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THE UNDERGROUND CORROSION OF SELECTED TYPE 300 STAINLESS STEELS AFTER 34 YEARS

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ABSTRACT

Recently, interest in long-term underground corrosion has greatly increased because of the ongoing need to dispose of nuclear waste. Additionally, the Nuclear Waste Policy Act of 1982 requires disposal of high-level nuclear waste in an underground repository. Current contaminant release and transport models use limited available short-term underground corrosion rates when considering container and waste form degradation. Consequently, the resulting models oversimplify the complex mechanisms of underground metal corrosion. The complexity of stainless steel corrosion mechanisms and the processes by which corrosion products migrate from their source are not well depicted by a corrosion rate based on general attack. The research presented here is the analysis of austenitic stainless steels after 33½ years of burial. In this research, the corrosion specimens were analyzed using applicable ASTM standards as well as microscopic and X-ray examination to determine the mechanisms of underground stainless steel corrosion. As presented, the differences in the corrosion mechanisms vary with the type of stainless steel and the treatment of the samples. The uniqueness of the long sampling time allows for further understanding of the actual stainless steel corrosion mechanisms, and when applied back into predictive models, will assist in reduction of the uncertainty in parameters for predicting long-term fate and transport.

Keywords: stainless steel, underground corrosion.

INTRODUCTION

The Department of Energy (DOE) Environmental Management (EM) Program is responsible for cleaning up 114 sites (over 2 million acres) contaminated during the production and testing of nuclear weapons and energy research activities. Hundreds of containers containing highly activated wastes, including non-fuel activated reactor components and other metal alloys, have been disposed since the early 1950s. The primary materials are

AISI Types 304 and 316 stainless steels (UNS S30400 and UNS S31600) from core barrels and core rod assemblies, aluminum fuel end boxes, beryllium reflectors and shims, and zirconium alloys and nickel alloys primarily from end boxes and assemblies. Overall, activated stainless steel and aluminum alloys are the largest contributors and will be the major source of the radiological activity in the subsurface environment.[1]

A growing environmental concern is the contamination of soil and groundwater by radionuclides and hazardous chemicals released from corroding metal waste forms and containers. Corrosion causes release of contamination in two ways: (1) via leaks from aging tanks or waste containers, where contaminants become readily available for transport; and (2) via the corrosion process itself, where the contamination becomes available for transport as the surface of the buried contaminated bulk metal waste is oxidized by chemical and physical attacks. The natural processes that release these contaminants to the environment and the rates at which the releases occur are poorly understood and inadequately defined, partly due to a paucity or complete lack of corrosion data.[2] Understanding the corrosion mechanisms, release, and transport processes is critical to predicting soil and groundwater contamination.

The National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards – NBS) has been actively involved in underground corrosion studies since 1910, when it was authorized by Congress to study the deterioration of underground structures. In 1970, an extensive program, sponsored by the American Iron & Steel Institute (AISI) and performed by the NBS, was undertaken to study the underground corrosion of martensitic, ferritic, and austenitic stainless steels.[3,4] Thousands of stainless steel specimens were buried at six test sites in the United States. During the first eight years of the study, only four of the five planned removals were completed, leaving one set of stainless steel specimens at each of the six test sites. These specimens are AISI Types 200, 300, and 400-series stainless steels and special high-alloy stainless steels in U-bend, sheet, and tube forms in annealed, cold worked, and sensitized conditions, with and without welds and crevices.

As part of the Environmental Science Management Program (ESMP)-sponsored basic research grant, the Idaho National Laboratory (INL) has recovered and analyzed some of the corrosion samples from one of the NIST sites. This research directly applies to environmental management operational corrosion issues and long-term stewardship scientific needs for understanding the behavior of waste forms and their near-field contaminant transport of chemical and radiological contaminants at nuclear disposal sites. As such, the research offers the best comparative study available for DOE waste metals and containers that have been disposed of and have been buried for more than 30 years. The long burial time for the specimens in this study allows for further understanding of the actual stainless steel corrosion mechanisms, and when applied to predictive models, will assist in reduction of the uncertainty in parameters for predicting long-term fate and transport. This paper briefly describes the corrosion analysis results of the AISI Type 301 (UNS S30100), Type 304 (UNS S30400), and Type 316 (UNS S31600) stainless steel sheet specimens recovered from the partial sampling of the first test site.

