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Tritium Aging Effects on Fracture Toughness of Stainless Steel Weldments

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The long-term embrittlement effects of tritium and decay helium on the structural properties of stainless steels have been studied for years at Savannah River to provide required data for establishing safe operating conditions and lifetimes of pressure vessels used to contain tritium gas. In this study, the fracture toughness properties of the longest-aged tritium-precharged stainless-steel base metals and weldments tested at Savannah River were measured and compared to earlier results. The fracture toughness values were the lowest recorded here for tritium-exposed stainless steel. As-forged and as-welded specimens were thermally precharging with tritium gas at 34.5 MPa and 623 K, then aged for up to 17 years to build-in decay helium prior to testing. ASTM J-Integral fracture mechanics analyses, transmission electron microscopy (TEM), and small angle neutron scattering (SANS) examinations were conducted to characterize the effects of tritium and its radioactive decay product, helium-3. Results show that the fracture toughness values were reduced to less than 2-4% of the as-forged values for specimens with more than 1300 appm helium from tritium decay. The trend of decreasing fracture toughness values with increasing helium content was consistent with earlier observations, and the data show that Type 304L stainless steel is more resistant to tritium-induced cracking than Type 21-6-9 stainless at similar decay helium levels. The fracture toughness properties of long-aged weldments were also affected, but the reductions were not as severe over time because weldments did not retain as much tritium as did the base metals. TEM observations were used to characterize the effects of decay helium bubbles on the deformation substructures, but nanometer-sized helium bubbles were not easily resolved because of high dislocation densities within the forged microstructures. SANS results are presented that suggest the technique can provide information on decay helium bubble size, spacing, and distribution in these steels.

KEYWORDS: TRITIUM, FRACTURE MECHANICS, TOUGHNESS, EMBRITTLEMENT, STEEL

I. INTRODUCTION

Tritium handling and storage for fusion power and other applications requires large scale tritium processing facilities that will be constructed from stainless steels because of their good compatibility with tritium. These steels are highly resistant to the embrittling effects of hydrogen isotopes and helium from tritium decay; however, they are not immune [1-5]. Fracture toughness is reduced by exposure to tritium and the reduction increases with time as helium-3 builds into the material from tritium diffusion and radioactive decay.

Where available, fracture toughness properties and fracture mechanics analyses may be used to inform design and minimize tritium-induced crack growth tritium service. Fracture toughness data is available for some tritium-exposed steels, but is limited, especially for welded steels with long exposure times. The purpose of this work was to extend measurements the effects of tritium and decay helium on the fracture toughness properties of types 304L and 21-6-9 stainless steel weldments to higher helium contents than measured in previous works. Type 304L is commonly used in tritium applications and Type 21-6-9, a nitrogen-strengthened alloy, has been used for high-strength applications. Additionally, of interest in this work was the measurement of helium bubble size distributions and their arrangement in the steel microstructure. These data are needed for developing deformation and cracking models for stainless steel in tritium service. Transmission electron microscopy has been used to characterize helium bubble microstructures in tritium charged stainless steels [6] but the technique is unable to resolve bubbles that are smaller than 1 nm, nor can it easily resolve bubbles that are in heavily dislocated microstructures like forged steels. Additionally, TEM can only examine a small volume of material, limiting the statistical power of the measurement. Small angle neutron scattering (SANS) has been shown to be able to measure implanted helium bubbles in metals [7-10], and is explored here for the characterization of tritium decay derived helium in these stainless steels.

II. MATERIALS AND METHODS

Fracture toughness samples were fabricated from base metals and weldments of Types 304L and 21-6-9 Stainless Steel. Details on composition and sample preparation have been reported previously [11]. Samples of both steels were tested in air at ambient temperature in the as-forged and as-welded conditions. Companion samples were exposed to tritium gas at 623 K and a pressure of 34.5 MPa and then stored in air at 193 K. The conditions of exposure were designed to saturate the samples with tritium while minimizing changes in the steel microstructure. The storage temperature was selected to limit tritium off-gassing and allow for the build-in of helium from tritium decay until testing was performed. Testing of the tritium-charged samples was conducted over a period of years to measure the effect of increasing decay helium on the fracture toughness properties.

