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STRESS CORROSION CRACKING IN TEAR DROP SPECIMENS†

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ABSTRACT

Laboratory tests were conducted to investigate the stress corrosion cracking (SCC) of 304L stainless steel used to construct the containment vessels for the storage of plutonium-bearing materials. The tear drop corrosion specimens each with an autogenous weld in the center were placed in contact with moist plutonium oxide and chloride salt mixtures. Cracking was found in two of the specimens in the heat affected zone (HAZ) at the apex area. Finite element analysis was performed to simulate the specimen fabrication for determining the internal stress which caused SCC to occur. It was found that the tensile stress at the crack initiation site was about 30% lower than the highest stress which had been shifted to the shoulders of the specimen due to the specimen fabrication process. This finding appears to indicate that the SCC initiation took place in favor of the possibly weaker weld/base metal interface at a sufficiently high level of background stress. The base material, even subject to a higher tensile stress, was not cracked. The relieving of tensile stress due to SCC initiation and growth in the HAZ and the weld might have foreclosed the potential for cracking at the specimen shoulders where higher stress was found.

INTRODUCTION

Laboratory corrosion tests were conducted to investigate the corrosivity of moist plutonium oxide/chloride (PuO_2/Cl^-) salt mixtures on 304L and 316L stainless steel coupons. The tests exposed flat coupons for pitting evaluation and "tear drop" stressed coupons (Figure 1) for stress corrosion cracking (SCC) evaluation in 24 containers at room temperature to various mixtures of PuO_2 and chloride-bearing salts. An autogenous weld is located at the center of the tear drop specimen and was made by fusing the base 304L alloy without filler metal (Figure 2) on what is to become the outside face of the specimen. Each container held one flat coupon of each alloy and two tear drop specimens of 304L stainless steel (except for one container with two 316L stainless steel tear drop specimens). The two flat coupons were placed so that the solid oxide/salt mixture contacted

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about one half of the coupon surface. One tear drop specimen was placed in contact with solid mixture; the second tear drop specimen was in contact with the headspace gas only. The chloride salts were composed of sodium chloride (NaCl) and potassium chloride (KCl) only or NaCl and KCl with additions of calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$). The mixtures were loaded with nominally 0.5 wt % water under a helium atmosphere. Test durations for these containers ranged from 150 to 506 days. The coupons have been examined visually and microscopically for corrosion, the headspace gas pressures and compositions have been determined, and accurate water loading analyses have been performed.

Observations of corrosion ranged from superficial staining to pitting and SCC. The extent of corrosion depended on the total salt concentration and on the composition of the salt. The most significant corrosion was found in coupons that were exposed to 98 wt % PuO_2, 2 wt % chloride salt mixtures that contained $CaCl_2$. SCC was observed in two 304L stainless steel tear drop specimens exposed in solid contact to the mixture of 98 wt % PuO_2, 0.9 wt % NaCl, 0.9 wt % KCl, and 0.2 wt % $CaCl_2$. The cracking was associated with the heat-affected zone of an autogenous weld that ran across the center of the coupon. Cracking was not observed in a 316L coupon exposed in solid contact to this mixture. Cracking was not observed in 304L coupons exposed to the headspace gas above the mixture, nor in the 304L coupons exposed to any other test mixture. This paper is focused on the 304L tear drop specimens which experienced SCC.

A detailed specimen fabrication process was simulated by the finite element method to estimate the initial stress in the 304L tear drop specimens for which the cracking occurred. It was determined that this stress level is about 483 MPa (70 ksi). However, the location of the highest stress in the specimen is not in the apex region where the weld is located. The maximum stress location has been shifted away from the apex as the specimen is being formed with a rigid mandrel. The base material in the shoulder region of the specimens were subject to a higher tensile principal stress of 731 MPa (106 ksi), but was not cracked. The relieving of tensile stress due to crack initiation and growth in the HAZ and the weld might have foreclosed the potential for cracking.