EXPERIMENTAL PROCEDURE

For this research paper topic, the scope is limited to one test site and only the Types 301, 304, and 316 stainless steel sheet specimens, annealed and sensitized. The corrosion specimens were analyzed using applicable American Society for Testing and Materials (ASTM) standards as well as microscopic and X-ray examination to determine the mechanisms of stainless steel corrosion. The experimental procedure consisted of three stages:

The first stage was the experimental procedure established by NIST in 1970 for preparing the specimens and then burial at the test site.

The second stage was the experimental procedure established by NIST following the recovery of specimens during the test intervals of 1, 2, 4, and 8 years.[4] The procedure NIST established is the basis for direct corrosion testing using buried coupons and is the most widely used and simplest method of underground corrosion testing.[5] For this research, the elements that were applied herein for testing the stainless steel coupons are: (1) measurements for calculating the corrosion rate of the specimens and (2) observations of the localized corrosion of the specimens following exposure. These elements have been reported for the test intervals of 1, 2, 4, and 8 years for the AISI Types 301, 304, and 316 stainless steel sheet specimens.[4] The procedures used by NIST helped establish the ASTM procedures now in use.

The third stage was the experimental procedure used by the INL following the recovery of AISI Types 301, 304, and 316 stainless steel sheet specimens after exposure for 33½ years. The elements for the testing are to follow ASTM procedure G 1 for measuring the corrosion rate of the specimens and to examine the extent of the localized corrosion using microscopic and X-ray techniques following exposure.

NIST Experimental Procedure for Preparation and Burial of the Specimens

NIST identified the test location as "Site D, Lakewood Sand." The description simply was white, loose sand with some black streaks that supports an abundant growth of beach grass. The Lakewood site is near the New Jersey coast but is not subject to overflow from the ocean except under unusual flood conditions. In 1970, the sand had a pH of 5.7 and the resistivity ranged from 13,800 to 57,500 ohm-cm. The level of the groundwater ebbed and flowed annually, so the specimens could have been covered for some part of the year.

NIST devised the sample set to simulate some of the conditions that may be encountered with components fabricated from stainless steels. The materials discussed in this paper are the annealed and sensitized flat sheet specimens of the Types 301, 304, and 316 stainless steels buried in 1970. The applicable stainless steel systems buried at the test site with their treatments and preparation are given in Table 1. The chemical analysis of each alloy is in Table 2.

Each specimen (approximately 0.06 in. (0.15 cm) thick) was received from the stainless steel producers as flat sheets with sheared deburred edges. The sheets were stamped with identification numbers using chromium-plated steel dies, degreased, passivated, scrubbed with a fiber brush, rinsed thoroughly with water, and air dried.

At the test site, the specimens were buried in trenches approximately 2½ ft (0.76 m) deep and 2 ft (0.61 m) wide. The specimens were placed about 1 ft (0.30 m) apart. The 8 in. x 12 in. (20.32 cm x 30.48 cm) sheets buried in September 1970 were placed in the trench in an upright vertical position with the short dimension horizontal. Sufficient specimens were buried at the test site to permit recovery of a complete set at each of five specific intervals–after 1, 2, 4, and 8 years with the final set to be removed at a later date.

NIST Experimental Procedure for Analyzing the Specimens

Upon removal from the trench after burial for 1, 2, 4 and 8 years, the specimens were returned to the NIST laboratory in Gaithersburg, Maryland. In the laboratory, the specimens were rinsed in tap water to remove adhering soil particles. They were examined visually prior to further cleaning. All specimens were then further cleaned ultrasonically using a 10% nitric acid solution heated to 120° – 130 °F (49°– 54 °C) for 20 to 30 minutes. After cleaning, the specimens were rinsed in hot tap water and air-dried. The sheets were then weighed and their weight loss was determined. The average loss in weight of similar unexposed (control) specimens given the identical cleaning process was subtracted from the weight loss of the exposed specimens. Pit depth determinations were obtained for all of the sheet specimens.