J-integral tests were conducted at room temperature in air using a screw-driven load frame and a crosshead speed of 0.002 mm/s while recording load, load-line displacement, and crack length. Crack length was monitored using an alternating DC potential drop system and guidelines from ASTM E647-95 [12]. The J-Integral versus crack length increase (J vs. da) curves were constructed using ASTM E1820-99 [13]. The J_Q value is defined as the material fracture toughness value and was obtained from the intercept of an offset from the crack tip blunting line with the J-da curve.

The specimens were analyzed for decay-helium content by isotope-dilution gas mass spectrometry following vaporization in a resistance-heated graphite crucible in a vacuum furnace. Small angel neutron scattering (SANS) was used to probe tritium exposed steels and decay helium bubble size, spacing and distribution. SANS measurements were performed on tritium exposed stainless steel samples on beamline CG-2 at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Lab (ORNL). For SANS measurements, the samples were electrical discharge machined from previously studied fracture toughness specimens and were contained in gas tight cells with neutron transparent windows.

III. RESULTS AND DISCUSSION

The helium concentration for the specimens of earlier studies ranged from about 80 to 600 appm, depending on the steel type, weld ferrite content, and aging time. For these new results, the longest-age base metals are estimated to have more than 1400 appm helium. The long-aged weldments have lower hydrogen solubility and faster off-gassing and were estimated to have ~600 appm helium. All measured decay helium levels were lower than estimated from calculated equilibrium tritium concentration from charging. In the decay helium measurement technique, small pieces were cut from the near-surface corners which have lower decay helium levels than the bulk because they are subject to increased tritium off-gassing during the furnace cooldown after charging. Also, these pieces would have increased off-gassing losses during aging compared to the bulk. The data in this study estimates the decay helium levels from these measured values, although the specimens could contain more helium than these. For more discussion: see [14]. Thus, the values reported herein are anticipated to be conservative.

Fracture toughness properties and fractography for the as fabricated base metals and weldments of both steels have been reported previously. The as-welded samples had average J_Q fracture-toughness values two-to-three times higher than base metal. The presence of ductile delta-ferrite phase in the microstructure at these levels (5-8% by volume) and recrystallization and recovery in the weld zone has a beneficial effect on fracture toughness for the unexposed weldments [11]. The base metal samples exhibited signs of dimpled rupture: microvoids nucleated at nonmetallic inclusions in the steels and grew under strain until their coalescence lead to fracture. Welding produces a dispersion of fine inclusions whose size and distribution can affect fracture toughness. In this case, the inclusions serve as microvoid nucleation sites during the dimpled rupture fracture process but don't significantly reduce fracture toughness from the base metal because of the presence of the discontinuous and ductile skeletal ferrite phase. Type 304L and 21-6-9 steels and weldments had similar fracture modes.

Hydrogen charging lowers the resistance of the steel to crack initiation and growth as indicated by the lower J_Q values and the less-steep J-da curves in figure 1. The effect increases as the charging pressure increased from 34.5 MPa to 69 MPa [11].

The effect of tritium exposure on Type 21-6-9 stainless steel J-da behavior is also shown in figure 1. Representative fractography is shown in figure 2. Tritium charged samples had lower fracture toughness than samples similarly charged with hydrogen because of the presence of helium from tritium decay. Figure 3 shows the increasing embrittlement with increasing helium content from tritium aging for 304L stainless steel. After exposure, hydrogen- and tritium-charged base metal fracture surfaces had a much smaller microvoid size and finer spacing (figure 2) than what was seen in the unexposed samples. Cracking along ferrite/austenite interfaces or through the ferrite is observed in the weld fractography of samples exposed to tritium (figure 2 bottom right). All the results from tests on these samples from this publication and those published earlier [11, 14] are summarized in figure 4. The J_Q fracture toughness values decreased further with increasing decay helium content (figures 3-4). After helium builds in from tritium decay the initially high weldment fracture toughness of both steels is reduced to values similar to those of the reduced base metal values, as any increase in toughness from the ferrite phase in the weld samples is lost.

