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Characterization of Stainless Steel 304 Tubing

A.J. Sunwoo, M.A. Brooks, and J.E. Kervin

SUMMARY

Earlier studies have shown that stainless steel 304 (SS304) containing martensite is susceptible to hydrogen embrittlement. This generated concern regarding the structural integrity of SS304 tubing we use in the W87 pit tube. During surveillance operations, the pit tube undergoes a series of bending and straightening as it goes through a number of surveillance cycles. This motivated the study to characterize austenitic SS304 tubing obtained from Rocky Flats. The tubes continued to display structural soundness even after numerous repeated bending and straightening cycles. The minimum and maximum number of bends to failure occurred after 13 and 16 cycles, respectively. After 5 bends, both the inner and outer surfaces of the tubing showed no microcracks. When the bent tubing samples were pressurized and tested using deuterium at 74°C and at -78°C, they failed away from the bent area. Thus deuterium embrittlement of the bent SS304 tubing should not be a problem. Moreover, to increase our 95% confidence level to 5 bends, we are planning to perform at least four additional bends to failure tests.

INTRODUCTION

Austenitic stainless steel 304 (SS304) is widely used in industry for its superior corrosion and oxidation resistance, and mechanical properties. Superior corrosion and oxidation resistance is imparted by the composition, and the mechanical properties are in part governed by the amount of cold work. Austenitic stainless steels are considered "metastable" types because plastic deformation triggers transformation from austenite to martensite. This composite microstructure of austenite and martensite exhibits higher strength and hardness than in the annealed condition. Martensite, on the other hand, is more susceptible to hydrogen embrittlement (HE) than austenite.

For our applications, SS304 tubing is used in the W87 pit tube. During surveillance operations, the pit tube undergoes repeated bending and straightening as it goes through a number of surveillance cycles. The combined effects of deformation and susceptibility to hydrogen (H) or deuterium (D₂) embrittlement on the structural integrity of the tube are a concern and the motivation for this study.

Earlier studies have shown that 304 containing martensite is susceptible to hydrogen embrittlement. However, the martensite contribution to HE is inconclusive at this time. The most detrimental effects of hydrogen on 304 are a decrease in ductility (as measured by a loss of reduction in area) and an enhanced crack propagation rate of preexisting cracks [1]. The decrease in ductility is thought to result from inhomogeneous deformation of the composite microstructure. Austenitic SS304 (γ phase) has a face centered cubic (FCC) crystal structure and the martensite of concern is a body centered cubic (BCC) α' phase. This α' martensite forms long, narrow plates on the $\{111\}_{\text{FCC}}$ slip plane in the $[110]_{\text{FCC}}$ slip direction [2]. Differences in deformation mechanisms of austenite and martensite may exist, and it has been suggested that the hydrogen cracking in these austenitic steels arises from the fact that the dislocation motion is in a planar mode rather than a cross-slip [3]. This could allow very high stress concentrations at the interfaces. If the stresses at the interfaces are greater than the flow stress of neighboring grains, then the localized stresses can help to nucleate cracks, which may ultimately propagate to failure.

For the martensite-enhanced HE, a possible failure mechanism is that the presence of these long, narrow α' plates on the slip planes of the austenitic grains may provide easier transport of H into

internal microvoids [1]. There, the atomically dissolved H may react with iron or other elements to increase the local stress. As the internal stress continues to build, these microvoids will enlarge and subsequently coalesce to failure. Another possible failure mechanism could be the way H interacts with two different crystal lattices. Consequently, the fracture initiation site is determined by the relative effect of H on its entrapments and on the deformation modes of austenite [4,5]. The typical H entrapments in the material are dislocations, impurity atoms, inclusion particles, interfaces, internal microvoid, and grain boundaries. Thus, the HE failure mode of 304 could exhibit either transgranular cleavage, intergranular, or ductile fracture.

The probability of HE occurring in SS304 depends on combination of many factors: initial microstructure and alloy strength, preexisting microcracks, external mechanical loading, temperature, and the source of H. Some of these factors are interrelated and have to occur simultaneously. However, SS304 benefits from its high chromium content (18-20 wt-%) which forms a very stable surface oxide. In service, this chromium oxide layer will prevent H absorption. For internal H, since H absorption in the steel is a reversible process, the 304 can be annealed in high vacuum to outgas the H.

