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LOCALIZED CORROSION OF AUSTENITIC STAINLESS STEEL
EXPOSED TO MIXTURES OF PLUTONIUM OXIDE AND CHLORIDE SALTS

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ABSTRACT

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 “teardrop” stressed coupons for stress corrosion cracking (SCC) evaluation at room temperature to various mixtures of PuO_2 and chloride-bearing salts for periods up to 500 days. The two flat coupons were placed so that the solid oxide/salt mixture contacted about one half of the coupon surface. One teardrop coupon was placed in contact with solid mixture; the second teardrop was in contact with the headspace gas only. The mixtures were loaded with nominally 0.5 wt % water under a helium atmosphere. 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 calcium chloride. SCC was observed in two 304L stainless steel teardrop coupons exposed in solid contact to a 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 coupons exposed to the headspace gas, nor in coupons exposed to other mixtures with either 0.92 wt % CaCl_2 or no CaCl_2 . The corrosion results point to the significance of the interaction between water loading and the concentration of the hydrating salt CaCl_2 in the susceptibility of austenitic stainless steels to corrosion.

Keywords: stress corrosion cracking, pitting, radiation

INTRODUCTION

The United States Department of Energy Standard DOE-STD-3013-2004 “Stabilization, Packaging and Storage of Plutonium-Bearing Materials” (the ‘3013’ standard) specifies that certain oxides of plutonium be heat treated to reduce water content and packaged and stored in at least two nested, welded containers fabricated from corrosion resistant alloy(s).¹ In practice the inner of the two containers has been fabricated from either 304L or 316L stainless steel, and the outer has been fabricated of 316L stainless steel. The oxide heat-treatment requires heating to 950°C for at least two hours in an oxidizing atmosphere. The heat-treated material is to contain less than 0.5% by weight water, and that limit must be maintained through the packaging and sealing of the material within the two containers. Both inner and outer containers are sealed by welding, and the 3013 standard specifies leak-tightness limits.

A portion of the plutonium oxide inventory may contain chloride salts in significant concentration, so that there is the potential of an aqueous electrolyte containing chloride ions in contact with the stainless steel containers.¹ For austenitic stainless steels, such an electrolyte can induce the localized modes of corrosion: pitting and stress corrosion cracking, as well as crevice corrosion. Previous limited experimentation demonstrated the corrosivity of PuO_2/Cl^- salt mixtures to austenitic (300-series) stainless steels. Localized corrosion in the form of pitting was discovered in small-scale 304L stainless steel

vessels containing a PuO₂ chloride salt mixture after 90 days' exposure.² Pitting depths up to 100 μm were observed on the metal surface in contact with the solid oxide and up to 25 μm on metal exposed to the vapor space above the solid. Subsequent flat coupon tests showed that a 304L stainless steel coupon exposed at 55°C with approximately 0.5 wt % moisture for various periods up to 6 months suffered pitting corrosion to a maximum depth of 30 μm in an area at the bottom of the coupon (in contact with the solid mixture).³ A 316L coupon had a small area (2 by 4 mm) of pitting of about 10 μm in depth. Coupons of both 304L and 316L stainless steel exposed at room temperature for the same durations were either not corroded or had barely detectable attack. Specimens under tensile stress were not investigated in those tests.

The present paper describes the results of coupon immersion tests conducted to investigate stress corrosion cracking as well as pitting in moist plutonium oxide/chloride salt mixtures. The objective was to determine the effects of chloride salt composition and radiation on the corrosion of 304L and 316L austenitic stainless steel and to refine the understanding of the relative importance of the concentrations of NaCl, KCl, MgCl₂, and CaCl₂, water content, and radiation dose.

The small-scale test program described in this paper included the following five test series (Table 1):

Series 1 included one test container (series 1a) with a PuO₂ sample with no chloride salts as an experimental control. The two other containers in this series (series 1b) contain a composition of PuO₂ with 28 wt % chloride salts composed largely of non-hydrating NaCl and KCl with some CaCl₂ and MgCl₂. The isotopic mix of plutonium in this test series and in test series 2 through 4 contained predominantly Pu-239.

Series 2a tests contained PuO₂ with 5 wt % NaCl and 5 wt % KCl.

The Series 3 tests were to evaluate the impact of the hydrating salt MgCl₂ on the corrosion of stainless steel using a laboratory-prepared surrogate of PuO₂ and salts intended to be representative of salts produced by the electrorefining process (termed 'ER' salt). Three compositions of the PuO₂/ER salt mixture that contained equal weight NaCl/KCl and MgCl₂ equal to one tenth of the total salt content were tested:

Series 3a) 90 wt % PuO₂ + 10 wt % ER salt

Series 3b) 95 wt % PuO₂ + 5 wt % ER salt

Series 3c) 98 wt % PuO₂ + 2 wt % ER salt

Series 4 tests were intended to assess the role of another hydrating salt, CaCl₂, versus that of MgCl₂ in the overall salt composition. The total salt concentration was 2 wt % in the series 4 tests, with two variants containing different concentrations of CaCl₂. Series 4a contained 0.2 wt % CaCl₂, and series 4b 0.92 wt % CaCl₂.

The purpose of the series 5a tests was to evaluate the impact of an increased alpha radiation dose on corrosion during exposure to a selected oxide/salt composition. The principal radioactivity from plutonium isotopes is due to alpha decay. Series 5a used a 5 wt % MgCl₂-rich ER salt with the plutonium's specific radioactivity increased by the addition of Pu-238 and Am-241 to that isotopic mixture used in the series 1 through 4 tests. The addition of Pu-238 and Am-241 increased the thermal power of this isotopic mixture from 2.26 W/kg Pu for the series 1 through 4 tests to 5.09 W/kg Pu in the series 5a tests.

TABLE 1
TEST SERIES SOLID MIXTURE COMPOSITIONS (WEIGHT %)

Series	Description	PuO ₂	NaCl	KCl	MgCl ₂	CaCl ₂
1a	Control, 0% salt	100	–	–	–	–
1b	master blend	72	11.7	14.8	1.1	0.4
2a	10% NaCl/KCl	90	5.0	5.0	–	–
3a	10% ER Salt	90	4.5	4.5	1.0	–
3b	5% ER Salt	95	2.25	2.25	0.50	–
3c	2% ER Salt	98	0.90	0.90	0.20	–
4a	2% Ca Salt	98	0.90	0.90	–	0.20
4b	2% 11589 Salt	98	0.54	0.54	–	0.92
5a	5% ER Salt	95	2.25	2.25	0.5	–

EXPERIMENTAL PROCEDURE

The corrosion tests used 304L and 316L stainless steel coupons purchased from Metal Samples Inc., Munford AL. Pitting corrosion was evaluated with 1-inch by 2-inch by 0.06-inch flat coupons with a longitudinally centered autogenous weld (ground flat to the coupon surface with a 600-grit finish). SCC was evaluated with a “teardrop” specimen, a type of compact U-bend specimen with its ends welded together to hold the stressed bend. The metal was plastically deformed during bending and the resulting principal tensile stresses on the outer curved surface were well above the material’s yield stress (manufacturers’ test report values of 50900 and 52300 psi for the 304L heats and 51400 psi for the 316L heat).⁴ Finite element stress analysis indicates that the principal tensile stress at the outer curved surface of the 304L teardrop is $\geq 70,000$ psi.⁵ The teardrop specimens had a transverse autogenous weld at the center of curvature.