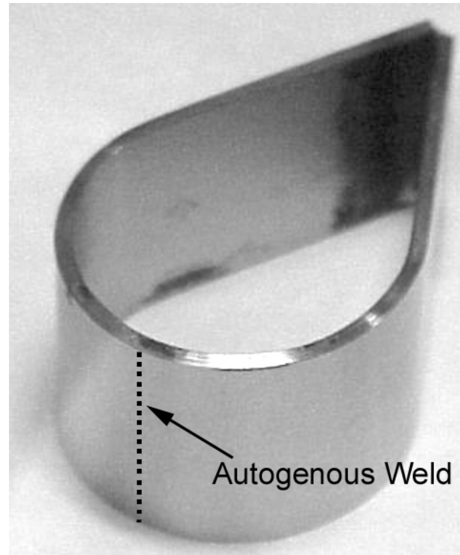


Figure 1 Tear drop specimen for stress corrosion cracking tests with the autogenous weld centerline indicated by the dotted line.

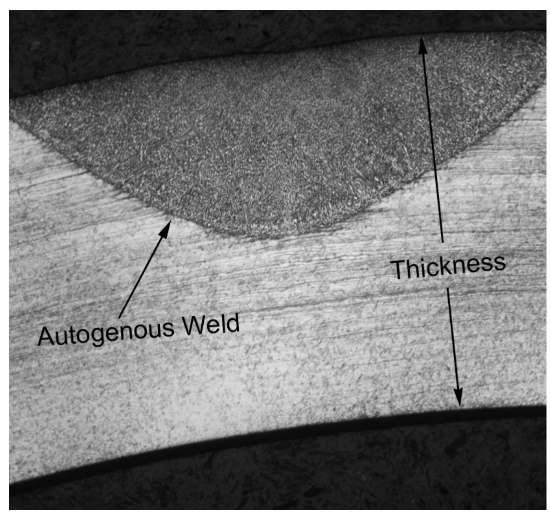


Figure 2 Micrograph of a cross-section of a 304L stainless steel tear drop specimen showing the autogenous weld at the apex of the specimen (~50X magnification). Note that the thickness of the specimen is 1.47 mm (0.058 in.), the deepest penetration of the weld is about 0.69±0.05 mm (0.027±0.002 in.), and the width of the weld is about 2.29 mm (0.09 in.).

EXPERIMENTAL SETUP

The test container is a stainless steel can with a diameter of approximately 50.8 mm (2 in.) and a height of 63.5 mm (2.5 in.). The container is sealed with a metal gasket and is equipped with a pressure transducer for continuous pressure monitoring during an exposure and a valve for acquiring gas samples periodically (Figure 3). Glass inserts were used to hold small (several cubic-centimeters) volumes of oxide/salt mixture in close contact with the test coupons to maximize the number of vessels allowed under the fissile material limit of the laboratory.