INL Experimental Procedure for Recovery and Analyzing the Specimens

The INL arrived at NIST's "Site D, Lakewood Sand" in April of 2004 to do environmental sampling and recover specimens that were buried in 1970. The soil fit the NIST description; however the abundant growth of beach grass had been replaced with thirty years of trees, shrubs and undergrowth typical of coastal progression. The site may not have been subject to ocean flooding; however, the specimens were in saturated soil conditions due to the high groundwater. The sand, in 2004, had a pH of 6.19 with a resistivity of 59,000 ohm-cm and the groundwater had a pH of 4.76.

The specimens analyzed for this research paper were recovered from one of the two trenches emplaced in 1970. NIST provided a map of Site D and the marker posts, for the most part, survived so the trenches were identifiable. The recovery occurred after 33½ years of exposure. From the one trench, the annealed and sensitized sheet specimens of AISI Types 301, 304, and 316 stainless steels were recovered.

Upon removal from the trench, the specimens were air-dried and any loosely adhering sand removed. The specimens were then appropriate packaged and sent to the INL in Idaho Falls, Idaho. In the laboratory, the specimens were visually examined before any cleaning was done and then again after the specimens were rinsed in demineralized, deionized water to remove adhering soil particles.

Changes at NIST since 1970 created two profound conundrums for this research. The first is that the original unexposed control specimens were no longer available. To compensate for this, cleaning blanks of closely matching materials were substituted (see Table 3). However, even using these closely matching substitutes added to the uncertainty when the specimens were subjected to the ASTM G1-03 standard proceedures[6] for cleaning the corrosion specimens. The second is that the records for original pre-exposure sheet mass measurements were no longer available. Since the original mass data were not available, mass loss could not be determined with great accuracy. Fortunately, the specimens were recovered in a condition where the original rolling marks and edges could still be seen on the surface of each of the specimens. For each specimen the volume was determined using the following procedure:

1. Measure the specimen length at 1-in. (2.5-cm) intervals across the 8-in. (20.32-cm) width (using a vernier caliper).
2. Measure the specimen width at 1-in. intervals (2.5 cm) along the 12-in. (30.48-cm) length (using a vernier caliper).
3. Measure the specimen thickness at 10 places with a micrometer.
4. Average the measured lengths, widths, and thicknesses and multiply those averages together to obtain a volume.

Once each volume was calculated, the mass was determined by taking the density values from textbooks and supplier websites.

After cleaning, pit depth analysis on each of the specimens was conducted using a vertical scanning interferometer. Additionally, X-ray examinations were performed on each of the sheet specimens while microscopic examinations were performed on selected sheet specimens.

RESULTS AND DISCUSSION

In April 2004 stainless steel specimens were recovered from the NIST underground corrosion research test Site D. Among the specimens, 12 sheet specimens of AISI series Type 300 stainless steel (UNS S30100, UNS S30400, and UNS S31600) were exhumed. The results of the corrosion evaluation are presented here. The specimens were examined visually, measured to evaluate mass loss, X-rayed, and in specific cases microscopically analyzed. The visual examination summary (see Table 4) includes the earlier NIST results along with the results of the specimens buried for 33½ years.

As is expected of stainless steels, corrosion effects are localized and are generally confined to a small area. As was reported for the earlier observations by Gerhold et al., "…one specimen may have only one corrosion pit which caused perforation of the specimen, while there was little or no corrosion observed on companion specimens exposed for the same period of time in the same environment."[4] This observation holds true with the results of the same companion specimens over time. Localized attack of the stainless steel has the same basic influences as was observed in the Gerhold et al. report as summarized as follows.[4]

1. Inhomogeneities in the metal surface.
2. Concentration cell effects due to adhering soil particles or crevices where stagnant conditions may exist.
3. Presences of chlorides in the soil.

4. Microbiological organisms.
5. Abrasion of the metal surface by soil particles, roots, or foreign debris.

To document the differences and similarities among the material types, treatments, and exposure time, this paper will group results by the three metal types. The results from each metal type will have discussions on visual examination (summary combines the results from Gerhold et al.[4]), X-ray, and microscopic examinations (when performed).