The test container for the small-scale tests was a 2-inch-diameter, 2.5-inch-tall stainless steel can sealed with a metal gasket. The container was equipped with a pressure transducer for continuous pressure monitoring during an exposure and a valve for acquiring gas samples periodically (Figure 1). Glass inserts were used to hold small (several cubic-centimeter) volumes of oxide/salt mixture in close contact with the test coupons.

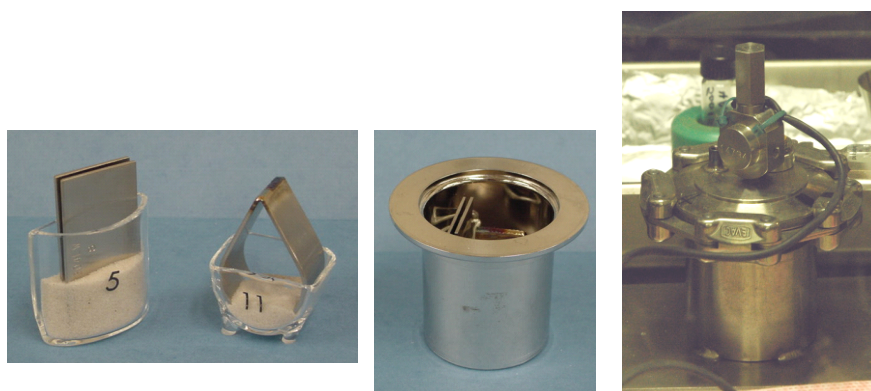


Figure 1. Flat and teardrop coupons in glass inserts, open test container, and sealed container.

Figure 1 shows the coupons in their glass boats or inserts 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 teardrop coupon. The two glass inserts were placed side by side in the vessel. A second teardrop coupon was then placed on top of the first such that it rested in the headspace position without contact with the solid mixture.

PuO₂ was prepared by anion exchange purification, oxalate precipitation, and calcination in a dry air purge for two hours at 950°C. Various salt mixtures having the desired ratios of NaCl, KCl, MgCl₂, and CaCl₂ were prepared by combining the required amounts of each salt in a dry argon glovebox. The dry salt mixtures were then removed from the argon glovebox in a desiccator and heated in a static air atmosphere to between 820°C and 850°C for two hours to melt the salts together. While still warm, the fused salts were placed back in the desiccator and transferred back to the dry argon box where they were ground and pre-weighed into screw-cap glass vials. The pre-weighed salt mixtures were transferred to a plutonium glovebox where they were combined with pre-weighed amounts of PuO₂ in screw-cap jars, mixed briefly with the jars capped, then transferred to a crucible and placed directly in a warm furnace. The PuO₂/salt mixtures were heated in a static air atmosphere at 850°C for two hours, cooled to approximately 300°C, and transferred to screw-cap glass jars.

A helium-purged glove bag deployed inside a plutonium glovebox was used to provide a helium atmosphere for loading PuO₂/salt mixtures and corrosion test coupons into the test containers. The glove bag was first purged with helium until the relative humidity (RH) was below 10%. PuO₂/salt mixtures were then weighed into glass inserts containing the corrosion test coupons as previously described. The two glass inserts in each sample set were placed in small stainless steel pans for ease of handling. The RH in the glove bag was gradually increased by bubbling helium through a container of distilled water and/or by moistening absorbent wipes with water and spreading them out in a large stainless steel pan to speed evaporation of water. The small stainless steel pans holding the sample sets were weighed periodically in the humidified helium atmosphere until the weight gain of each sample set corresponded to uptake of about 0.5 wt% water. A “blank” consisting of pan, glass inserts, and test coupons with no PuO₂/salt mixture was weighed along with each set of exposed samples to estimate the amount of water adsorbed by the container and coupons surfaces. The maximum RH required for samples to reach the target moisture loading in a nominal eight-hour shift was between 58% and 94%. The containers were closed and transferred to air atmosphere gloveboxes for ambient temperature staging.

RESULTS AND DISCUSSION

This section discusses the corrosion observations and the analysis of water contents from the test containers that have completed their exposures and have been opened. These containers had been at ambient glovebox temperature for between 150 and 506 days. Prior to opening each container, the headspace gas in the container was diluted with helium and sampled for analysis. The post-exposure water content of samples of the PuO₂/salt mixtures was measured by thermogravimetric analysis coupled with mass spectrometric detection (TGA-MS), typically within one to three days after opening the container. During this interval the samples were in screw-lid sealed glass vials.

Corrosion Results

The stainless steel coupons from 13 containers were examined visually and photographed. The coupons were lightly brushed to remove oxide/salt mixture, and cleaned of corrosion product with 0.1 M nitric acid. Coupons from four containers have received preliminary microscopic examinations. Observations of corrosion are summarized in Table 7 below. Corrosion ranged from slight, superficial staining in the series 1 tests to pitting with measurable depth and SCC in the 304L coupons in the series 4a containers.

Optical microscopy was used to measure pit depths. The minimum pit depth measurable with the microscope was about 20 μm. Initial measurements of pit depths from two test containers (4a-2 and 4b-1) only are reported below. Cracked coupons have been and will be sectioned for optical metallography. The SCC observations and evidence are detailed after the discussion of pitting results.

The observations in Table 7 for the flat coupons apply to both 304L and 316L stainless steels. There is no significant qualitative difference in the attack on the two alloys, and the depth of attack was comparable in the coupons that have been examined to date microscopically. The only extensive pitting has been seen in coupons exposed in the 4a and 4b series tests, that is, to PuO₂/Cl⁻ salt mixtures with 2 wt % total salt that included CaCl₂.