A simple experiment was proposed to assess the possible effect of hydrogen on repeatedly bent SS304 tubing. The integrity of the tubes was determined by pressure burst tests. Prior to pressure tests, a set of bent tubes was D₂ charged at 100 psi for various temperatures and times.

EXPERIMENTAL PROCEDURES

SS304 vacuum induction melted-vacuum arc remelted (VIM-VAR) sample tubing was obtained from Rocky Flats to compare previous studies done on tubing found at Lawrence Livermore National Laboratory (LLNL) [6]. The diameter and wall thickness of the tubing were 3.175 mm (0.125 inch) and 0.711 mm (0.028 inch), respectively. The as-received tubing was characterized first for composition and tensile properties. Then, they were all cut to 152.4 mm (6 inch).

Two different types of bending and straightening tools are used in an assembly. The one we named "final bend" tooling is used for the last bend (90° bend), while the "other bend" tooling is used for all prior bends. For this study, only the "final bend" tooling was used and the schematic of the tool design is shown in Figure 1. The bending and straightening process tested consisted of first securing the tool in a bench vice, fitting a sample tubing into the tubing clamp, bending it to 90°, and then straightening it as best as the final bend tool will allow. The tool has two tube clamps (as shown in Fig. 1): one is tightly secured, another is allowed to slide freely.

The first series of tests was done to determine the number of bends to failure using the final bend tooling. The major and minor diameters as well as the length of the bent samples were measured using a 152 mm (6 inch) caliper. To document the deformation-enhanced-martensitic transformation, two different instruments were used to measure permeability: magne-gage and permeability indicator. The magne-gage, which is more sensitive to small changes in permeability, measures the force required to separate a calibrated magnet from a magnetic sample, utilizing dual vernier type dials for continuous reading. The dial readings are then converted to ferrite numbers using a simple linear calibration equation ($y=33.139-0.29083x$). The permeability indicator, on the other hand, uses discrete interchangeable permeability reference standards on a magnetic balance and is more suited for bulk material measurements with significant changes in magnetism. Using both instruments, measurements were taken on the inside, side, and outside radius of the bend area after every bending and straightening cycle. The effect of repeated cycles on the microstructure was also microstructurally characterized on a 5 bend-cycled sample.

Samples were then prepared for the pressure burst tests to assess system hydrogen embrittlement concerns. Except for the as-received condition, all the tubing samples were cycled either 5 or 8

times and were tested in bent condition. A first set of pressure burst tests was performed at ambient temperature using helium for the samples of 0, 5, and 8 bends. The second set of tests for the 5 and 8 bend tubing was held at 74° C at 100 psig for 2 h in D₂ gas and then pressurized at 5 ksi/min to bursting pressure. To create more adverse condition, a last set of tests was held at a constant pressure of 100 psig at 74° C for 2 h in D₂ gas, followed by holding at -78°C for 5 min to stabilize to temperature and then pressurizing at 5 ksi/min to bursting pressure.

RESULTS and DISCUSSION

Chemical analysis of 304 stainless steel tubes was performed using LECO combustion technique and spectroscopy by Anamet Laboratories. Compared to what is considered a nominal composition limit for SS304, our tubing is a high purity, enriched alloying addition material. The purpose of this analysis was to determine, in particular, residual hydrogen in the alloy. In addition, knowing the precise amounts of alloying elements in the tubing, we were able to estimate the deformation-enhanced-transformation temperature (M_d). We calculated an approximate temperature at which 50% of austenite would transform to martensite during a tensile test at a true strain of 0.3 (eng. strain = 35%) by substituting the composition data from Table 1 into the predictive transformation formula [7]. A below freezing temperature transformation was predicted. Note that this calculated temperature should not be considered as an actual transformation temperature since it will vary with testing conditions.

$$M_d (^{\circ}\text{C}) = 413 - 462 (\text{C} + \text{N}) - 9.2 (\text{Si}) - 8.1 (\text{Mn}) - 13.7 (\text{Cr}) - 9.5 (\text{Ni}) - 18.5 (\text{Mo}) \\ = -1.22^{\circ}\text{C} (-34.2^{\circ}\text{F})$$

