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Title: Tritium embrittlement of austenitic stainless-steel tubing at low helium contents

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1. *Abstract*

Austenitic stainless steels are the standard materials for containment of hydrogen and tritium because of their resistance to mechanical property degradation in those environments. The mechanical performance of the primary containment material is critical for tritium handling, processing, and storage, thus comprehensive understanding of the processes of tritium embrittlement is an enabling capability for fusion energy. This work describes the investigation of the effects of low levels of tritium-decay-helium ingrowth on 304L tubes. Long-term aging with tritium leads to high helium contents in austenitic stainless steels and can reduce fracture toughness by 95%, but the details of behavior at low helium contents are not as well characterized. Here, we present results from tensile testing of tritium pre-charged 304L tube specimens with a variety of starting microstructures that all contain a low level of helium. The results of the tritium exposed-and-aged materials are compared to previously reported results on similar specimens tested in an unexposed condition as well as the hydrogen precharged condition. Tritium precharging and aging for a short duration resulted in increased yield strengths, ultimate tensile strengths and slightly increased elongation to failure, comparable to higher concentrations of hydrogen precharging.

2. *Keywords*

Austenitic Stainless Steel, Hydrogen, Tritium, Embrittlement

3. *Introduction*

Hydrogen and tritium handling infrastructure typically requires extensive gas manifolds. Type 300-series austenitic stainless steels are preferred for these systems due to their resistance to hydrogen isotope embrittlement. Additionally, their weldability is advantageous because welding is the preferred joining strategy whenever possible, as it is generally less leak prone than mechanical fittings. However, despite their good resistance to hydrogen embrittlement, materials like 304L stainless steels are not immune, and exposure to tritium and its decay product helium synergistically reduces toughness (*1-3*). Additionally, thermal history associated with welding tends to create microstructures and internal stresses that can be more sensitive to hydrogen-isotope embrittlement (*4, 5*).

The effects of hydrogen isotopes on the mechanical properties of stainless steel have been studied for many years (*6-8*). Thus, information on performance of various alloys in hydrogen is available, and certain general relationships including a direct correlation of embrittlement with hydrogen content and a positive effect of increasing nickel content have been established (*9-11*). However, until recently (*10, 12*), there has been a lack of systematic studies focused on the effect that microstructural variation has on susceptibility to hydrogen embrittlement. Tritium embrittlement is complicated by the combined effects of the hydrogen isotope and the aging effect of tritium's helium decay product. Because helium is less soluble in the atomic lattice than hydrogen isotopes, mobile atomic helium ultimately becomes trapped as high-pressure nanoscale helium bubbles, impeding dislocation motion and altering plastic deformation. Due to the additional difficulties of experimental studies utilizing tritium, data on its effects are less prevalent. Whereas the mechanisms of embrittlement in tritium environments are more complicated than for hydrogen, similar relationships have been established comparing composition and processing effects to mechanical performance in tritium environments (*5, 13-15*).

This manuscript reports the tensile properties of tritium-exposed and aged type 304L microstructures to extend work previously performed at Sandia National Laboratories on the effects of hydrogen (*10, 12*). Previous work demonstrated that internal hydrogen-induced losses in ductility could be correlated with differences in yield strength despite significant microstructural differences in compositionally identical material. Herein, the effect of tritium precharging and aging on the tensile response of type 304L tubing is presented. The materials were saturated with tritium at elevated temperature and subsequently aged at low temperature for 6 months, resulting in nominally 100 atomic parts per million (appm) of helium derived from tritium decay.

4. Materials and Methods

The testing described in this report was conducted on commercially available 3.175 mm outer diameter 304L stainless steel tubing with 0.7 mm wall thickness. The nominal composition of the tubing as given by the manufacturer is shown in Table 1.

Table 1 - nominal alloy composition (wt.%) from manufacturer

alloy	Cr	Ni	Mn	Mo	Si	C	S	P	Fe
304L	18.6	11.7	1.7	0.08	0.43	0.021	0.0004	0.017	Bal.