TABLE 2
SUMMARY OF CORROSION OBSERVATIONS

Test Container	Salt Content	Days Sealed	Corrosion Observations		Maximum Pit Depth in μm
			Flat Coupons	Tear Drop Coupons	
1a-1	None	325	slight stain	slight stain	
1b-1	28% salt	489	slight stain	slight stain	
1b-2		150	slight stain	slight stain	
3c-1	2% ER Salt	274	stain, local corrosion at bottom edge	stain in 304L in solid contact region	
4a-1	2% Salt with 0.2% CaCl_2	506	pitting mostly in solid contact region, stain	pitting, no cracking in 316L in solid contact region	to be evaluated
4a-2		335	pitting in headspace region, edge attack in solid contact	pitting and cracking in 304L in solid contact region	to be evaluated
4a-3		166	pitting mostly in headspace region, edge attack in solid contact	pitting and cracking in 304L in solid contact region	100
4b-1	2% Salt with 0.9% CaCl_2	193	pitting only in solid contact region	pitting in 304L in solid contact	60
4b-2		340	pitting only in solid contact region	pitting in 304L in solid contact	to be evaluated
4b-3		496	pitting only in solid contact region	pitting, no cracking in 304L solid contact region	to be evaluated
5a-1	5% ER Salt with increased α -dose	352	stain, edge attack	stain, pitting in 304L solid contact region	to be evaluated
5a-2		168	stain, possible pitting solid contact region	stain, pitting in 304L solid contact region	to be evaluated
5a-3		470	stain, edge attack	stain, possible in 304L pitting solid contact region	

Figures 2 through 12 show macro-photographs of the front and back faces of selected flat coupons, which show the range of corrosion results from very slight attack to measurable pitting that are listed in Table 2. Most figures show two images of each coupon face, taken with a digital camera through a glovebox window with fluorescent light illumination. The two images were taken at different angles with respect to the coupon in order to obtain the best photographic contrast to reveal features of interest on the highly reflective surfaces. A red line or curve on an image marks the approximate location on the coupon of the irregular top of the solid mixture. Due to bridging in the oxide/salt mixture, the mixture surface was not usually level. The interface between the top of the mixture and the headspace gas usually made itself evident on the coupon through a change in color, reflectivity, or distribution of corrosion. As mentioned above, these coupons contained longitudinal autogenous welds. The preliminary examination of the coupons showed neither preferential attack nor immunity from corrosion associated with the weld of any flat coupon.

Figures 2 and 3 show coupons 304L-12 and 316L – 81 from container 1b-2 respectively after exposure to the high-salt-content mixture for 150 days. The coupons appear uncorroded, with only slight staining or altering of reflectivity to indicate contact with the solid mixture. Neither coupon had measurable pits. Microscopic examination confirmed that the visible spot on the back of 304L – 12 was not a pit with measurable depth but is a stain. Scratches in the headspace area of the coupons were caused by post-exposure handling.

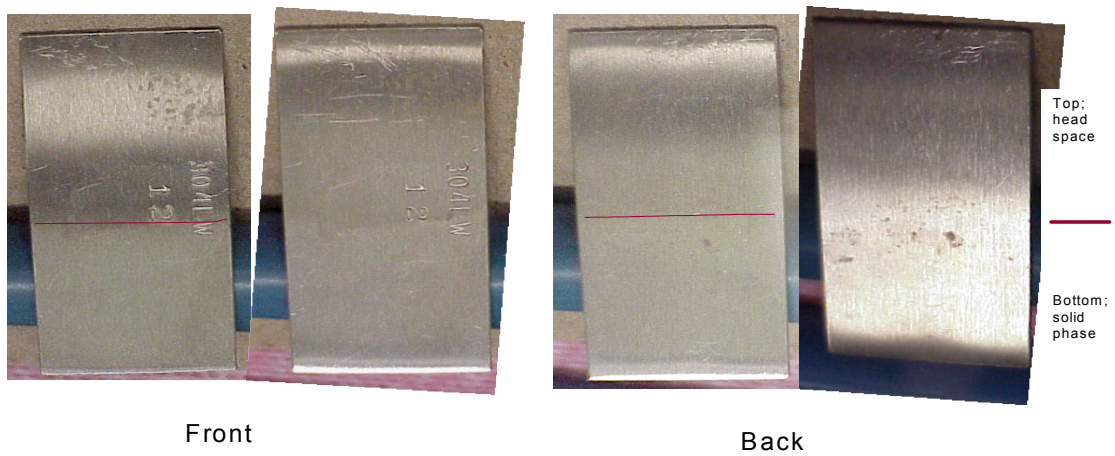


Figure 2. Flat coupon 304L – 12 from container 1b-2, with slight staining; scratches from post-test handling. In this and subsequent figures, the red line or curve denotes the highest level of the plutonium oxide/chloride salt mixture on the coupon.

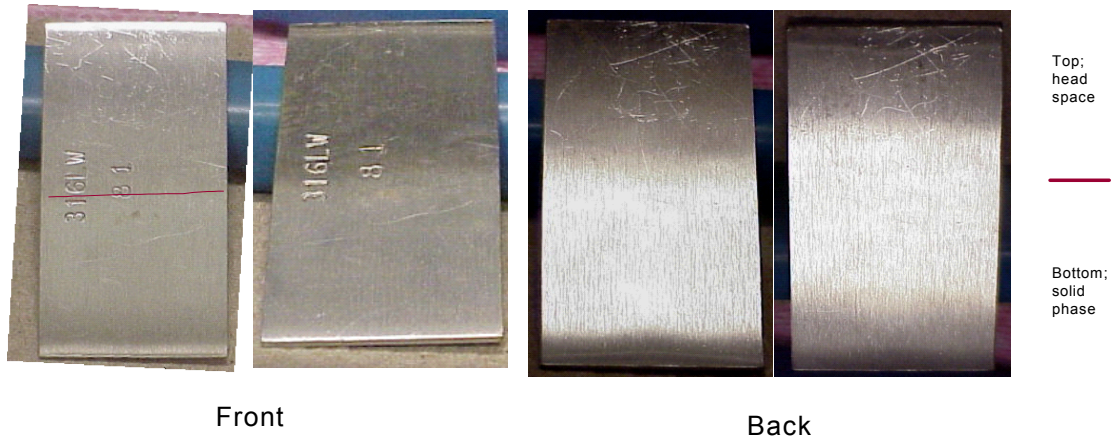


Figure 3. Flat coupon 316L – 81 from container 1b-2,, no corrosion; scratches from post-test handling.

Figures 4 and 5 show images of coupons 304L – 73 and 316L – 13 from container 5a-2 exposed to a 5 wt % magnesium-rich ER salt for 168 days. Both coupons showed considerable staining of the metal that was in contact with solid mixture. Microscopic examination revealed no measurable pitting. There is some attack at the bottom edge of both coupons, but corrosion at edges is not quantified because of the indeterminate starting surface for the attack.

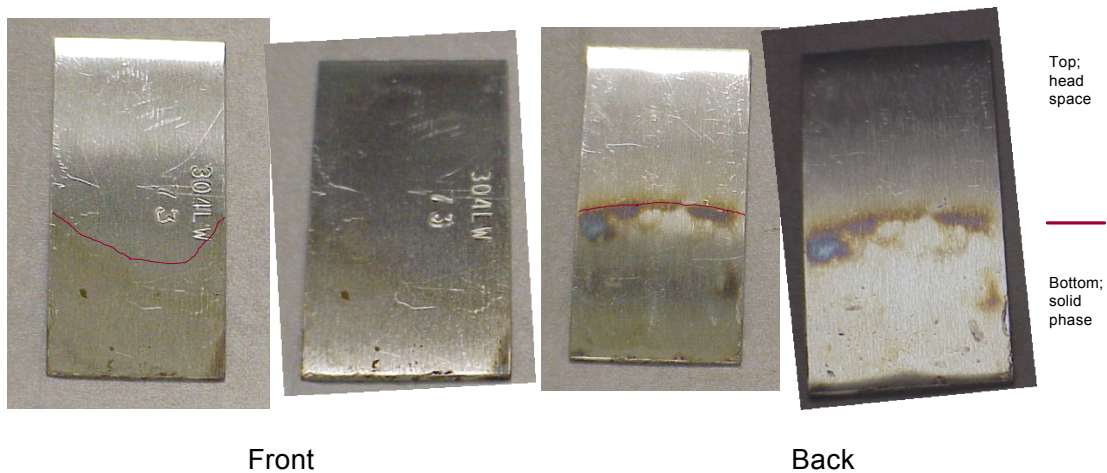


Figure 4. Coupon 304L – 73 from container 5a-2, staining at and below interface between solid mixture and headspace gas.