The effect of ferrite on weldment toughness agrees with the literature [15-17]. Brooks [15] shows the ductile ferrite phase blunts propagating cracks and forces a tortuous path through the weld microstructure. Mills [16]shows that at ambient and elevated temperatures, the ferrite phase behaves in a ductile manner, and welds are more resistant to fracture. However, ferrite displays a ductile to brittle transition temperature, and brittle fracture in welds may be seen below ambient temperatures. The weldments' toughness seen in this study is analogous to the fracture process that Mills describes as the ferrite phase is embrittled by tritium and helium. The fracture of these weldments is consistent with Brooks [17] as tritium and decay helium embrittlement-induced fracture occurs along or near the austenite-ferrite interface in welds.

Reduced SANS data was analyzed with SasView. From the reduced and fitted data, several observations can be made. In figure 5, reduced SANS data from a hydrogen charged weld sample and a tritium charged and aged weld sample are plotted. For these samples, two separate fitting functions are used. The hydrogen charged weld is well fit by a Gunier-Porod model, with the bulk of the scattering due to the complex microstructure of the weld sample. In the tritium charged and aged sample, significant additional scattering can be seen which can be fit with a hard sphere model. In fitting this data set, the two critical parameters are the radius of gyration, corresponding to the average bubble size, and the scattering length density, which directly relates to the helium pressure inside the bubbles. For this sample, a radius of gyration of 2.3 nanometers and a pressure of ~3 GPa were used, which agree with other measurements in the literature [7-10], and match closely to observations from TEM micrographs [6].

An additional observation to be made from these data is in the background at high Q. The hydrogen charged sample exhibits 10-20 times as much incoherent scattering background as the tritium charged sample, despite nominally identical hydrogen isotope concentrations and microstructures except for decay helium bubbles. This might be attributed to two combined effects: the decay of tritium in 17 years will have reduced concentrations by more than a factor of 2 and additionally, protium has an incoherent scattering cross section substantially higher than tritium. Because this background represents an additional source of information, an additional series of measurements were conducted in the form of small angle incoherent neutron scattering (SAINS) scans across these welds. A short measurement was taken at a series of locations linearly across each sample, and the background can be summed into a measure of total counts at each location, representing the incoherent scattering. This technique follows work from ORNL [18]. The scans for clean, protium charged, and tritium charged weld samples are shown in figure 6.

IV. CONCLUSIONS

[1]. For types 304L and 21-6-9 stainless steels, the fracture toughness of weldments is two to three times higher than that of the base metal. The toughness increase is attributed to the ductile ferrite phase formed in the microstructure through the welding process.

[2]. Hydrogen and tritium exposure lowered the fracture toughness properties of both base metals and weldments to similar values, having relatively larger effect on the weldments. Toughness decreased with increasing helium content from tritium decay.

[3]. Fracture occurred by microvoid nucleation, growth and coalescence. Hydrogen and tritium fracture surfaces have a finer void size and spacing than unexposed fracture surfaces. Weld fracture surfaces showed evidence for tritium-induced cracking through ferrite or along ferrite-austenite interfaces.

[4]. Fracture toughness continues to decrease with increasing decay helium contents. The very long ages with >1000 appm helium reported in this work lead to >90% loss in fracture toughness compared to the base metal.

[5]. Small angle neutron scattering measurements offer a new way to investigate bubble micro/nano structures on a broad statistical level even in highly strained materials, and agree with evidence in the literature for bubble sizes of one to several nanometers and pressures of several gigapascals. Related SAINS measurements may also provide a route to characterizing the distribution of hydrogen and its isotopes in nonhomogeneous samples. More work is required to refine both of these techniques.

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REFERENCES

[1] G. R. Caskey, "Hydrogen Effects in Stainless Steel," in *Hydrogen Degradation of Ferrous Alloys*, R. A. Oriani, J. P. Hirth, and M. A. Smialowski, Eds., ed Park Ridge, NJ: Noyes Publishing, 1985, pp. 822-862.

[2] G. Caskey Jr, "Tritium-helium effects in metals," *Fusion Technology,* vol. 8, pp. 2293-2298, 1985.

[3] M. J. Morgan and M. H. Tosten, "Tritium and decay helium effects on the fracture toughness properties of types 316L, 304L and 21Cr-6Ni-9Mn stainless steels," in *Hydrogen Effects in Materials*, ed Warrendale, PA: TMS, 1996, pp. 873-882.