The type 304L tubing was received in a strain-hardened condition. Samples were heat treated to vary the microstructure and strength of the tubing without changing the composition. The heat treatment conditions were chosen to achieve five qualitatively different microstructural conditions: (i) partially recovered (866K / 60 min), (ii) fully recovered (1000 K / 30 min), (iii) partially recrystallized (1033 K / 30 min), (iv) fully recrystallized (1116K / 60 min), and (v) fully annealed (1311 K / 60 min). The microstructures of the as-received and heat treated materials are shown in Figure 1.

Samples were thermally precharged with hydrogen at 138 MPa and 573 K for 10 days to allow uniform saturation of the tubes. Tritium precharging was conducted at 34.5 MPa and 623 K for 14 days. At 573 K, uniform saturation of a solid cylinder with diameter of 3.175 mm would occur in 2-3 days; however, often times precharging runs contain multiple specimen geometries and the length of the precharging run is dictated by the largest sample. Therefore the samples in both hydrogen and tritium were fully and uniformly saturated given the long precharging times. The tubes precharged with tritium were subsequently aged at low temperature (193 K) for 6 months to permit approximately 100 appm helium to accumulate in the material (along with a concomitant reduction in tritium content to 3600 appm). We call this condition the tritium-aged condition to distinguish it from the hydrogen precharged condition. These two sets of charging conditions result in nominally 7700 and 3700 appm hydrogen and tritium respectively, due to the differences in pressures and temperatures. Additional details of the preparation and testing of samples in the non-charged and hydrogen-precharged condition are described in (*10, 12*).

The conditions of the tensile testing of the tritium-aged samples were nominally the same as for the non-charged and hydrogen precharged conditions. Tritium-aged specimens were tested at ambient laboratory conditions with a 25.4 mm gauge length extensometer and 2.54 mm/minute displacement rate in an electromechanical screw driven load frame, with each specimen tested to failure. Specimens were gripped over lengths of approximately 25.4 mm using pin inserts in the grip region to prevent tube collapse as suggested in ASTM E8.

5. Results

The heat treatments resulted in microstructures as shown in Figure 1. Proceeding through the microstructural images in Figure 1, the “As Received” material has small, equiaxed grains. The “Partially Recovered” microstructure displays evidence of polygonization, but as will be shown in the mechanical properties, the material only slightly softened. The “Fully Recovered” microstructure advances the recovery process further, while the “Partially Recrystallized” microstructure displays the beginning of the formation of new grains, with nominally complete recrystallization in the “Fully Recrystallized” microstructure. Finally, the “Fully Annealed” microstructure displays significant grain growth after recrystallization.