Visual Observations Type 301 (UNS S30100)

Visual observations were performed for the Type 301 sheets and compared with earlier observations by NIST (Gerhold et al.[4]) in Table 4. Photographs showing the front side of the two annealed Type 301 sheets are on the left sides of Figures 1 and 2, while the sensitized Type 301 sheets are depicted on the left sides of Figures 3 and 4. Surface attack (e.g., iridescent film and staining) was observed primarily on the 33½-year annealed and sensitized specimens although limited staining was observed on both the 4-year annealed specimens and the 8-year sensitized specimens. Staining was readily removed during the cleaning process. Pitting was observed in the 1 and 2-year annealed specimens; this was the only type of invasive[(1)] attack observed on the early-retrieval annealed specimens. Sensitized specimens showed some pitting at every test interval. Blistering was observed in the sensitized specimens quite early in the test (after 2 years), but not for the annealed specimens until 33½ years. Except for pitting and blistering, other forms of invasive attack are not visually observed on the sensitized specimens with a notable exception of an edge effect perforation for the 33½-year specimen. No tunneling was observed in the 1, 2, 4, and 8-year specimens. Tunneling was observed only in the 33½-year specimens and only in the annealed specimens along the edge.

Mass Loss Type 301 (UNS S30100)

The data for the estimated original mass and post-cleaning mass for the Type 301 specimens are in Table 5. The post-clean mass for the annealed Type 301 specimens are within the range of the estimated original mass. The mass loss for sensitized Type 301 specimens after 33½ years of burial is estimated at 10 to 32 g for specimen 53D19, and 20 to 42 g for specimen 53D20.

X-ray Observations Type 301 (UNS S30100)

X-ray observations for annealed Type 301 samples recovered after 33½ years are found on the right half of Figure 1 and 2. There are few pits and tunnels visible on the X-rays of the annealed specimens that are not discernable from the visual examination. In Figures 1 and 2, the tunneling runs horizontally. Close inspection of the specimen surface disclosed that the rolling direction for all of the Type 301 specimens was in the horizontal direction. This is unlike the Types 304 and 316 stainless steel specimens, for which the rolling direction was in the vertical axis of the specimens when buried. This shows that the tunneling in Type 301 preferentially follows the rolling direction. There is very little tunneling at the cut edges of the annealed specimens. The visual examination of the 8-year annealed specimens disclosed no indications of invasive attack. By contrast, the 33½-year specimens showed blistering, tunneling, and pitting. This indicates that the type of corrosion seen in Figures 1 and 2 had not occurred or was just starting.

X-ray observations for sensitized Type 301 specimens recovered after 33½ years are found on the right half of Figures 3 and 4. In Figures 3 and 4 there are four distinctive features:

1. Black spots, which visual observation confirm are pits;
2. Grey spots that surround the pits but are darker than that of the rest of the sheet, which visual observation confirm are blisters;

[(1)] For this research paper, invasive corrosion attack is defined as attack that penetrates the specimen surface. This includes pitting, tunneling, blistering and cloud-like formations. Iridescent surface stains and intergranular corrosion on the surface are not considered invasive corrosion attack

3. Off-white, cloud-like formations that extend over most of the area of the Type 301 sensitized specimens and are unique to these specimens; and
4. White areas that are in uncorroded areas of the sheets.

Destructive Examination of Sensitized Type 301 (UNS S30100)

To obtain a better understanding of the features and corrosion mechanisms of the sensitized Type 301 specimens, a destructive examination was performed on the sheet in Figure 3. In the lower right hand corner of the sheet, a large blister appears lighter in color than the other blisters due to lighting during photography. This lighter-colored blister has small cracks that radiate from the central surface pit. The blister, measuring between 0.015 and 0.019 in. (390 and 480 μm) tall, was scored and pried open as illustrated in Figure 5. The underside of the blister and the "hinge" (see Figure 6) were corroded intergranularly. Examination at higher magnification disclosed that there was no plastic deformation on either the hinge or the underside of the large blister with the exception of a small area of cup-and-cone fracture at the intersection of the hinge and underside, between the "780.12" and "856.98" markings in Figure 6.

When a chamber or void was found underlying the blister after being pried open, additional examination was conducted. Metallographic sectioning of another large blister of similar size disclosed that the chamber walls were heavily intergranularly corroded (Figure 7). This is not surprising when considering the sensitizing heat treatment given to this alloy (Table 1). Grain dropout, due to the sensitized grain boundaries' being completely corroded away, is very evident in Figure 8 as dark spots in the white matrix. The chambers associated with the blisters were almost exactly in the middle of the sheet thickness (see Figure 7). Measurements made on the two layers enclosing the chamber disclosed that the sum of their thicknesses was only 20 μm more than the average thickness of the sheet away from the chamber (0.060 in. [1524 μm]). This indicates that layers of whole grains were not corroded to form the chamber. If the chambers were formed in this manner, they would show up on X-rays as darker circles. That they do not confirms that the chamber formation does not involve an appreciable loss of material thickness.