[4] M. J. Morgan and M. H. Tosten, "Tritium and decay helium effects on the fracture toughness properties of types 316L, 304L and 21Cr-6Ni-9Mn stainless steels," Westinghouse Savannah River Co., Aiken No. SRTC-MTS--94-3036; CONF-940945--2, 1994.

[5] M. J. Morgan and M. H. Tosten, "Tritium and decay helium effects on cracking thresholds and velocities in stainless steel," *Fusion Technology,* vol. 39, pp. 590-595, 2001.

[6] M. H. Tosten and M. J. Morgan, "Transmission Electron Microscopy Study of Helium Bearing Fusion Welds," in *2008 Int. Hydrogen Conf. - Effect of Hydrogen on Materials*, Materials Park, OH, 2009, pp. 694-701.

[7] Qiang-Li, W. Kesternich, H. Schroeder, D. Schwahn, and H. Ullmaier, "Gas densities in helium bubbles in nickel measured by small angle neutron scattering," *Acta Metallurgica et Materialia,* vol. 38, pp. 2383-2392, 1990.

[8] D. Schwahn, H. Ullmaier, J. Schelten, and W. Kesternich, "Gas densities in he bubbles and their size distribution in nickel measured by neutron scattering," *Acta Metallurgica,* vol. 31, pp. 2003-2011, 1983.

[9] R. Coppola, M. Klimiankou, M. Magnani, A. Möslang, and M. Valli, "Helium bubble evolution in F82H-mod – correlation between SANS and TEM," *Journal of Nuclear Materials,* vol. 329-333, pp. 1057-1061, 2004/08/01/ 2004.

[10] R. Coppola, R. Lindau, R. P. May, A. Möslang, and M. Valli, "Investigation of microstructural evolution under neutron irradiation in Eurofer97 steel by means of small-angle neutron scattering," *Journal of Nuclear Materials,* vol. 386-388, pp. 195-198, 2009/04/30/ 2009.

[11] M. J. Morgan, S. L. West, and M. H. Tosten, "Effect of Tritium and Decay Helium on the Fracture Toughness Properties of Stainless Steel Weldments," in *Proceedings of the 8th Int. Conf. on Tritium Science and Technology,*, Rochester, NY, USA, 2008, pp. 501-505.

[12] "ASTM E647-95a Standard Test Method for MEasurement of Fatigue Crack Growth Rates," in *1999 Annual Book of ASTM Standard Volume 3.01 Metals-Mechanical Testing; Elevated and Low-Temperature Tests; Metallography* vol. ASTM E647-95a, ed, 1999.

[13] "ASTM E1820-99 "Standard Test Method for Measurement of Fracture Toughness"," in *1999 Annual Book of ASTM Standards Volume 3.01: Metals-Mechanical Testing; Elevated and Low-Temperature Tests; Metallography;*, ed: American Society for Testing and Materials, 1999.

[14] M. J. Morgan, D. Hitchcock, T. Krentz, J. McNamara, and A. Duncan, "2017 Accomplishments– Tritium Aging Studies on Stainless Steel Weldments and Heat-Affected Zones," Savannah River Site (SRS), Aiken, SC (United States)2018.

[15] J. Brooks, A. Thompson, and J. Williams, "A fundamental study of the beneficial effects of delta ferrite in reducing weld cracking," 1984.

[16] W. Mills, "Fracture toughness of type 304 and 316 stainless steels and their welds," *International Materials Reviews,* vol. 42, pp. 45-82, 1997.

[17] J. A. Brooks and A. J. West, "Hydrogen induced ductility losses in austenitic stainless steel welds," *Metallurgical Transactions A,* vol. 12, pp. 213-223, 1981.

[18] Y. Q. Yan, S; Littrell, K; Parish, C M; Plummer, L K, "Fast, quantitative, and nondestructive evaluation of hydrided LWR fuel cladding by small angle incoherent neutron scattering of hydrogen.," *Journal of Nuclear Materials,* vol. 460, pp. 114-121, 2015.