It has been observed that if an austenitic SS is plastically strained 15% at 60°C and cooled to -30°C under the applied stress, the amount of α' martensite produced is much less than if the material is plastically deformed at -30°C [8]. However, small amounts of prestrain (about 2-4%) above, but in the vicinity of, M_d stimulates subsequent transformation, increasing the amount of α' produced, while about 10-15% prestrain suppresses the subsequent transformation [8,9]. Suppression of the martensitic transformation is attributed to strengthening and partitioning of austenite, so that α' crystal growth is impaired [10,11].

Table 2 lists tensile properties of various tempers and presents tensile test data of our tubing. The test results confirmed our tubing temper as 1/4 Hard, since there was initially uncertainty as which temper it was. The tubing was purchased in the 1/4 Hard condition at the request of the valve designers at Sandia National Laboratories-California. This condition facilitates a cleaner cutting of the tubing. On the other hand, Los Alamos National Laboratory (LANL) used their tubing in the annealed condition.

To determine the bending limit, four tubing samples were cycled to failure, and the results are summarized in Table 3. Minimum bends to failure occurred after 13 cycles and all the tubing failed at the inside radius during straightening. Figure 2 shows the increases in ferrite number (FN) as a function of number of bends for both inside and outside radius. FN is a good qualitative indicator of amount of martensite present in the bent surface of the tubing. As the number of bends increased, FN increased almost linearly, reaching a limit for the magne-gage of 36. The scatter in the data is attributed to difficulty in measuring the same location consistently. The figure clearly shows that there is a greater deformation occurring at the inside radius of the bent tube. Since the tube is repeatedly bent around 90° angle and straightened at the same location, the effects of work-hardening and fatiguing are greater at the inside radius. Similar results were also observed by Joe Petranto [12] at LANL, when he measured the hardness of both inside and outside radius of the bent tubing as a function of bends. He found higher hardness values at the inside radius than the outside. When these bent tubes were pneumatically pressurized and burst tested to 45+ ksig, they

did not burst. He concluded that our SS304 tubing that has been bent and rebent 10 times had no apparent deleterious effect on the structural integrity.

In reliability theory, wearout failure is usually approximated by Gaussian distributions. From the data in Table 3, normal probability functions can be calculated for the pit tube. If the sample statistics (mean = 14.75 bend cycles and standard deviation = 1.26) are representative of the stockpile, then we would expect no failures prior to the 10th cycle. But since we are not entirely sure that the sample statistics are the same as the population statistics, we applied confidence level analysis to them. The two confidence levels that we chose to apply were the 50% confidence level and 95% confidence level. The ratio of the difference between the observed average of a sample and the mean of its population to the sample standard deviation is distributed in a double sided Student's distribution. Based on this relationship, at a 50% confidence level the population mean is between 14.27 and 15.23 bend cycles. At the 95% confidence level, the uncertainty increases to between 12.75 and 16.75 bend cycles. The ratio of the product of the degrees of freedom and the sample variance to the population variance is distributed in a chi-squared distribution. Using this relationship, at the 50% confidence level the standard deviation is calculated to be between 1.08 and 1.98 bend cycles. At the 95% confidence level, this increases to between 0.72 and 4.69 bend cycles. With this data, it is possible to construct worst case failure estimates at each of these confidence levels by using the lowest end of the mean range and the highest end of the standard deviation. Thus, we can be sure at the 50% confidence level that failure will not occur before the 6th bend cycle, or at the 95% confidence level there is some small chance of failure (0.6%) that would occur on the first bend cycle. The probability of failure at the different confidence levels is graphed in Figure 3.

Figure 4 shows a cross-sectional view of the bent area of a tube after 5 bends. Both the internal and external surfaces of the bent tube exhibit no visible microcracks. It has been observed that α' martensite always formed at preferred sites, such as the intersection of two {111} faulted sheets of γ [2]. This tendency to nucleate at sheet intersections became more pronounced after deformation. Since the tubing is already a 1/4 Hard tempered material containing martensite, transformation of α' plates from γ should be easily accomplished and this is consistent with our FN measurements.