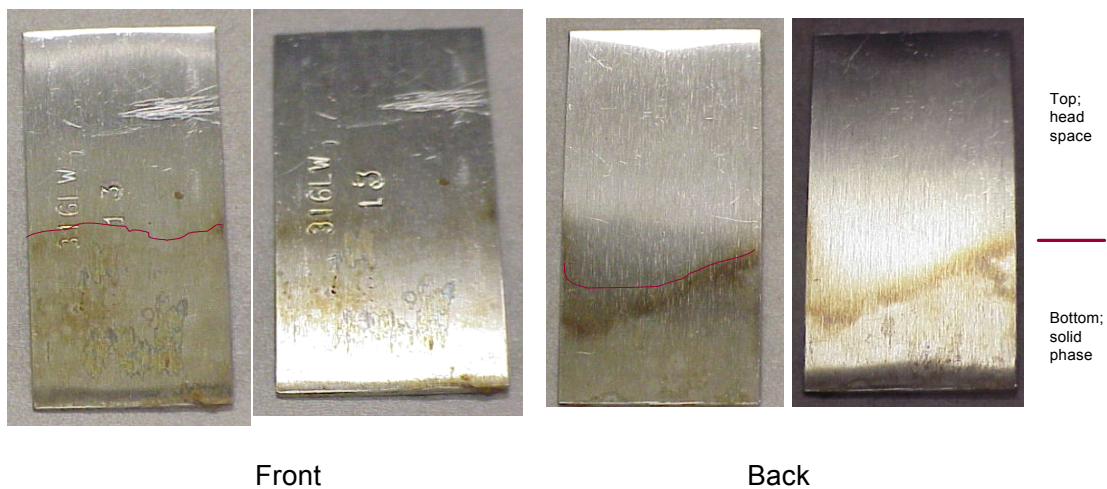


Figure 5. Coupon 316L – 13 from container 5a-2,, staining mainly at and below interface.

Coupons from containers 4a-3 (0.2 wt % CaCl_2) and 4b-1 (0.92 wt % CaCl_2) had obvious pitting corrosion along with a superficial general corrosion or staining. Figures 6 and 7 show images of the coupons from container 4a-3. Coupon 304L – 95 has extensive pitting on the back face in metal just above and following along the solid mixture/headspace gas interface (Figure 6). Pit depths ranged from 10 to 100 μm . There is also attack at the bottom edge of the coupon. Coupon 316L – 75 is similarly pitted (from 20 to 100 μm in depth) at and above the interface, but also has a large pit clearly visible on the front face in the solid contact region (Figure 7). That pit measured 80 μm in depth and is surrounded by a ring of deposited corrosion product. Edge attack at the bottom of 316L – 75 is also visible.

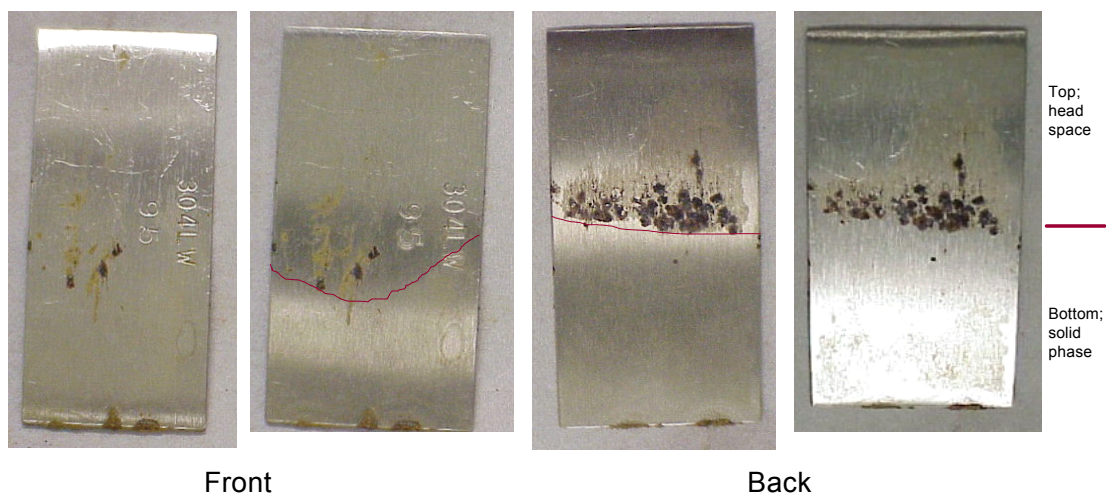


Figure 6. Coupon 304L – 95 from container 4a-3,, pitting in the headspace area, edge attack at bottom.

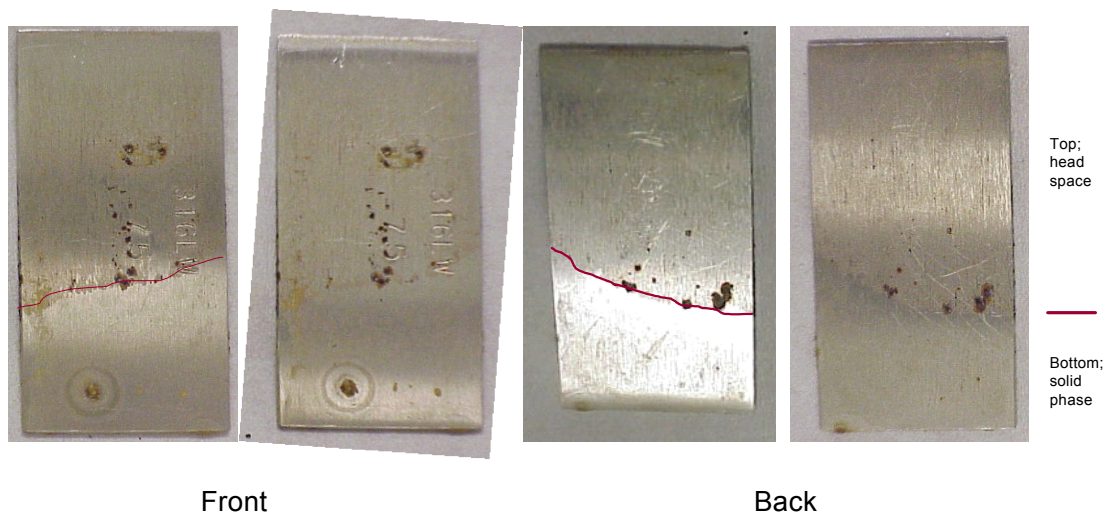


Figure 7. Coupon 316L – 75 from container 4a-3,, large pit on front face in solid contact area and pitting in the headspace region.