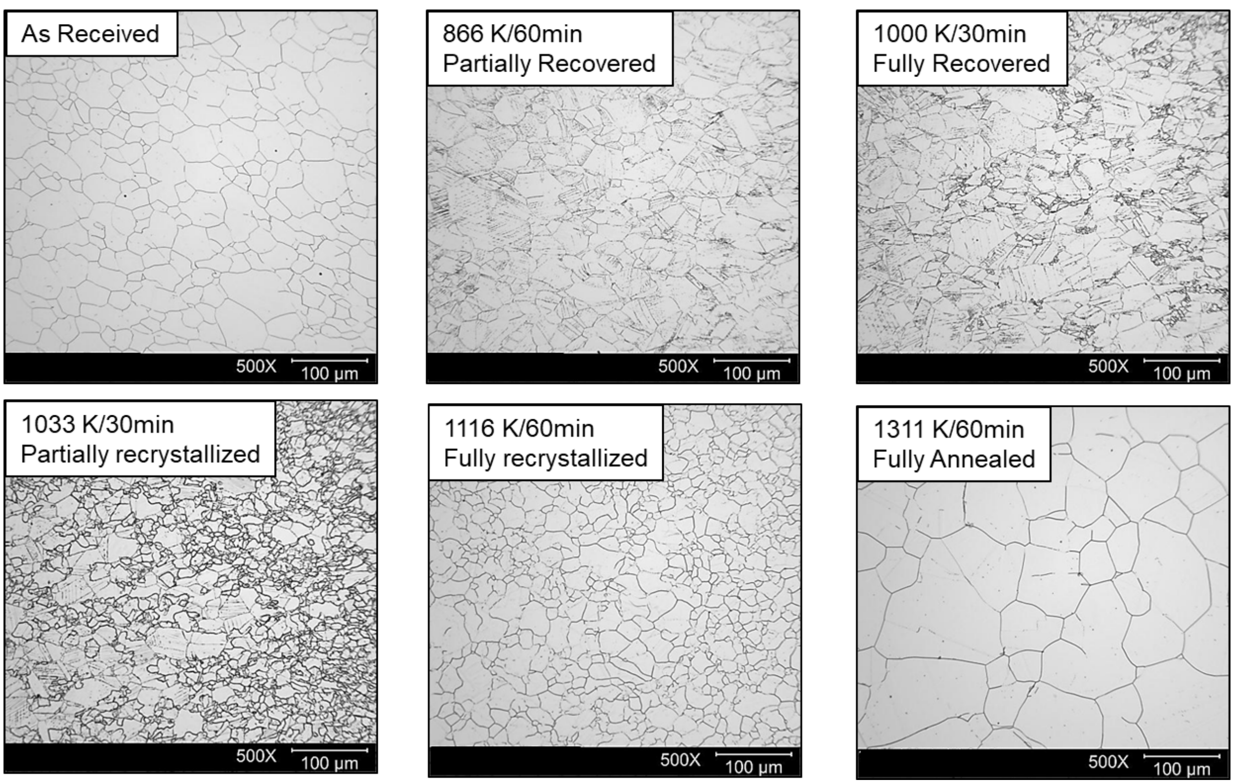

Figure 1 – micrographs of 304L tube microstructures based on different heat treatments. Further description in the text. Reproduced with permission from SNL/CA through SAND2020-8528 PE (16).

The tensile response of the non-charged samples are shown in Figure 2, as reported in (*10, 12*). The yield strengths range from 200 – 800 MPa and reflect the microstructures shown in Figure 1. The “As Received” material has a high yield strength near 700 MPa. The “Partially Recovered” material has a slightly reduced yield strength and marginally higher elongation to failure. Progressively, each subsequent heat-treated condition displays further reduction of yield strength and greater elongation to failure. The tensile response of the hydrogen-precharged samples measured are shown in Figure 3. In every case, hydrogen precharging increases yield strength, averaging a 19% increase over the noncharged controls. The ultimate tensile strength also increases with hydrogen precharging, on average by 10%. Finally, elongation to failure also increases on average by 14%. While elongation may increase after hydrogen precharging, the reduction of area is always reduced by internal hydrogen. The tritium-aged condition, with engineering stress-strain plots shown in Figure 4, shows comparable behavior to the hydrogen-precharged condition in each microstructure. Modest increases to yield (16%), ultimate tensile strength (5%), and elongation to failure (19%) were measured over the noncharged controls. Yield, ultimate tensile strength, and elongation values for all samples, as well as reduction of area measurements on non-charged and hydrogen-precharged samples, are tabulated in the appendix.

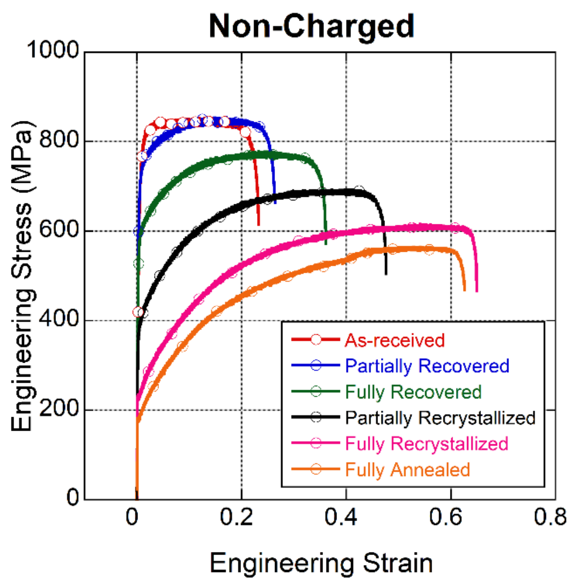

Figure 2 – Stress-Strain results from non-charged tube specimens. Reproduced from SAND2020-8528 PE(16)

