tension test specimens are used for pipe wall thicknesses over 1.0 in. [25.4 mm], the mid-length of the longitudinal axis of such test specimens shall be from a location midway between the inside and outside surfaces of the pipe.

23.3 Test specimens for the bend test specified in Section 11 and for the flattening tests shall consist of sections cut from a pipe. Specimens for flattening tests shall be smooth on the ends and free from burrs, except when made on crop ends.

23.4 Test specimens for the bend test specified in 11.2 shall be cut from one end of the pipe and, unless otherwise specified, shall be taken in a transverse direction. One test specimen shall be taken as close to the outer surface as possible and another from as close to the inner surface as possible. The specimens shall be either ½ by ½ in. [12.5 by 12.5 mm] in section or 1 by ½ in. [25 by 12.5 mm] in section with the corners rounded to a radius not over ⅛ in. [1.6 mm] and need not exceed 6 in. [150 mm] in length. The side of the samples placed in tension during the bend shall be the side closest to the inner and outer surface of the pipe respectively.

23.5 All routine check tests shall be made at room temperature.

24. Certification

24.1 When test reports are requested, in addition to the requirements of Specification A530/A530M, the producer or supplier shall furnish to the purchaser a chemical analysis report for the elements specified in Table 1.

25. Product Marking

25.1 In addition to the marking prescribed in Specification A530/A530M, the marking shall include heat number, the information as per Table 4, an additional symbol “S” if one or

TABLE 4 Marking

Hydro	NDE	Marking
Yes	No	Test Pressure
No	Yes	NDE
No	No	NH
Yes	Yes	Test Pressure/NDE

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more of the supplementary requirements apply; the length, OD 1 %, if ordered as special outside diameter tolerance pipe; ID 1 %, if ordered as special inside diameter tolerance pipe; the schedule number, weight class, or nominal wall thickness; and, for sizes larger than NPS 4 [DN 100], the weight. Length shall be marked in feet and tenths of a foot [metres to two decimal places], depending on the units to which the material was ordered, or other marking subject to agreement. For sizes NPS 1½, 1¼, 1, and ¾ [DN 40, 32, 25, and 20], each length shall be marked as prescribed in Specification **A530/A530M**. These sizes shall be bundled in accordance with standard mill practice and the total bundle footage marked on the bundle tag; individual lengths of pipe need not be marked with footage. For sizes less than NPS ¾ [DN 20], all the required markings shall be on the bundle tag or on each length of pipe and shall include the total footage; individual lengths of pipe need not be marked with footage. If not marked on the bundle tag, all required marking shall be on each length.

25.2 When pipe sections are cut into shorter lengths by a subsequent processor for resale as material, the processor shall transfer complete identifying information, including the name or brand of the manufacturer to each unmarked cut length, or to metal tags securely attached to bundles of unmarked small diameter pipe. The same material designation shall be included with the information transferred, and the processor's name, trademark, or brand shall be added.

25.3 *Bar Coding*—In addition to the requirements in 25.1 and 25.2, bar coding is acceptable as a supplementary identification method. The purchaser may specify in the order a specific bar coding system to be used.

26. Government Procurement

26.1 When specified in the contract, material shall be preserved, packaged, and packed in accordance with the requirements of **MIL-STD-163**. The applicable levels shall be as specified in the contract. Marking for the shipment of such material shall be in accordance with **Fed. Std. No. 123** for civil agencies and **MIL-STD-129** or **Fed. Std. No. 183** if continuous marking is required for military agencies.

26.2 *Inspection*—Unless otherwise specified in the contract, the producer is responsible for the performance of all inspection and test requirements specified herein. Except as otherwise specified in the contract, the producer shall use his own, or any other suitable facilities for the performance of the inspection and test requirements specified herein, unless disapproved by the purchaser. The purchaser shall have the right to perform any of the inspections and tests set forth in this specification where such inspections are deemed necessary to ensure that the material conforms to the prescribed requirements.