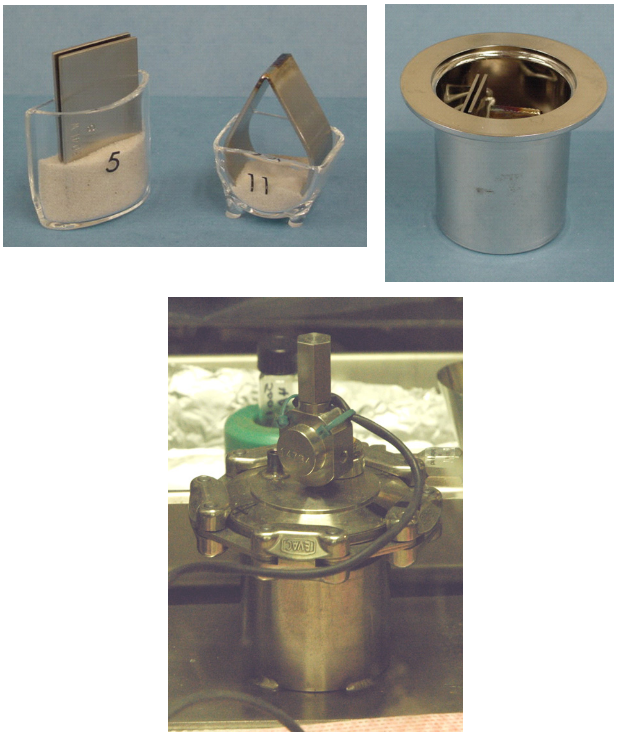


Figure 3 Flat and tear drop coupons in glass inserts, open test container, and sealed container.

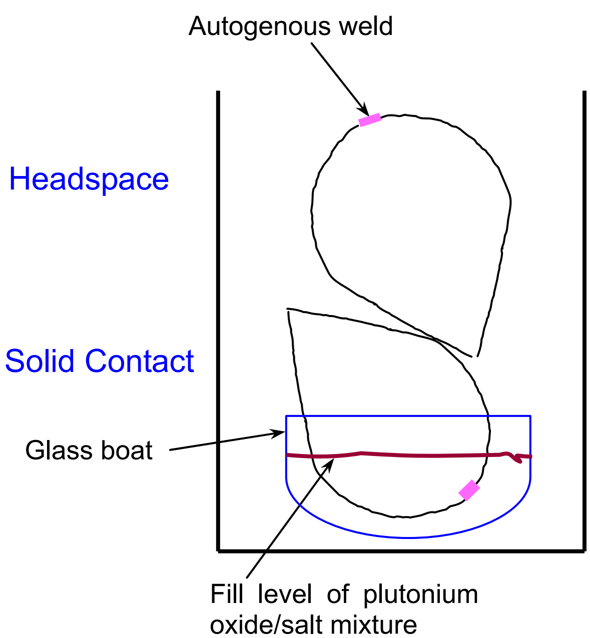


Figure 4 Arrangement of 304L tear drop specimens within a container.

The free volume of the test container loaded with glass inserts containing oxide and test coupons is nominally 100 cubic centimeters (cm^3). The containers were staged at ambient temperature in gloveboxes. Figure 3 shows the coupons in their glass boats or inserts (with sand substituting for the oxide salt mixture) and an open test container with coupons. One 304L flat coupon and one 316L flat coupon were placed side by side in one glass insert. Enough oxide/salt mixture was added between and around the coupons to cover the lower half of each coupon. Several grams of oxide/salt mixture were added to a second glass insert, and one teardrop coupon was placed in this second glass insert on top of the oxide/salt mixture. Several more grams of oxide/salt mixture were added inside the closed loop of the tear drop specimen. The two glass inserts were placed side by side in the vessel. A second tear drop specimen was then placed on top of the first such that it rested in the headspace position without contact with the solid mixture, as shown in the diagram in Figure 4.

STRESS CORROSION TEST RESULTS

As noted earlier, the tear drop specimens were used to assess the susceptibility of 304L stainless steel to SCC induced by the moist oxide/salt mixture. Two specimens were found to have undergone SCC after 166 and 335 days of exposure, respectively, in the solid contact position. Cracking was not observed in the solid contact position coupons from any other container opened to date, nor was cracking seen in any headspace position coupon.

Optical microscopy, scanning electron microscopy, and optical metallography have been performed to examine the path and nature of the cracking in the tear drop specimen which was exposed for 166 days. The cracking extended across more than half the width of the coupon and was associated with the transverse autogenous weld. Figure 5 is an optical micrograph that shows the cracking apparently originating at the edge of the coupon in what may be characterized as a localized area of general corrosion (rather than pitting). The cracking propagated along the interface between the weld and the parent metal. The region in the parent metal along this interface is the heat-affected zone, where the weld heat may induce compositional changes in the alloy. The multiply-branched cracking crossed the weld and propagated along the other interface. Optical metallography of one cross-section of the coupon reveals the propagation of the crack along the interface (Figure 6) and, in a second cross-section, propagation through the weld metal into the parent metal (Figure 7). The enlargement in Figure 7 shows transgranular cracking. The highest magnification image shows the extensive cracking paths across parent metal grains. This transgranular nature is characteristic of chloride-induced SCC in austenitic stainless steel.