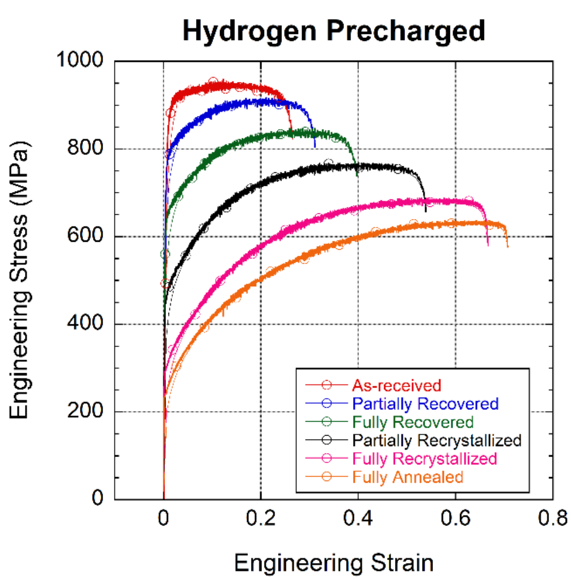

Figure 3 – Stress-Strain results from hydrogen precharged tube specimens. Reproduced from SAND2020-8528 PE(16)

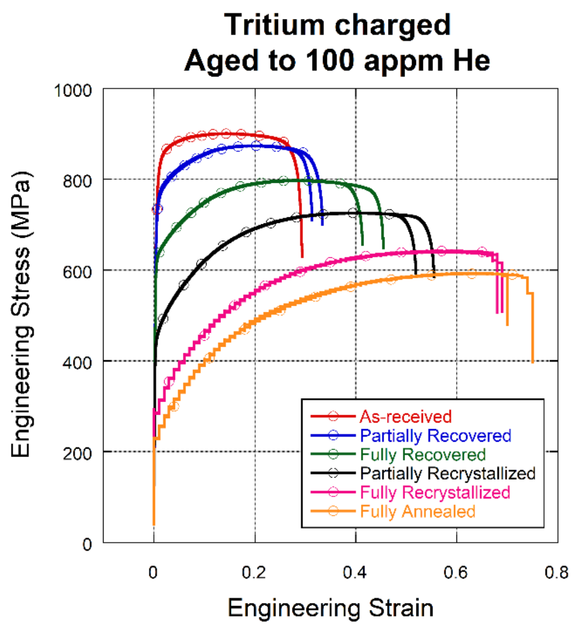

Figure 4 – Stress-Strain results from the first aging of tritium pre-charged tube specimens (6 months aging to attain ~ 100 appm helium).

The yield and tensile strength of the tritium-aged condition is generally slightly lower than the hydrogen precharged condition. In considering these mechanical test results, it is important to note that the hydrogen precharging condition leads to a nominal hydrogen content of 7700 appm, while the tritium-aged condition retains 3600 appm of tritium and develops 100 appm helium. Recently published data demonstrate an approximately linear relationship between strength (as well as ductility) and hydrogen concentration (*17*). As well, low levels of just a few hundred appm helium or less can have significant impacts on the fracture toughness of austenitic stainless steels (*18*). Moreover, such low helium levels can lead to embrittlement similar to that seen in steels with significantly higher hydrogen isotope contents (*19*). The measurements presented here qualitatively agree with these previous data, where the lower hydrogen isotope concentration in the tritium-aged condition is mostly offset by the hardening due to helium buildup.

While the small increases to yield and ultimate tensile strength are expected and reflect established embrittlement behavior, the increases to elongation are unexpected. They may be due the effects of the tube geometry presenting thinner walls and an additional free surface combined with altered strain hardening due to hydrogen and tritium. Regardless, reduction in area measurements (reproduced from (*16*) in the appendix) conducted on non-charged and hydrogen-precharged specimens reveal that ductility is still reduced by internal hydrogen. Finally, Figure 5 shows the percent change in yield strength over the noncharged condition for both hydrogen-precharged and tritium-aged samples. These data indicate some degree of microstructural dependence on the relative yield strength-due to hydrogen, where partially recovered microstructures are somewhat less sensitive to hydrogen, while more complete recrystallization and annealing is as sensitive or more sensitive than the strain hardened microstructure. The same systematic variation with microstructure is not seen for elongation or ultimate tensile strength. These results are preliminary, and more work is required to explain this behavior.