Table 1 – fracture toughness values for the alloys plotted in Figure 4. Helium contents are rounded to the nearest 100 appm for convenience of representation (* - indicates a single sample tested at this age. All others average at least 2 tests)

appm Helium	0	100	200	300	400	600	800	900	1000	1200	1400
21-6-9 100 KSI yield	370		96*			24				7*	
21-6-9 90 KSI yield	350	245*		96*			21				10
21-6-9/308L weldment	654	281*			74				51		
304L 75 KSI yield	296	179*	195*		158			95			
304L/308L weldment	870	330	201		165	132					

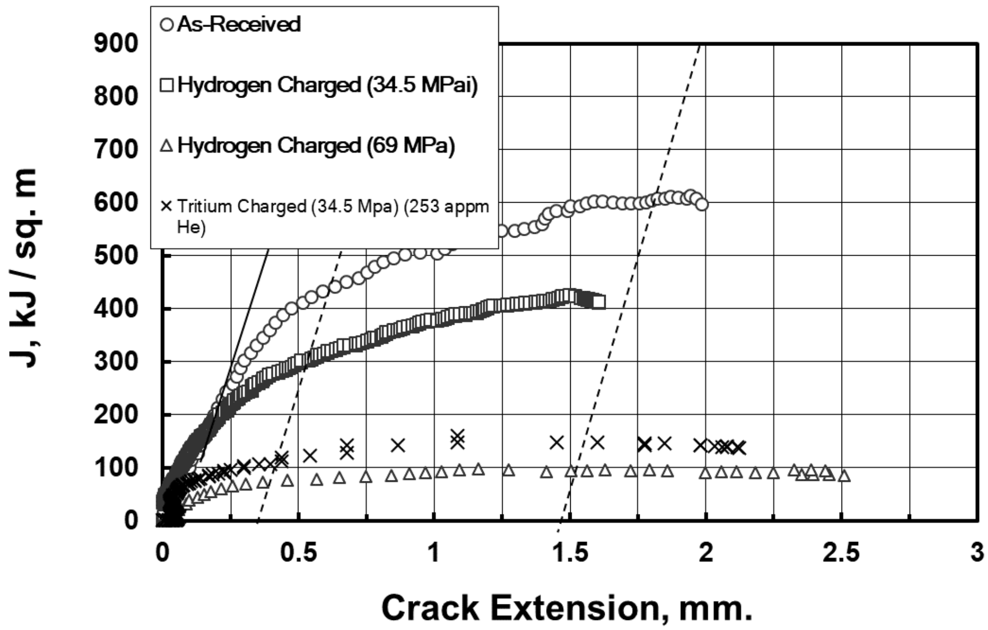

Figure 1 - Effect of Hydrogen and Tritium on J-da Behavior of Type 21-6-9 Stainless Steel. (adapted from data published in [11])