Coupons from container 4b-1 were exposed to the oxide/salt mixture for 193 days. As in the container 4a-3 coupons, there was considerable pitting, as Figures 8 and 19 show for coupons 304L – 19 and 316L – 88, respectively. However, the pitting attack in these coupons was seen entirely in the solid contact region, with no attack in the headspace gas region. The coupons were also generally stained or discolored in the solid contact region, but not in the headspace gas region. Pit depths ranged from 20 to 40 μm in coupon 304L – 19 and from 20 to 60 μm in 316L – 88.

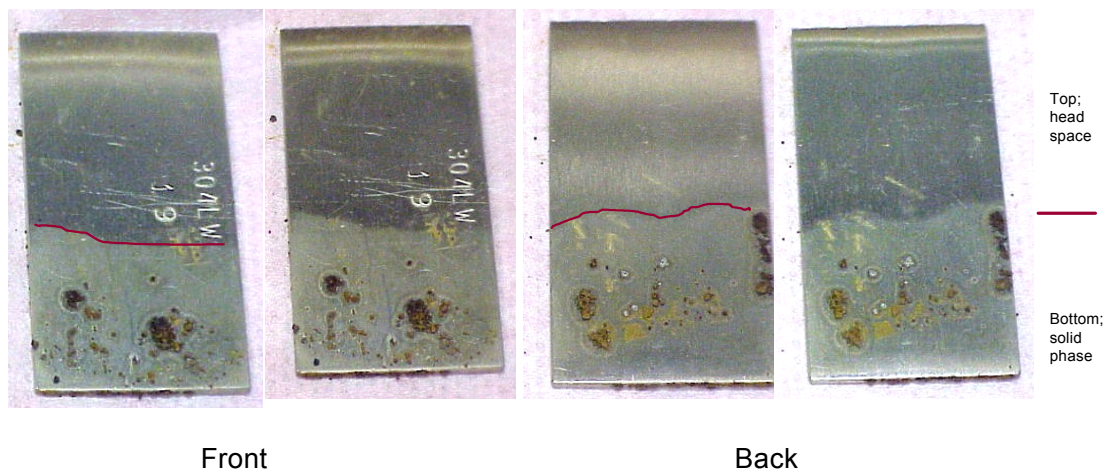


Figure 8. Coupon 304L – 19 from container 4b-1, , extensive pitting in the solid contact region, but not in the headspace region.

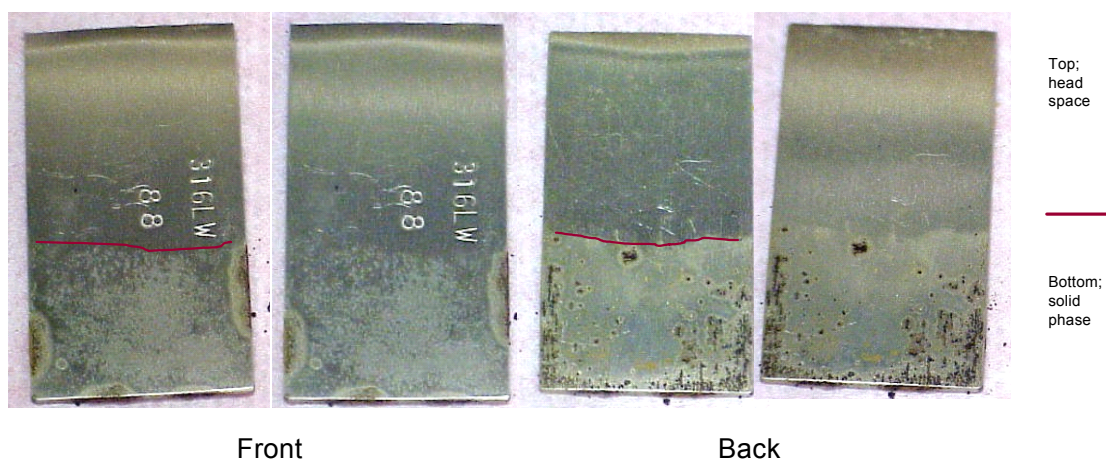


Figure 9. Coupon 316L – 88 from container 4b-1,, pitting in the solid contact region, but no attack in headspace gas region.

The observations to date show that the most extensive pitting was found in coupons exposed to PuO_2/Cl^- salt mixtures that contained relatively high concentrations of CaCl_2 with a relatively low total salt concentration, that is in coupons exposed to the 2 wt % total salt mixtures 4a (0.2 wt % CaCl_2) and 4b (0.92 wt % CaCl_2). Coupons exposed to MgCl_2 -bearing mixtures with 2 wt % total salt (3c) or coupons exposed to higher total salt concentration mixtures (1b with 28 wt % total salt and 5a with 5 wt % total salt) had only staining or perhaps slight pitting.

The result from container 5a-2 indicates that MgCl_2 may not be as corrosive as CaCl_2 . However the presence of CaCl_2 in mixture 1b did not result in pitting attack in the 1b-1 and 1b-2 coupons. This suggests that corrosion in the PuO_2/Cl^- salt system is a product of a complex interaction between the salt composition and the available water that is essential to form a corrosive aqueous electrolyte. Both CaCl_2 and MgCl_2 can bind waters of hydration (NaCl and KCl cannot). Although both the 1b series mixtures had relatively high calculated initial water contents of about 1%, this water content was well below the value required to fully hydrate the MgCl_2 and CaCl_2 present (see Table 3 below).

The relative level of hydration of CaCl_2 appears to play a role in the character of the pitting attack in the series 4a and 4b exposures through its control of the relative humidity of the headspace gas. As Figures 6 and 8 show, the pitting attack in the 304L flat coupon exposed to mixture 4a-3 is predominantly found in the region of headspace contact, while the pitting in the 304L coupon exposed to mixture 4b-1 is predominantly in the solid contact region. The associated 316L flat coupons show a similar but less pronounced tendency. Table 3 shows that the calculated initial water content for the 4a-3 mixture greatly exceeded the water content for full hydration of the 0.2 wt % CaCl_2 . In the case of mixture 4b-1, the water loading was not sufficient to fully hydrate the 0.92 wt % CaCl_2 . Thus the water content in container 4a-3 that was in excess of that needed for full hydration of the CaCl_2 would have been available to raise the humidity of the headspace gas. The water content in container 4b-1 however would have been mostly captured by the hydration of the higher CaCl_2 concentration. Container 4b-1's headspace gas would have a lower relative humidity. The higher relative humidity may have then led to the formation of a corrosive electrolyte on the stainless steel in contact with the headspace gas in container 4a-3. Such a corrosive electrolyte could have been absent in the drier atmosphere of container 4b-1, leading to the observed distribution of pitting.