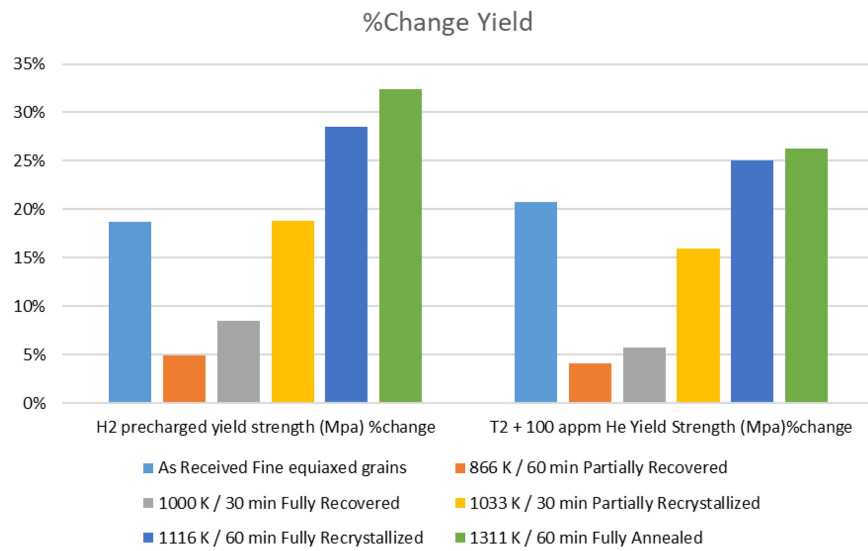

Figure 5 – Percent changes in yield strength over the noncharged condition for thermally hydrogen precharged and tritium precharged samples

The welded samples exhibit interesting trends that highlight the mechanics of the specimens. The fusion zone of the weld has significantly lower strength than the base materials for the strain-hardened (as-received) and fully recovered condition as shown in Figure 6. As a consequence, the yield strength is dominated by the strength of the fusion zone, which is similar to the recrystallized material. The large difference between the strength of the base material and the fusion zone causes the deformation to be restricted to the fusion zone, because the stresses never exceed the yield strength of the base material. In other words, loading in the base material remains elastic and the effective gauge length is reduced to the length of the fusion zone; however, we used the same extensometer for the welds as we did for the base metals. The result is highly non-uniform deformation in the weld samples and an artificially low apparent elongation in Table 3. The ductility of the welded specimens, however, remains high as the RA measures the deformation that is localized in the fusion zone of the weld. The RA is approximately the same in the welds as the fully annealed material for both the noncharged and H-precharged conditions. In the case of the welded, fully annealed tubing, the weld and base material have similar properties, thus the strength and ductility properties for all conditions reflect the behavior of the fully annealed tubing. Taken together, these observations suggest that the behavior of the welds in the helium-aged condition is analogous to the behavior of the fully-annealed material in the same helium-aged condition.