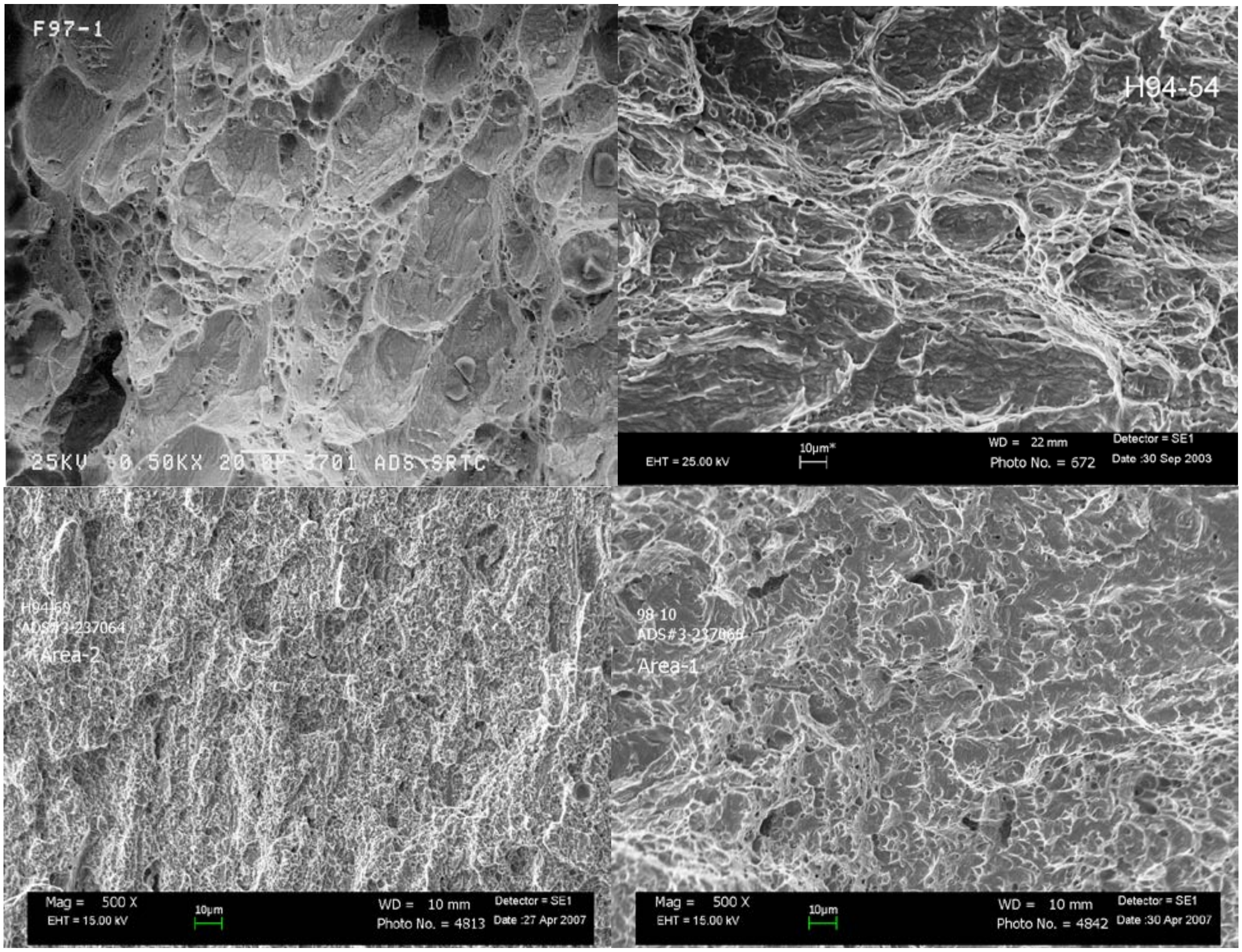

Figure 2 - Fracture Appearance of Type 21-6-9 Stainless Steel: (Top Left) Un exposed steel; (Top Right) Hydrogen charged at 34.5 MPa; (Bottom Left) Tritium-Charged at 34.5 MPa and Aged [253 appm Helium]; and (Bottom Right) Tritium-Exposed-and-Aged Type 21-6-9 Weldment (485 appm Helium)