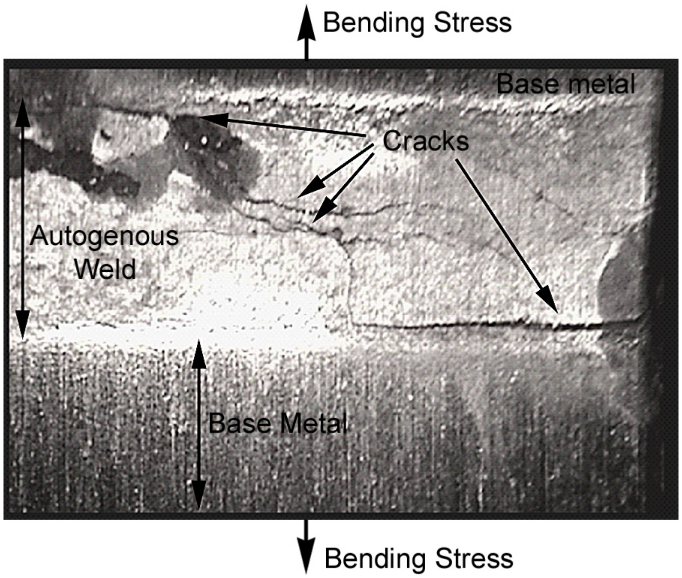


Figure 5 Stress corrosion cracking in a tear drop specimen associated with the autogenous weld (~8X magnification) [1] as viewed into the apex area toward the dotted line in Figure 1.