For comparative purposes one of the smaller blisters (see Figure 9) was metallographically sectioned. The small blisters are slightly less than 0.006 in. (143 μm) in height and occur within about 0.006 in. (150 μm) of the surface. From Figure 9, note that grain drop out does not occur at the surface of the sensitized Type 301 specimens. This could be due to a high annealing temperature, which decarburized the surface grains.[7] Low carbon in the surface grains lead to fewer carbides being produced during the sensitization treatment, which, in turn, resulted in less grain boundary attack during the 33½-year burial.

Unlike the pits and the blisters, the cloud-like formations seen in Figures 3 and 4 are not very dark indicating that they do not represent a great loss in thickness. The slight darkening associated with the cloud-like formations is thought to be intergranular corrosion. Therefore, metal overlying those cloud-like formations should have little if any ductility. This deduction was confirmed with metallographic sectioning (see Figure 8, corroded areas) and when the specimen 53D19 cracked in a brittle manner just outside the vise jaws holding the specimen while sectioning. The intergranular crack stopped at the clear, white section in Figure 8 (uncorroded area). Furthermore, the uncorroded corner of specimen 53D19 (the lower left corner of the sheet in Figure 3) was plastically deformed with a pair of pliers and no cracking resulted.

Discussion – Annealed Type 301 (UNS S30100)

X-ray examinations of the annealed Type 301 specimens disclosed a few pits and tunnels that were not apparent from the visual examination. Interestingly, the pits and tunnels preferentially follow the rolling direction (horizontally orientated), which is the direction in which the imperfections and impurities in the metal surface are propagated during fabrication. This observation is particularly significant when the Type 301 specimens are compared with other specimens recovered in this research. The previous theory for pit and tunnel progression in stainless steels supported gravity as the primary influencing factor. When looking strictly at those specimens positioned with the rolling direction vertically, the forces of gravity appears to influence the progression. Although gravity may indeed have some influence, when compared to the Type 301 specimens, all the specimens showed pitting and tunneling following the rolling direction. Another observation supporting the rolling direction as the primary influencing factor in tunneling propagation direction is that the pit initiation sites, pits and tunnels are located indiscriminately across the specimens and not specific to the bottom or bottom half of the sheets (as they were placed in the experiment).

Discussion – Sensitized Type 301 (UNS S30100)

Based on the visual and X-ray observations along with the sectioning and microscopy work conducted during this research, the following is proposed as a mechanism for corrosion in the sensitized Type 301 specimens: a pit forms and propagates perpendicular to the surface to the center of the sheet thickness (Figure 10). The conditions in the pit promote intergranular corrosion, which spreads laterally from the pit (Figure 11 and 12) and toward the surfaces (Figure 13). It has been proposed that the corrosion in sensitized Type 301 initially occurs quickly (pitting and initial spreading), but that it slows down as transport of reactants in the corroded grain boundary channels becomes more difficult. Corrosion products clogging the channels further slows the corrosion process.[8, (2)]

The attack at the center of the sheet is due to segregation of various solute elements (e.g., chromium, nickel, and manganese) and tramp elements (e.g., sulfur) toward the center of the ingot during ingot solidification.[8] This segregation can persist into the wrought product.[9] This segregation, along with the conditions associated with the pit (low pH, high chlorides and metal ions), combine to cause intergranular corrosion of the sensitized grain boundaries. The oxides of iron, chromium, and nickel have molar volumes that are greater than their respective metals. When the intergranular corrosion emerges at the sheet surface, the oxide products are extruded out of the corroded grain boundaries. This explains why the reddish-brown iron oxide stains on both sides of the pre-cleaned sensitized Type 301 (53D19) specimen correspond almost exactly to the cloud-like formations in the X-ray (Figure 14). If the corrosion products were extruded through the pit in the specimen surface, there would be a ring of corrosion products, which would not have taken the configuration of the corroded area of the specimen. Also, the stains would have been on only one side of the sheet, the side with the pit.