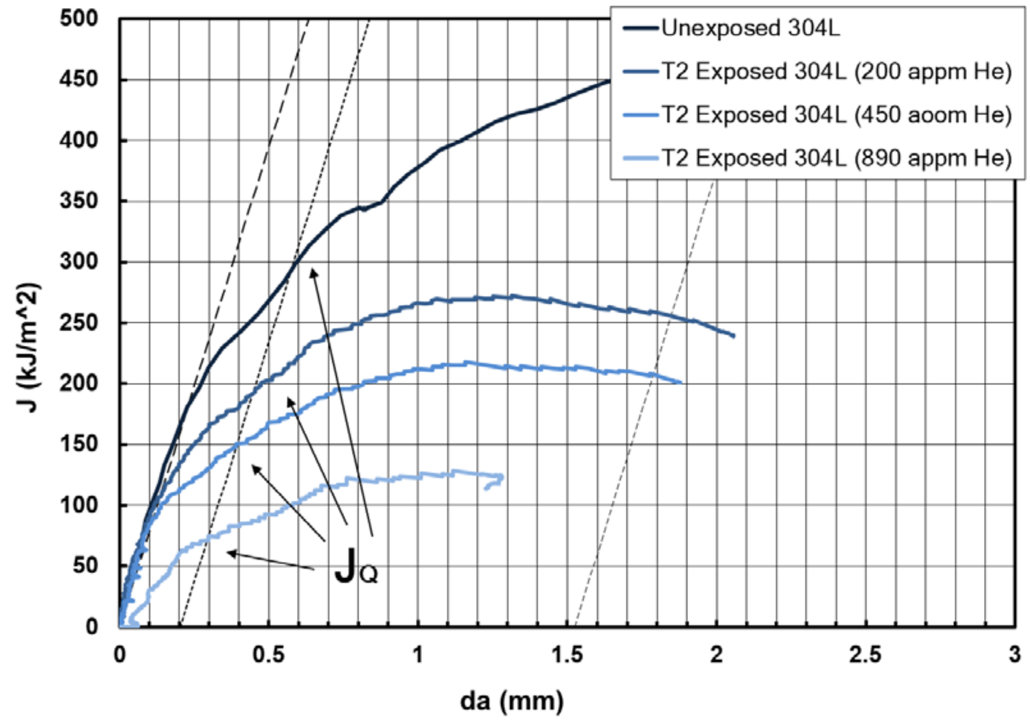

Figure 3 - Effect of Tritium and Decay Helium on the J-da Behavior of 304L Stainless Steel

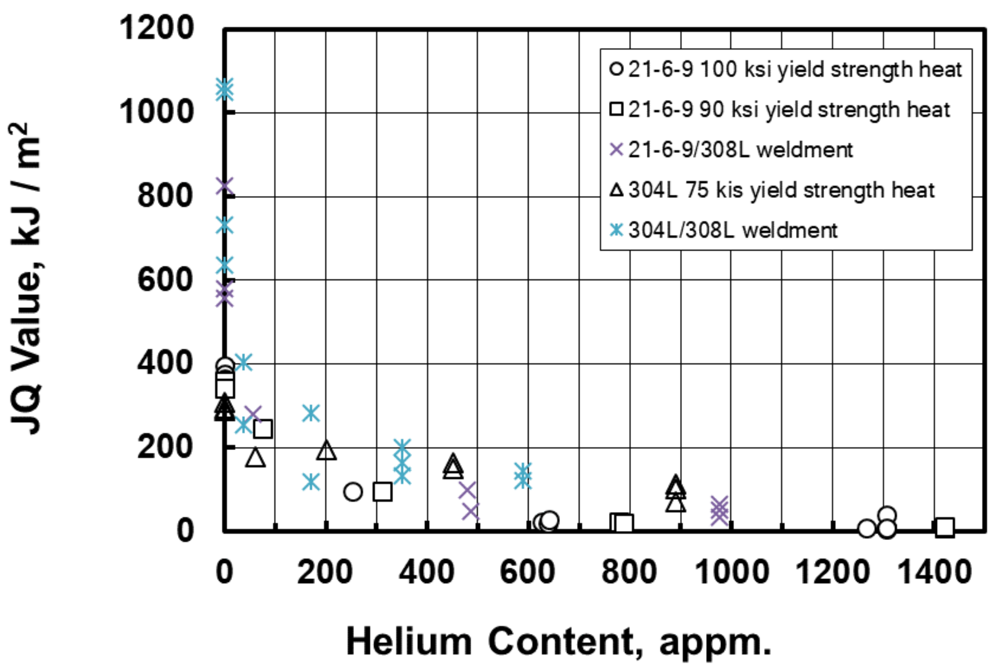

Figure 4 - Effect of Decay Helium Content on the JQ Value of Types 304L and 21-6-9 Stainless Steels and their Weldments