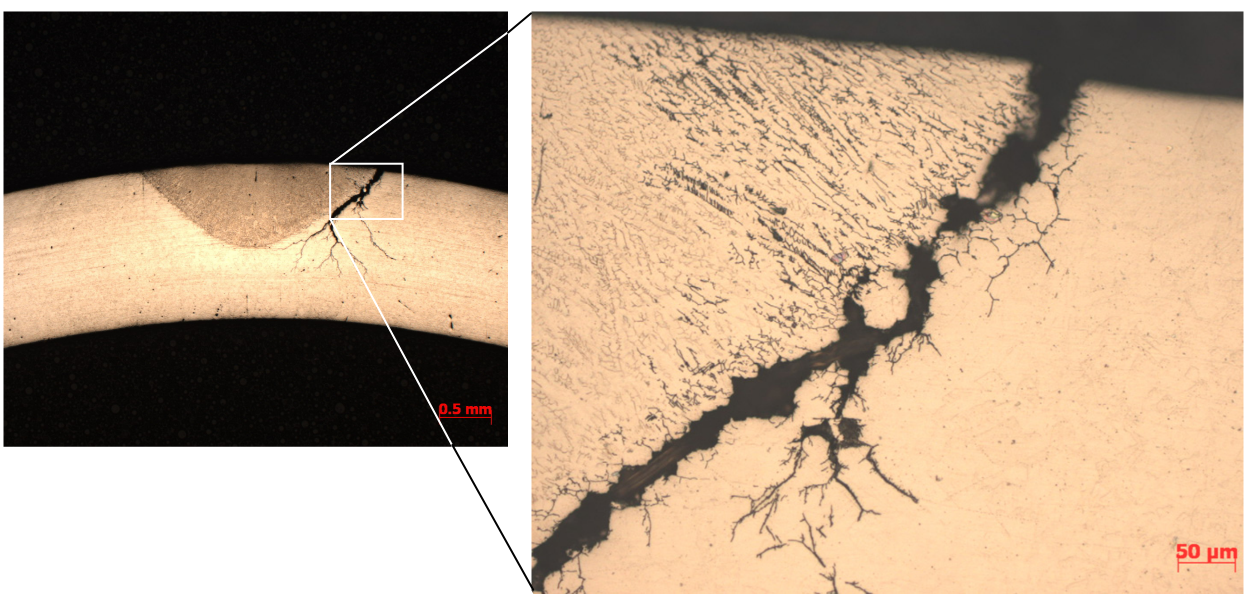
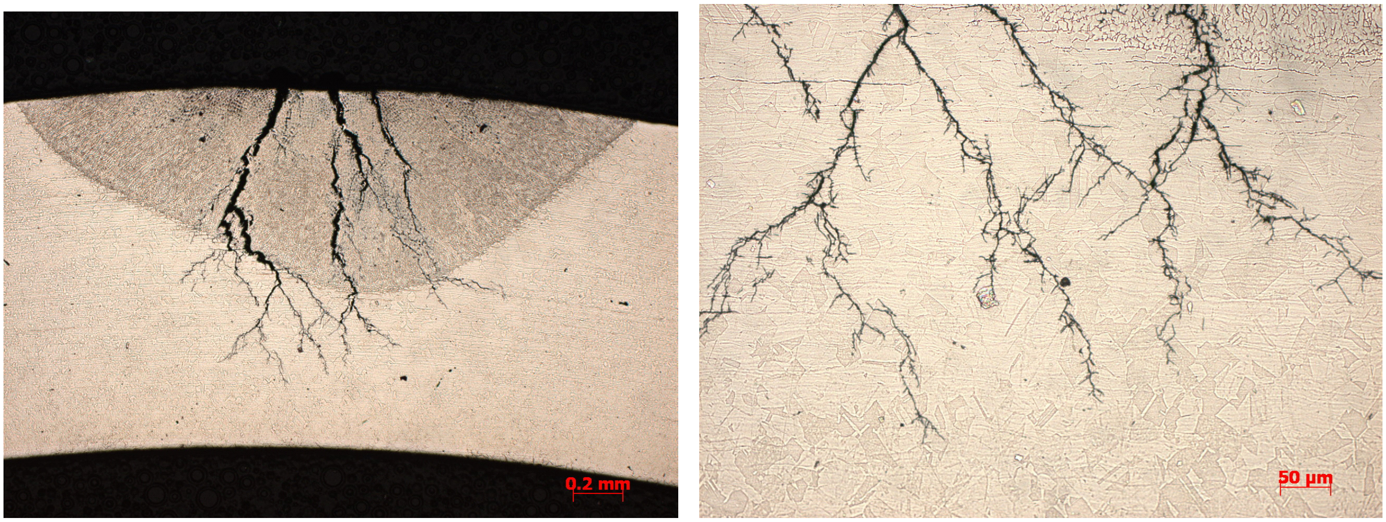


Figure 6 Optical micrographs of a cross-section through teardrop specimen showing cracking along the weld/parent metal interface.



(a) (b)

Figure 7 Propagation of multiple cracks through the weld metal into the base metal (a) and the enlargement (b) shows the transgranular nature of stress corrosion cracking.

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FINITE ELEMENT ANALYSIS

The ABAQUS program [3] was used to perform the finite element analysis. Only one-half of the 304L strip and one-half of the mandrel are needed in the finite element calculation because of geometric symmetry. The model contains 3600 four-noded plane strain elements (Type CPE4R with reduced integration) and 4010 nodes with 9 elements across the specimen thickness (1.47 mm or 0.058 in.). The undeformed stainless strip (outlined with blue) is shown in Figure 8. The mandrel is assumed to be rigid and is fixed in space while the metal strip is forced to bend around the mandrel until the ends of the strip are in contact. The specimen ends are then fixed in space to simulate the welded joint by which the specimen is maintained in the stressed condition. Finally, the rigid mandrel is removed from the model and the internal stresses in the specimen are self-equilibrated. The final shape of the deformed model (tear drop specimen) is also shown in Figure 8 (red). Because large displacement is involved in this fabrication process, the finite strain and large deformation finite element algorithm in ABAQUS was invoked.