The above model for the corrosion of the sensitized Type 301 could also explain the presence of the chambers. During the initial lateral spread of intergranular corrosion from the pit (Figure 12), the oxide products have no place to go because intergranular corrosion has not propagated to the surface. The oxide products cause swelling of the metal, and the chamber forms. Powder found inside the chamber was examined under the scanning electron microscope and found to be individual grains of sensitized Type 301 stainless steel. These grains dropped out of the matrix because their sensitized grain boundaries had been completely corroded away. This occurs in acid solutions, which is the environment found in pits in stainless steels.[10]

If the above model is correct, the amount of the sheet corroded and the location of the corroded areas are dependent on the pit formation. If there are no pits, there will be no corrosion per the model; it could however be argued that the uncorroded areas (white in the X-rays) are not sensitized; however, metallographic sectioning and etching has disclosed that the white areas are indeed sensitized. Also, one could argue that intergranular corrosion could occur generally on the whole surface. However, the white areas in Figures 3 and 4 show no intergranular corrosion at the surface. Furthermore, there is no grain drop at the surface of the sensitized Type 301 specimens. This could be due to a high annealing temperature, which caused decarburization of the surface. This decarburization leads to a low carbon content in the surface grains, which, in turn, leads to less sensitization and thus less intergranular attack.

It should be noted that the cloud-like formations do not appear to be influenced by gravity. This is probably due to the corrosion proceeding along the grain boundaries, which are so narrow that the capillary effect far outweighs the effect of gravity.

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(2) The channels' being cut off from the surrounding environment promotes pit conditions—hydrolysis of metal oxide products, attraction and concentration of chlorides into the channels, low oxygen, and production of low-pH conditions. This makes the corrosion process autocatalytic.

The lower sides of Figures 3 and 4 do not have the cloud-like formations and are distinctively white in the photographs and X-rays. These areas correspond to the lower portion of the specimens as they stood in the trench. The absence of the cloud-like formations in these regions is probably related to the lack of pits. The proposed mechanism of corrosion described above makes pitting the first step in producing centerline intergranular corrosion and the cloud-like formations. Without pitting, the cloud-like formations do not form. The cloud-free areas were sensitized (as were the areas with the cloud-like formations), but for some unknown reason, pitting did not occur on the lower portions of the sensitized Type 301 stainless steel specimens (53D19 and 53D20).

Pitting attack in stainless steels usually occurs in aerated solutions, so perhaps one could argue that the water contacting the lower portion of the sensitized Type 301 samples was not aerated. Two things mitigate against this. First, there are pitted portions at the lower edge of specimens 53D19 and 53D20. Second, overall pitting was observed on other metal type specimens recovered at the test site. Since all the specimens were buried at the same depth, the conditions at the test site (i.e., amount of oxygen in water at a given depth) would be consistent given the amount of ebb and flow that probably occurred over the 33½-year burial.

One now can compare the 33½-year specimens to those recovered after 8 years of burial at Site D. After 8 years, the sensitized Type 301 stainless steels suffered pitting, blistering, cracking, and rust stains (see Table 4). The pitting, blistering, and cracking are indications that the chambers under the blisters had formed. The cracking implies that complete loss of ductility associated with intergranular corrosion had occurred above the chambers. Since X-rays of the 8-year specimens were not taken, it is not known if the associated cloud-like structure observed in the 33½-year specimens had developed; however, it is likely that it was at least starting at that time. Therefore, from the observations conducted on the 8-year specimens, one can argue that chambers had developed and intergranular corrosion between the chambers and the sheet surface also had occurred at the 8-year test interval.

Determining mass loss is the first step in calculating the general corrosion rate. For the sensitized Type 301 specimens after 33½years of burial, the mass loss is relatively low (10 to 32 g for 53D19, and 20 to 42 g for 53D20 [see Table 5]) at about 1 to 5% of the original mass. The complete loss of ductility that occurred for this low a mass loss shows that assuming general corrosion drastically underestimates the damage from localized corrosion mechanisms such as pitting, tunneling, and intergranular corrosion.