The results of the pressure burst tests are summarized in Table 4. These extrinsic test parameters were chosen to simulate a possible service environment. It is difficult to develop a statistical analysis since we tested only one tubing sample for each condition. However, they provide assurance that the failure will not occur in the bent area of the tubing. In the most adverse condition of high temperature (74°C) pressurization and low temperature (-78°C) test, an 8 bend cycled tube failed prematurely due to a bad braze joint, where it exhibited 50+ ksig burst pressure. Work by Caskey [4] has suggested that for 300 series austenitic stainless steels, the severity of H damage as determined by tensile properties appears to correlate with composition, particularly the Ni content. As the Ni content increases from 8 to 14 percent, austenite stability increases and tensile ductility becomes less affected by H, especially at -23 to -73°C, where H damage is maximum. Although our tubing contains only 10.35 percent Ni, but in combination with high Cr content, they will provide austenite stability.

CONCLUSIONS

Characterization of austenitic SS304 tubing obtained from Rocky Flats displayed structural soundness even after numerous repeated bending and straightening cycles using the "final bend" tooling. Minimum bends to failure occurred after 13 cycles. After 5 bends, both the inner and outer surfaces of the tubing showed no microcracks. When the bent tubing samples were pressurized and tested using deuterium at 74°C and at -78°C, they failed away from the bent area. Thus deuterium embrittlement of the bent SS304 tubing should not be a problem.

FUTURE WORK

Available to us are the actual SS304 pit tubes removed from previous surveillance operations. We will be able to compare the deformation characteristics of the simulated tubing to those of the actual pit tubing. Moreover, we will perform at least four additional bends to failure tests to increase our 95% confidence level to 5 bends.

ACKNOWLEDGMENT

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Table 1. Nominal and analyzed composition of stainless steel 304.

wt-%	C	Si	Cr	Mn	Ni	P	N	H	S
nominal	0.08	1.0	18-20	2.0	8-10.5	0.045	0.1	-	0.03
actual	0.057	0.48	19.35	1.62	10.35	0.013	0.015	0.0006	0.003

Table 2. Tensile properties of hard drawn austenitic stainless steel tubing.

Temper	Ultimate Tensile Strength MPa (ksi)	Yield Strength MPa (ksi)	Elongation (%)
annealed	515 (75)	205 (30)	35
1/4 Hard	825 (120)	515 (75)	12
1/2 Hard	1035 (150)	760 (110)	7
LLNL (avg.)	725 (105)	550 (80)	35

Table 3. Number of bends to failure tests.

Specimen	Number of Bends	Location
20F1	16	inside radius during straightening
20F3	15	inside radius during straightening
20F4	13	inside radius during straightening
20F5	15	inside radius during straightening

Table 4. Pressure burst tests of bent tubes in various conditions.

Specimen	Condition	Gas	Temperature/ Pressure/Time	Burst Pressure, ksig	Location
200	as-received	He	ambient	59.71	baseline property
201	after 5 bends	He	ambient	60.93	away from bend area
202	after 8 bends	He	ambient	60.53	away from bend area
205	after 5 bends	D ₂	74°C at 100psig for 2h	56.5	away from bend area
206	after 8 bends	D ₂	74°C at 100psig for 2h	57	away from bend area
209	after 5 bends	D ₂	74°C at 100psig for 2h/ -78°C at 100psig for 5min	59	away from bend area
210	after 8 bends	D ₂	74°C at 100psig for 2h/ -78°C at 100psig for 5min	52	away from bend area, at braze joint

Figure 1. A schematic sketch of a "final bend" tooling used for the last bend (90° bend) in an assembly and also in our present study.

Stainless Steel 304 Tubing

Figure 2. Ferrite number (FN) of bent tubing as a function of number of bends for both inside and outside radius.

Probability That Pit Tube Will Have Failed By Given Bend Cycle

Figure 3. A graph shows the probability of failure at the different confidence levels.

Figure 4. A cross sectional view of a bent area of stainless steel tube after 5 cycles: a. inner diameter; b. outer diameter.