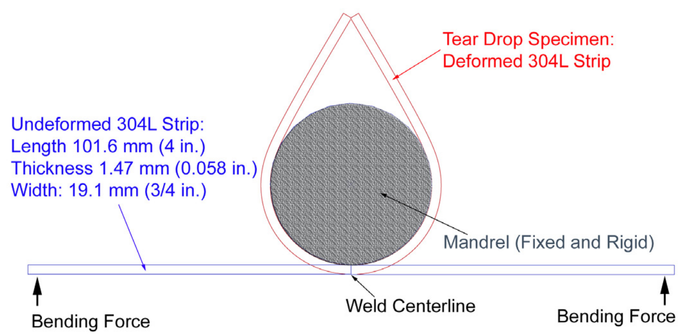

Figure 8 Finite element model to form tear drop specimen by deforming a rectangular strip of metal.

Material Tensile Properties

As specified in vendor certificate [2], the 0.2% offset yield stress for the 304L stainless steel is 351 MPa (50.93 ksi), the ultimate tensile strength (UTS) is 662 MPa (96.05 ksi), and the elongation (at break) with a 50.8 mm (2 in.) gage length is 45.85%. The full stress-strain curve necessary for the finite element analysis was not provided. For a preliminary assessment of the stress state of the tear drop specimen without elaborating material-specific testing, a stress-strain curve (Figure 9) with similar values of yield stress (455 MPa or 66 ksi) and UTS (689 MPa or 100 ksi) [4,5] is used for the present analysis. The tensile properties of the small volume of autogenous weld metal are assumed to be the same as those of the base metal (304L). For this large deformation finite element analysis, the true stress-true plastic strain curve must be used. The elastic-plastic material input for the ABAQUS finite element analysis is listed in Table 1, along with the Young's modulus and the Poisson's ratio which are, respectively, 193 GPa (28×10^6 psi) and 0.3.

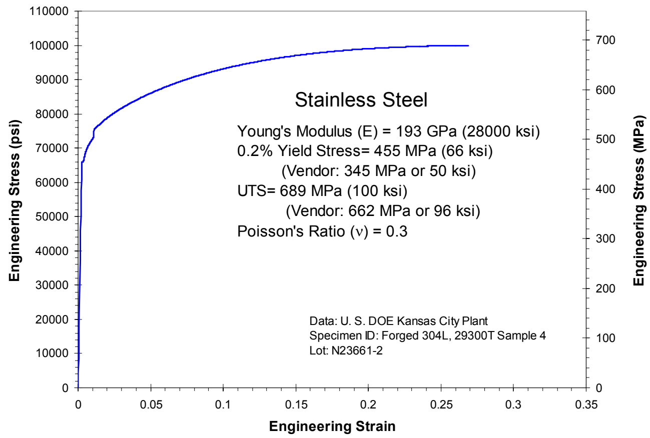

Figure 9 Engineering stress-strain curve for 304L stainless steel.

Table 1 Elastic-plastic material property input for finite element analysis

True Plastic Strain	True Stress
0	Yield= 455 MPa (66000 psi)
0.0057	498 MPa (72300 psi)
0.0169	554 MPa (80379 psi)
0.0510	634 MPa (91963 psi)
0.1010	721 MPa (104570 psi)
0.1510	788 MPa (114348 psi)
0.2013	844 MPa (122380 psi)
0.2337	UTS= 875 MPa (126840 psi)