27. Keywords

27.1 carbon steel pipe; seamless steel pipe; steel pipe

SUPPLEMENTARY REQUIREMENTS

One or more of the following supplementary requirements shall apply only when specified in the purchase order. The purchaser may specify a different frequency of test or analysis than is provided in the supplementary requirement. Subject to agreement between the purchaser and manufacturer, retest and retreatment provisions of these supplementary requirements may also be modified.

S1. Product Analysis

S1.1 Product analysis shall be made on each length of pipe. Individual lengths failing to conform to the chemical composition requirements shall be rejected.

S2. Transverse Tension Test

S2.1 A transverse tension test shall be made on a specimen from one end or both ends of each pipe NPS 8 [DN 200] and over. If this supplementary requirement is specified, the number of tests per pipe shall also be specified. If a specimen from any length fails to meet the required tensile properties (tensile, yield, and elongation), that length shall be rejected subject to retreatment in accordance with Specification **A530/A530M** and satisfactory retest.

S3. Flattening Test, Standard

S3.1 For pipe over NPS 2 [DN 50], a section of pipe not less than 2½ in. [63.5 mm] in length shall be flattened cold between parallel plates until the opposite walls of the pipe meet. Flattening tests shall be in accordance with Specification **A530/A530M**, except that in the formula used to calculate the “H” value, the following “e” constants shall be used:

0.08 for Grade A

0.07 for Grades B and C

S3.2 When low *D-to-t* ratio tubulars are tested, because the strain imposed due to geometry is unreasonably high on the inside surface at the six and twelve o'clock locations, cracks at these locations shall not be cause for rejection if the *D-to-t* ratio is less than ten.

S3.3 The flattening test shall be made on one length of pipe from each lot of 400 lengths or fraction thereof of each size over NPS 2 [DN 50], up to but not including NPS 6 [DN 150], and from each lot of 200 lengths or fraction thereof, of each size NPS 6 [DN 150] and over.

S3.4 Should a crop end of a finished pipe fail in the flattening test, one retest is permitted to be made from the failed end. Pipe shall be normalized either before or after the first test, but pipe shall be subjected to only two normalizing treatments.

S4. Flattening Test, Enhanced

S4.1 The flattening test of Specification **A530/A530M** shall be made on a specimen from one end or both ends of each pipe. Crop ends may be used. If this supplementary requirement is specified, the number of tests per pipe shall also be specified.

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If a specimen from any length fails because of lack of ductility prior to satisfactory completion of the first step of the flattening test requirement, that pipe shall be rejected subject to retreatment in accordance with Specification **A530/A530M** and satisfactory retest. If a specimen from any length of pipe fails because of a lack of soundness, that length shall be rejected, unless subsequent retesting indicates that the remaining length is sound.

S5. Metal Structure and Etching Test

S5.1 The steel shall be homogeneous as shown by etching tests conducted in accordance with the appropriate sections of Method **E381**. Etching tests shall be made on a cross section from one end or both ends of each pipe and shall show sound and reasonably uniform material free from injurious laminations, cracks, and similar objectionable defects. If this supplementary requirement is specified, the number of tests per pipe required shall also be specified. If a specimen from any length shows objectionable defects, the length shall be rejected, subject to removal of the defective end and subsequent retests indicating the remainder of the length to be sound and reasonably uniform material.

S6. Carbon Equivalent

S6.1 The steel shall conform to a carbon equivalent (CE) of 0.50 maximum as determined by the following formula:

$$CE = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%Mo + \%V}{5} + \frac{\%Ni + \%Cu}{15}$$

S6.2 A lower CE maximum may be agreed upon between the purchaser and the producer.

S6.3 The CE shall be reported on the test report.

S7. Heat Treated Test Specimens

S7.1 At the request of the purchaser, one tensile test shall be performed by the manufacturer on a test specimen from each heat of steel furnished which has been either stress relieved at 1250 °F or normalized at 1650 °F, as specified by the purchaser. Other stress relief or annealing temperatures, as

appropriate to the analysis, may be specified by agreement between the purchaser and the manufacturer. The results of this test shall meet the requirements of **Table 1**.