Stress Corrosion Cracking Observations

As noted above, teardrop coupons were used to assess the susceptibility of 304L stainless steel to SCC induced by the moist oxide/salt mixture. Two teardrop coupons, one from container 4a-3 and one from container 4a-2, were found to have undergone SCC after 166 and 335 days of exposure, respectively, in the solid contact position. Cracking was not observed in coupons in solid contact from any other container opened to date, nor was cracking seen in any headspace-position coupon. Nor was cracking observed in the 316L teardrop coupons exposed to mixture 4a-1.

In general, all teardrop coupons had staining and pitting similar in extent as was seen in their companion flat coupons. Some teardrop coupons had general staining or corrosion in the heat-affected zones of their closure weld. Figures 10 and 11 show examples of the pitting and staining in teardrop coupons exposed in the solid contact positions in containers 4a-3 and 4b-1. These images were made before acid cleaning of the coupons. Pitting is visible on the outer and inner curved surfaces of the coupons as well as at edges.

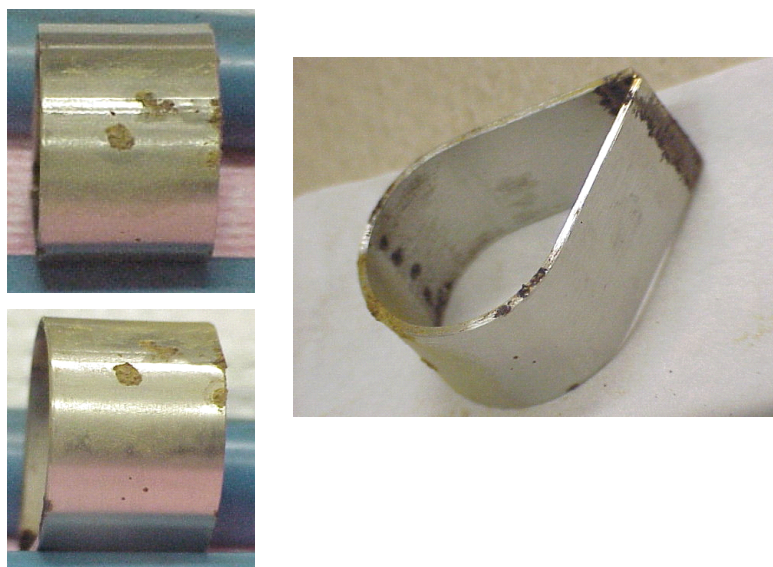


Figure 10. Container 4a-3 teardrop coupon 304L – 23 showing pitting in the metal in contact with the oxide/salt mixture. Corrosion is also evident in the heat-affected zone of the closure weld at the coupon tip, which was not in contact with the solid mixture.

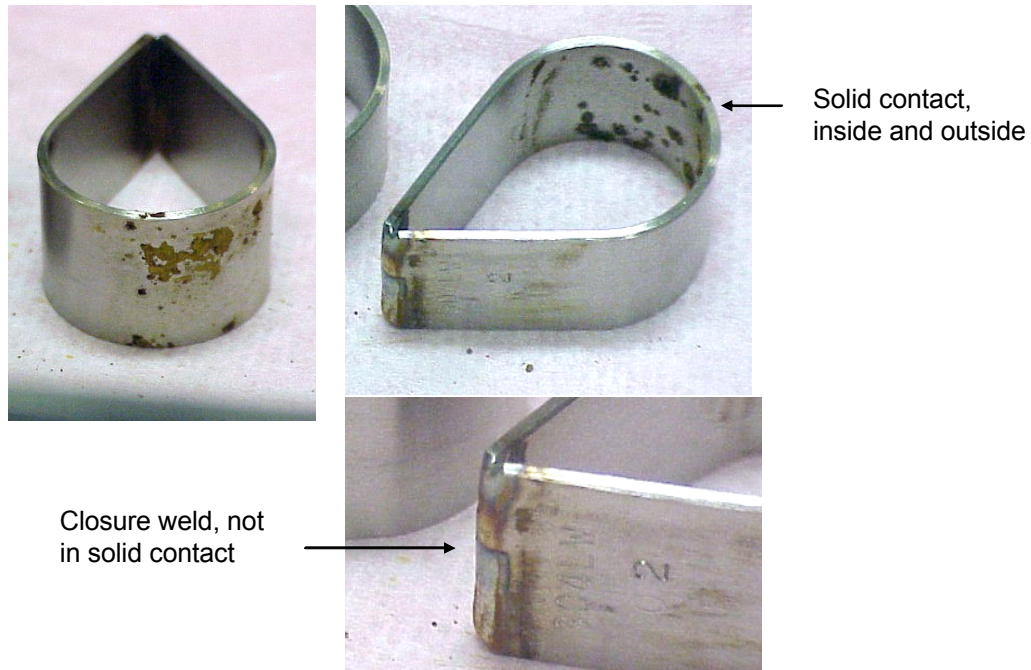


Figure 11. Container 4b-1 teardrop coupon 304L – 02 showing pitting inside and outside in metal in solid contact; no evidence of cracking; staining near closure weld.

Stress corrosion cracking was initially revealed in the container 4a-3 solid contact teardrop coupon 304L – 23, through dye penetrant testing. Optical microscopy, scanning electron microscopy, and optical metallography were used to examine the path and nature of the cracking. The cracking extended across more than half the width of the coupon and was associated with the transverse autogenous weld. Figure 12 is an optical micrograph that shows the cracking starting at the edge of the coupon in a localized area of general corrosion and propagating along the interface between the weld and the parent metal, that is in the weld heat-affected zone. Figure 13 shows the entire crack path on the coupon surface in a composite scanning electron micrograph. The crack was highly branched as it crossed through weld metal and continued its path along the opposite weld/parent metal interface. Optical metallography of one cross-section of the coupon reveals the propagation of the crack along the interface (Figure 14) and, in a second cross-section, propagation through the weld metal into the parent metal (Figures 15 and 16). The enlargement in Figure 14 shows what appears to be intergranular cracking. The highest magnification image (Figure 17) shows the extensive cracking paths across parent metal grains. This transgranular nature of the cracking is characteristic of chloride-induced SCC in austenitic stainless steel. The cracking terminates at a depth where stress analysis predicts that the tensile stress falls to zero.⁴