Numerical Results and Discussion

The sequence of forming a tear drop specimen by bending a flat strip of 304L around a rigid mandrel is shown in Figure 10 with the von Mises stress contour plotted. The Mises stress is an equivalent stress which represents the intensity of the multiaxial, general stress state of the deforming body. It can be seen that the maximum stress first occurs at the apex of the deforming strip (Figure 10b, warmer colors). As the strip continues to conform to the shape of the mandrel, the location of the maximum stress is shifted to the general area where new contact is made between the strip and the mandrel (Figure 10c). The stress at the apex is further relieved as more contact is made until the forming process is completed (Figure 10d); and finally the stress is re-distributed as the ends of the strip are welded and the mandrel is removed (Figure 10e).

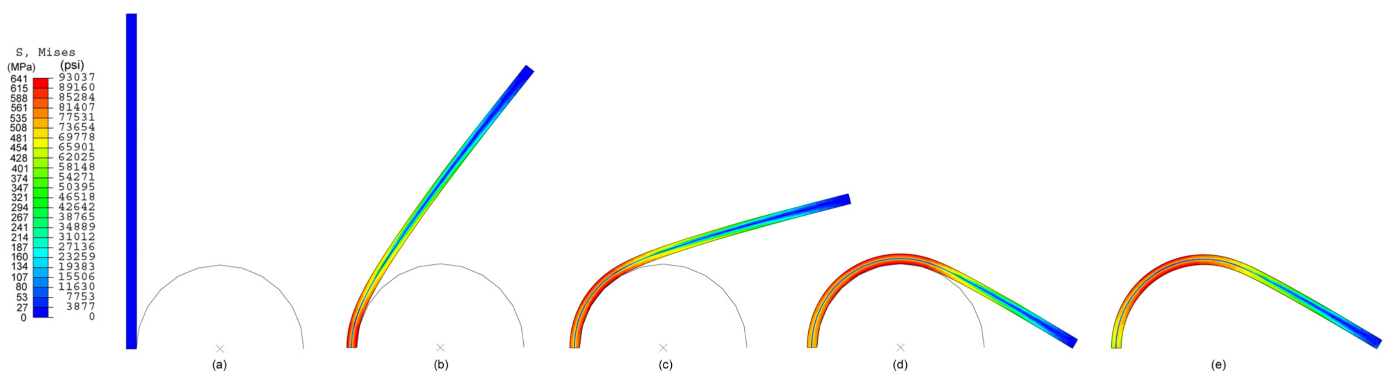

Figure 10 The Mises stress distribution during the fabrication of the tear drop specimen: (a) Undeformed state, (b) Maximum stress at the apex, (c) Maximum stress deviating from the apex when the strip continues to deform, (d) Specimen forming completed, and (e) Stress re-equilibrium upon completion of specimen fabrication.

Cracking has been found in the weld region (apex) of the tear drop specimen after exposure to the PuO_2-chloride salt mixture in the corrosion experiment [1]. These cracks appeared to be perpendicular to the bending stress in the outer fiber of the specimen (Figure 5). It may be concluded that the cracks were initiated and propagated mainly under the tensile bending stress. This bending stress component is equivalent to the maximum principal stress calculated in each element (or at any material point), and can be seen in Figure 11, in which the relative magnitude and the orientation of this stress component are plotted with double-headed arrows (black) in the enlarged regions of the apex and the highest stress location, respectively. For visual convenience, the contour of the bending stress (maximum in-plane principal stress) is superimposed on the photograph of the tear drop specimen (Figure 12). The location of the maximum bending stress is identified.

CONCLUSIONS

Laboratory corrosion tests at room temperature on 304L stainless steel coupons that were exposed to moist (nominally 0.5 wt % water) $PuO_2/CaCl_2$-bearing salt mixtures have shown that this alloy is susceptible to pitting and SCC under specific conditions of mixture water loading, total chloride salt concentration *and* composition, and physical contact with the solid mixture. The stress corrosion cracking was associated initially with the heat-affected zone at the interface between the specimens' parent metal and an autogenous weld. Subsequently the cracking propagated through the autogenous weld into the parent metal. The mixture that led to SCC contained 98 wt % PuO_2, 0.9 wt % NaCl, 0.9 wt % KCl, and 0.2 wt % $CaCl_2$ (total salt concentration of 2 wt %).