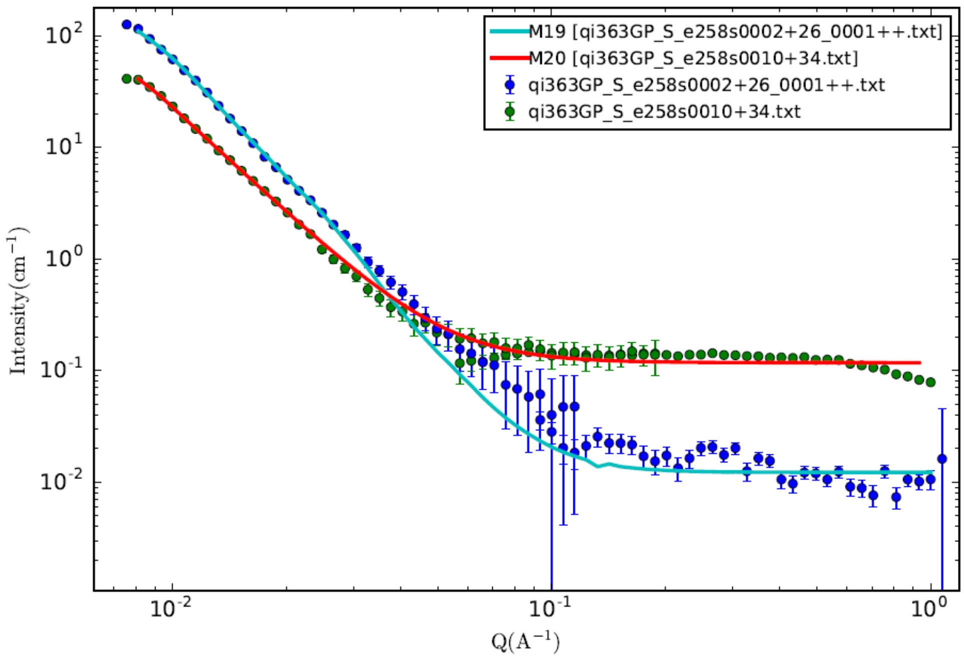

Figure 5 - Reduced and fitted data from a hydrogen charged weld (green with red fit) and tritium charged weld aged 3 years (blue with light blue fit).

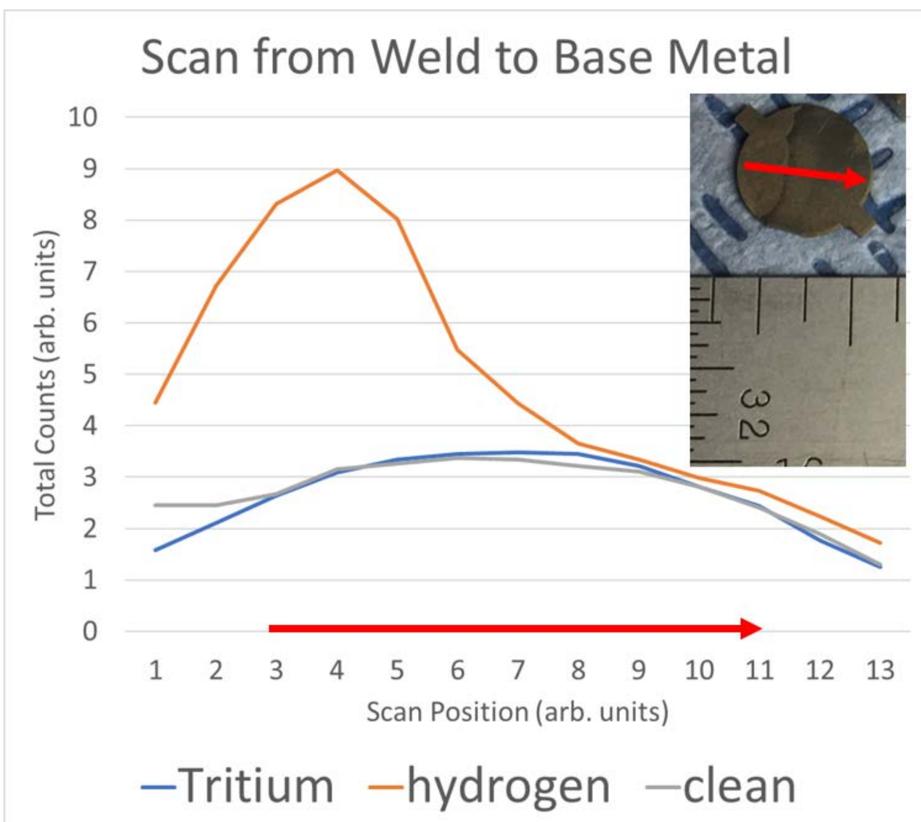

Figure 6 - Summed SAINS measurements conducted in a scan across weld (direction shown in insert)