S8. Internal Cleanliness—Government Orders

S8.1 The internal surface of hot finished ferritic steel pipe and tube shall be manufactured to a free of scale condition equivalent to the visual standard listed in **SSPC-SP 6**. Cleaning shall be performed in accordance with a written procedure that has been shown to be effective. This procedure shall be available for audit.

S9. Requirements for Carbon Steel Pipe for Hydrofluoric Acid Alkylation Service

S9.1 Pipe shall be provided in the normalized heat-treated condition.

S9.2 The carbon equivalent (CE), based upon heat analysis, shall not exceed 0.43 % if the specified wall thickness is equal to or less than 1 in. [25.4 mm] or 0.45 % if the specified wall thickness is greater than 1 in. [25.4 mm].

S9.3 The carbon equivalent (CE) shall be determined using the following formula:

$$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$$

S9.4 Based upon heat analysis in mass percent, the vanadium content shall not exceed 0.02 %, the niobium content shall not exceed 0.02 %, and the sum of the vanadium and niobium contents shall not exceed 0.03 %.

S9.5 Based upon heat analysis in mass percent, the sum of the nickel and copper contents shall not exceed 0.15 %.

S9.6 Based upon heat analysis in mass percent, the carbon content shall not be less than 0.18 %.

S9.7 Welding consumables of repair welds shall be of low hydrogen type. E60XX electrodes shall not be used and the resultant weld chemical composition shall meet the chemical composition requirements specified for the pipe.

S9.8 The designation “HF-N” shall be stamped or marked on each pipe to signify that the pipe complies with this supplementary requirement.

SUMMARY OF CHANGES

Committee A01 has identified the location of selected changes to this specification since the last issue, A106/A106M–10, that may impact the use of this specification. (Approved November 1, 2011)

(I) Revised Section 5 Heat Treatment to clarify that hot-finished pipe may be heat treated.

Committee A01 has identified the location of selected changes to this specification since the last issue, A106/A106M–08, that may impact the use of this specification. (Approved October 1, 2010)

(I) Added new Footnote B to be applied to grades B and C in **Table 1** and renumbered subsequent table footnotes.

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Vita

Maneel Bharadwaj was born in Palpa, Nepal to his parents Mr. Madhav Raj Sharma and Mrs. Kamala Devi Sharma. He has an older brother Mr. Maneesh Bharadwaj. After finishing his high school at Saints Xaviers School in Nepal, Maneel moved to the United States to pursue further education. After receiving his B.S. in Extractive Metallurgy from the University of Idaho Moscow, Idaho in 2008, Maneel worked as a Research Intern at Georgia Tech studying the estimation of the dihedral angle on W-Fe-Ni liquid phase sintered alloys where his desire for further education fortified, which, prompted him to apply at the University of Tennessee for the graduate program. Maneel decided to pursue his graduate school under the guidance of world renowned Professor Carl D. Lundin in the field of welding and physical metallurgy.

For his Masters research, Maneel studied High Temperature Hydrogen Attack (HTHA) on carbon steel and C- $\frac{1}{2}$ Mo steels a commonly known problem in the petrochemical industry. He has also published several publications in the welding research council bulletin for his work on C- $\frac{1}{2}$ Mo and HTHA damage. He is pursuing his Ph.D. in Metallurgical Engineering with Professor Lundin,

and intends to finish his degree by May, 2016. For his Ph.D., he is working on the development of toughness prediction factors for service-exposed C-½ Mo steels that are used in the hydrogen environment, which correlates microstructure, chemistry and other mechanical properties.

Apart from his research, Maneel has worked as a Teaching Assistant for various departmental courses including MSE-201 (Introduction to Materials Science and Engineering), MSE-370 (Materials Processing), MSE-480 (Material Selection and Design) and MSE-489 (Failure Analysis). MSE-480 and MSE-489 are the capstone courses for undergraduates at the department of material science and engineering. Maneel was also been involved with annual ASM Materials Camp assisting students with failure analysis projects.