The highest bending stress in the tear drop specimen is not located at the apex as normally expected. The finite element analysis showed that the apex stress is relieved and continuously redistributed as the 304L strip is being bent around the mandrel, and the location of the highest stress is shifted away from the apex to the specimen shoulders. This is caused by the increasing contact surface between the 304L strip and the mandrel in the course of forming the specimen, which effectively changes the bending moment of the system. However, the stress for the autogenous weld to crack in a corrosive environment is the stress estimated in the apex area. For this specimen geometry, this stress is about 483 MPa (70 ksi, see the apex stress in Figure 11 and Figure 12). The specimen fabrication process also results in a permanent deformation (maximum 5.5% true plastic strain), which is far below the elongation at break which is greater than 45% [2]. Nevertheless, it should be pointed out that the weld has already experienced a plastic deformation (about 5%) prior to the stress corrosion testing. Because the location of the maximum bending stress is away from the area of interest, it is recommended that inspection for base metal cracking be performed in the area of the maximum stress (see Figure 12).

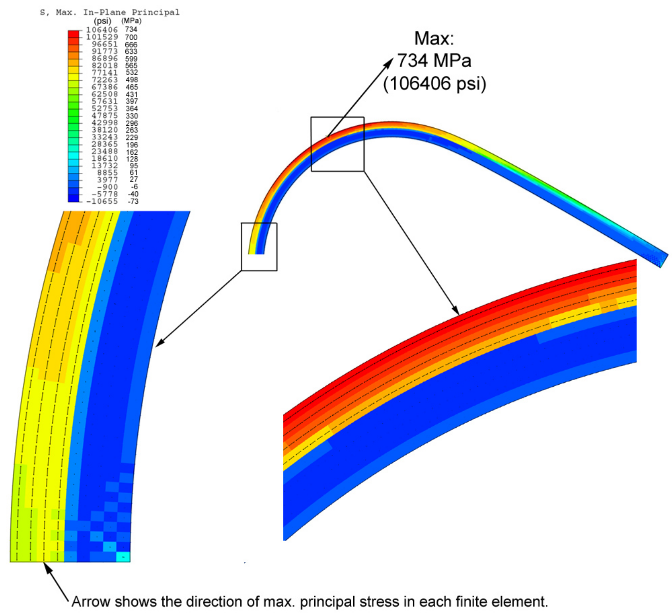

Figure 11 The maximum in-plane principal stress distribution in the tear drop specimen. The black arrows represent the orientation and the relative magnitude of the stress component.

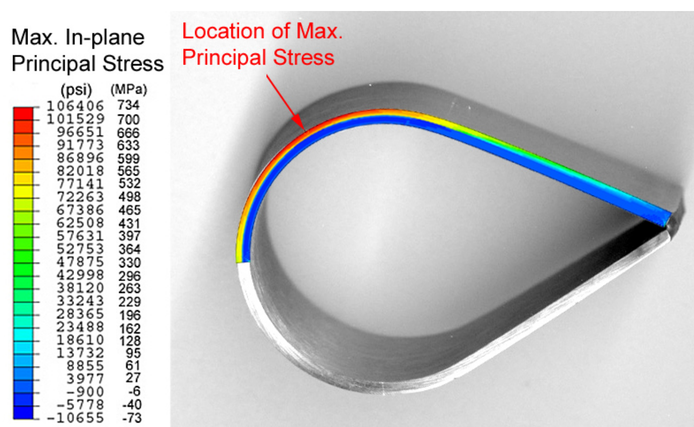

Figure 12 The location of maximum stress in the tear drop specimen.

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