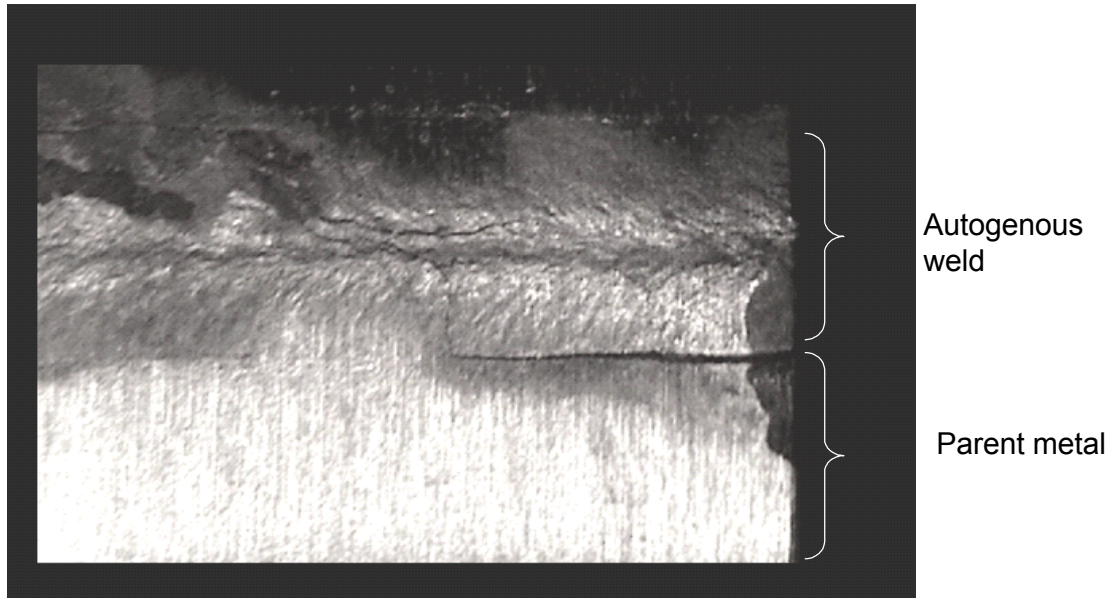


Figure 12. Photomicrograph of teardrop coupon 304L – 23, showing branched cracking near and within the autogenous weld; possible crack initiation site in area of localized corrosion at right edge of coupon. Approximately 10X magnification.

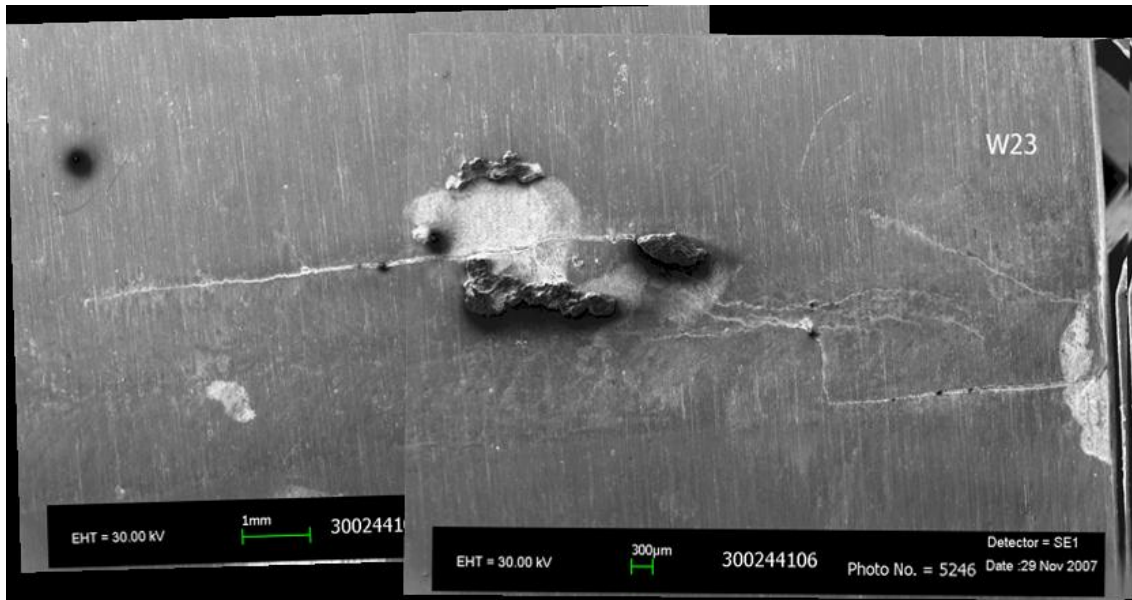


Figure 13. Composite scanning electron micrographs of coupon 304L-23 showing full extent of cracking on outside (convex) surface.

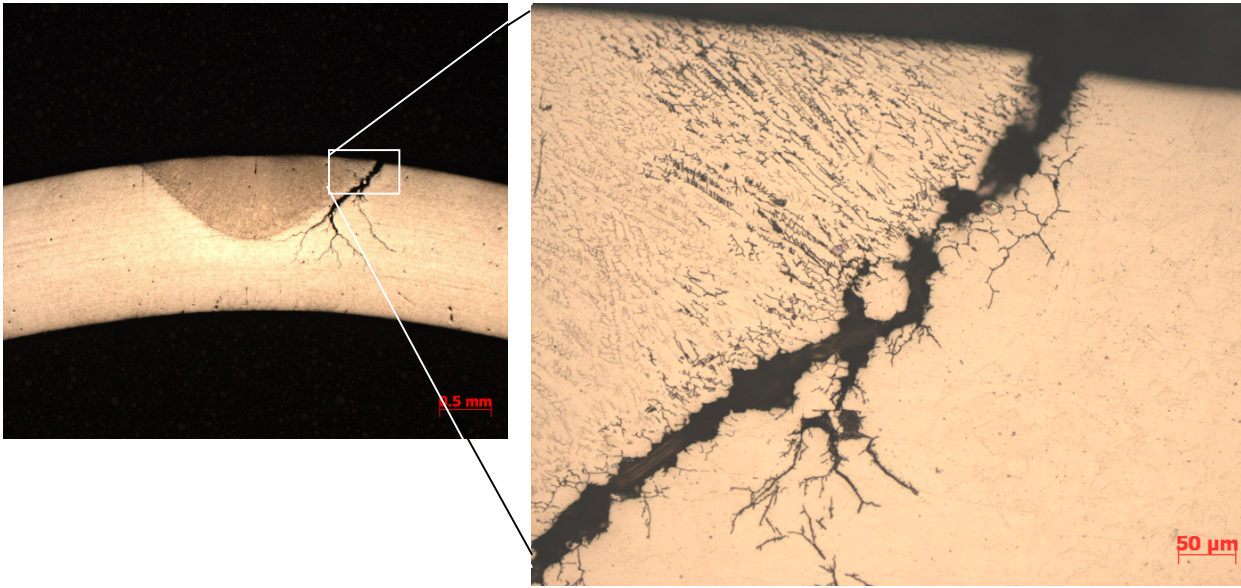


Figure 14. Optical micrographs of a cross-section through teardrop coupon 304L-23 showing cracking along the weld/parent metal interface.