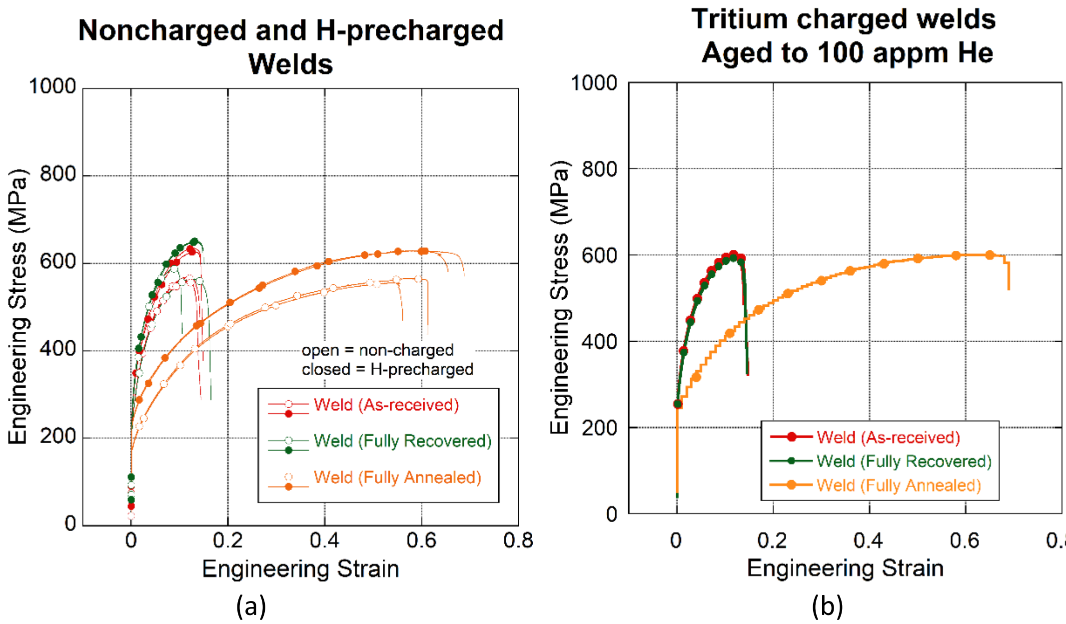

Figure 6 - Stress-Strain results from (a) noncharged and H-precharged welds, and (b) the first aging of tritium pre-charged tube welds (6 months aging to attain ~ 100 appm helium).

6. *Conclusions*

This work has presented initial results from tensile testing of 304L stainless steel tubing after a range of thermal processing and precharging with tritium. Building on earlier work investigating performance in hydrogen, it is shown that the development of nominally 100 appm tritium-decay-helium concentration leads to similar yield and tensile strength increases and changes in elongation to failure as seen with precharging to approximately twice the concentration with hydrogen. Embrittlement is seen regardless of microstructure in both hydrogen and tritium, however, these changes are smaller in recovered microstructures than they are in strain-hardened or fully recrystallized or annealed samples. Finally, mechanical behavior in welded sections behaves similarly in hydrogen and tritium to fully annealed material, regardless of the base microstructure. Future work will include additional aging of complementary coupons to be tested at 300 and 600 appm helium. These later tests will seek to investigate if various microstructures display differing sensitivity to tritium embrittlement as helium levels continue to rise with age.

7. *Acknowledgements*

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9. Appendix/supplementary info

Table 2 – Mechanical Properties of 304L tubing (n/m = not measured)

Microstructure	Environmental condition (wt ppm)	Yield Strength (MPa)	Tensile Strength (MPa)	Total Elongation (%)	Reduction of Area
Strain-hardened (as-received)	Non-charged	697 [664]	857 [844]	23	0.71
	H-precharged	788	945	27	0.50
	T + He	802	907	27	n/m
Partially recovered	Non-charged	678	854	27	0.68
	H-precharged	711	915	32	0.50
	T + He	706	874	34	n/m
Fully recovered	Non-charged	576	780	36	0.64
	H-precharged	625	850	41	0.54
	T + He	609	798	45	n/m
Partially recrystallized	Non-charged	377	692	47	0.70
	H-precharged	448	770	53	0.58
	T + He	437	726	54	n/m
Fully recrystallized	Non-charged	228	614	63	0.76
	H-precharged	293	688	67	0.65
	T + He	285	641	69	n/m
Fully Annealed	Non-charged	179	565	64	0.80
	H-precharged	237	636	71	0.66
	T + He	226	593	74	n/m

Table 3 – Mechanical Properties of 304L welded tubing

Microstructure	Environmental condition (wt ppm)	Yield Strength (MPa)	Tensile Strength (MPa)	Total Elongation (%)	Reduction of Area
As-received tubing welded	Non-charged	248	566	15	0.82
	H-precharged	287	631	15	0.62
	T + He	287	600	15	n/m
Fully recovered tubing welded	Non-charged	256	577	16	0.82
	H-precharged	296	651	15	0.67
	T + He	281	594	15	n/m
Fully annealed tubing welded	Non-charged	178	561	59	0.78
	H-precharged	239	630	67	0.65
	T + He	239	601	68	n/m