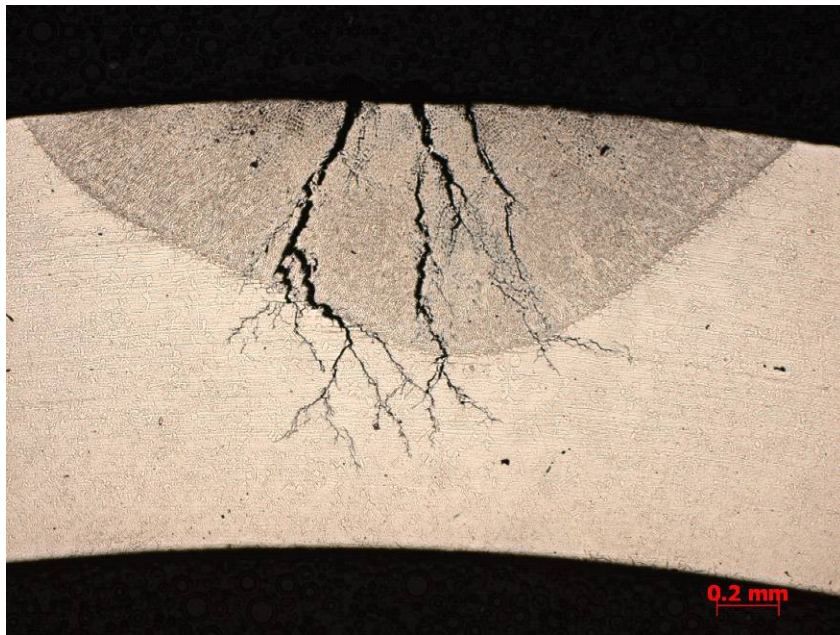


Figure 15. Optical micrograph of a second cross-section of coupon 304L – 23, showing propagation of multiple cracks through the weld metal into the parent metal.



Figure 16. Optical micrograph showing transgranular nature of the cracking.

As noted above the principal tensile stresses across the outer curved surface of the teardrop coupon were $\geq 70,000$ psi. Stress analysis revealed that the highest calculated stresses were of the order of 100,000 psi and located about 1 cm away from the transverse autogenous weld at the center of the coupon's bend. The fact that cracking appeared to initiate in corrosion at the weld metal/parent metal interface (essentially the weld's heat-affected zone) with its $\sim 70,000$ psi tensile stress rather than at some higher stress location suggests the special susceptibility of the weld and its interface to SCC.

SCC occurred in a second series 4a test coupon, 304L – 20 from container 4a-2, which was exposed for 335 days or about twice the exposure of container 4a-3. Figure 17 shows the prominent stress corrosion cracks at the weld metal/parent metal interfaces of the coupon. A third series 4a container, container 4a-1, held 316L stainless teardrop coupons in both the solid contact and headspace positions for 506 days. Although teardrop coupon 316L – 40 experienced extensive pitting and localized general corrosion visual inspection revealed no cracking.



Figure 17. Stress corrosion cracking along the autogenous weld in coupon 304L – 20 from container 4a-2

As stated above, SCC has not been observed in 304L teardrop coupons that were exposed in any containers other than 4a-2 and 4a-3. Notably, cracking was absent from coupons exposed in the 4b test containers, whose PuO_2/Cl^- salt mixtures did contain CaCl_2 at a concentration of 0.92 wt% compared with 0.2 wt% CaCl_2 in the 4a containers. Clearly a corrosive

electrolyte did form in container 4b-1, and considerable corrosion is evident in the stressed region of its teardrop coupon (Figure 11). The reason for the absence of cracking in this instance is not known, but further testing at elevated temperature (of the order of 70°C) must be conducted to draw conclusions on the corrosivity of the 0.92 wt% CaCl₂ mixture or, indeed, of those mixtures that contain MgCl₂.

Analysis of Water Content

Table 3 gives the analysis of the water content of materials removed from the 13 opened test containers. This net water loading assumes water content prior to exposure to humid atmosphere was negligible. As a cross-check of the initial water content of each sample that was determined by weight gain, the post-exposure water content was measured by TGA-MS analysis and then corrected for water loss via radiolytic or chemical hydrogen production on the basis of headspace gas analysis results. This correction is based on the assumptions that (1) water is the only significant source of hydrogen and (2) one mole of water yields one mole of hydrogen. This correction does not account for water that may have been consumed by chemical reactions to produce, for example, hydroxyl groups on the surface of PuO₂ or oxychloride compounds. The post-exposure moisture content by TGA-MS and the amount of water consumed by hydrogen production were summed to yield a calculated initial water content for each test container, which is the value listed in Table 3. The final column in Table 3 lists the theoretical water content needed to fully hydrate the MgCl₂ or CaCl₂ present in each container. These values are included for comparison to the measured water contents as an indication of the extent to which the alkaline earth salts were hydrated.

TABLE 3
WATER CONCENTRATION OF PUO₂/SALT MATERIALS (WEIGHT %)

Sample ID	Calculated Initial Water Content	Water Content Fully Hydrated ^a
1a-1	0.38	No salts to hydrate
1b-1	1.00	1.64
1b-2	0.94	1.64
3c-1	0.35	0.23
4a-1	0.58	0.19
4a-2	0.63	0.19
4a-3 ⁱ	0.50	0.19
4b-1	0.66	0.90
4b-2	0.61	0.90
4b-3	0.61	0.90
5a-1	0.49	0.57
5a-2	1.24	0.57
5a-3	0.45	0.57

^a Fully hydrated is assumed to mean six moles of water for each mole of MgCl₂ or CaCl₂.

Calculated initial water contents based on post-exposure water analyses were generally equal to or higher than values for initial water added based on weight gain. This is probably because most of the samples contained some amount of moisture prior to exposure to humidified helium. The calculated initial water contents are considered to be more accurate because of the difficulties associated with handling and weighing the samples in the helium glove bag, the high RH required to load up to 0.5 wt % water, and the possibility that some samples had measurable water content prior to moisture uptake.

CONCLUSIONS

Laboratory corrosion tests at room temperature on 304L stainless steel coupons that were exposed to moist (nominally 0.5 wt % water) PuO₂/CaCl₂-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. Cracking was associated with the heat-affected zone of an autogenous weld in the test coupons. The mixture that led to SCC contained 98 wt % PuO₂, 0.9 wt % NaCl, 0.9 wt % KCl, and 0.2 wt % CaCl₂ (total salt concentration of 2 wt %). Type 316L stainless steel was found to undergo pitting but not SCC when exposed to this same mixture with similar water loading as in the 304L tests. Type 304L stainless steel showed pitting but did not exhibit cracking under exposure to a mixture with an identical 2 wt % total salt concentration but with a higher CaCl₂ concentration of 0.92 wt %. A mixture with a very high total salt concentration of 28 wt % did not induce pitting or cracking. Cracking was not observed in any coupon that was contacted by headspace gas, but pitting was observed on areas of some coupons that were in headspace gas contact. Pitting measurements on coupons that have been examined microscopically to date showed depths up to 100 μm.

The corrosion tests were conducted in small stainless steel containers that were sealed under a helium atmosphere. At completion of the test, the headspace gas composition was determined, and the water loading of the PuO₂/Cl⁻ salt mixture was evaluated. Actual water loading of the PuO₂/Cl⁻ salt mixtures ranged from 0.35 to 1.24 wt %. These values represent gravimetric data corrected with the results of the headspace gas analysis, in particular analysis of hydrogen gas generation from water radiolysis.

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