Visual Observations Type 304 (UNS S30400)

Visual observations were performed for the Type 304 sheets and compared with earlier observations document by NIST (Gerhold et al.[4]) in Table 4. Photographs showing the front side of the two annealed Type 304 sheets are on the left sides of Figures 15 and 16, while the sensitized Type 304 sheets are depicted on the left sides of Figures 17 and 18. Surface attack (e.g., iridescent film and staining) was observed primarily on the 33½-year annealed and sensitized specimens although there was very limited dark staining on an annealed specimen after 4 years and iridescent film on both the annealed and sensitized specimens after one year. Staining was readily removed during the cleaning process.

Invasive attack in the form of pitting and blistering was observed only after 2 years for the sensitized specimens; invasive attack was also observed for the sensitized 4-year specimens. Pitting and tunneling were observed in both the 8 and 33½-year annealed and sensitized specimens. Sensitized specimens clearly show the greater amount of invasive corrosion with pitting, tunneling, blistering and perforation – particularly along the sheared edges.

Mass Loss Type 304 (UNS S30400)

The data for the estimated original mass and post-cleaning mass for the Type 304 specimens are in Table 5. The mass loss for annealed Type 304 specimens after 33½ years of burial is estimated at 2 to 16 g while the mass loss for sensitized Type 304 specimens after 33½ years of burial is estimated at 23 to 36 g for specimen 56D19 and 10 to 24 g for specimen 56D20.

X-ray Observations Type 304 (UNS S30400)

X-ray observations for annealed Type 304 samples recovered after 33½ years are found on the right half of Figure 15 and 16. There are few pits and tunnels visible on the X-rays of the annealed specimens that are not discernable from the visual examination. In Figures 15 and 16, the tunneling runs vertically. Close inspection of the specimen surface disclosed that the rolling direction for all of the Type 304 stainless steel specimens is in the vertical direction as placed in the trench. There is some tunneling at the cut edges of the annealed specimens particularly in specimen 55D19.

X-ray observations for sensitized Type 304 specimens recovered after 33½ years are found on the right half of Figures 17 and 18. The most striking thing about Figure 17 (specimen 56D19) is the long (8 in. [20.3 cm]) tunnel from the top of the specimen. The tunnel follows the rolling direction. As in the case of the sensitized Type 301 stainless steel, the metal covering the tunnel is thin enough in places to be punctured by a needle. In the photographs of Figures 17 and 18, surface discoloration follows the subsurface tunnel—probably an effect from the cleaning solution leaking from the tunnel.

Destructive Examination of Sensitized Type 304 (UNS S30400)

Sectioning the tunnels (Figures 19 and 20) disclosed that the layer of metal covering them was intergranularly corroded—much like the sensitized Type 301. However, the attack did not spread as extensively as in the case of the sensitized Type 301 as evidenced by the whiteness of the X-ray (Figures 17 and 18) and the ductility of the specimen away from the tunneling. At some points, the tunnels' height was almost the whole thickness of the sheet specimen, which is why they are so dark in the X-radiographs. The powder in the tunnels was stainless steel, so grain dropping due to intergranular corrosion occurred as it did in the sensitized Type 301. However, the morphology of attack was quite different—tunnels are much longer than they are wide and much of the thickness has been corroded away.

Discussion – Annealed Type 304 (UNS S30400)

X-ray observations of the annealed Type 304 specimens disclosed a few pits and tunnels that were not apparent from the visual examination. Again, as was observed in the annealed Type 301 specimens, the pits and tunnels preferentially follow the rolling direction. In the annealed Type 304 specimens, about half the tunnels are associated with a sheared specimen edge.

Determining mass loss is the first step in calculating the general corrosion rate and for the annealed Type 304 specimens after 33½ years of burial, the mass loss is relatively low: 2 to 16 g (see Table 5). By looking at the X-rays and photographs of the annealed Type 304 specimens, one clearly sees that generalized corrosion has not occurred and that the small amount of localized corrosion can be detected by using X-ray techniques.

Discussion – Sensitized Type 304 (UNS S30400)

Based on the visual and X-ray observations along with the sectioning and microscopy work conducted during this research, and as in the case of the annealed Type 304 stainless steel specimens, there are few tunnels in the sensitized Type 304 stainless steel. However, where they do occur, the tunnels in the sensitized Type 304 stainless steel are longer and more extensive and are more rounded than for the annealed Type 304. Most of the tunnels in sensitized Type 304 originate from, or are connected to, the sheared specimen edges.

The long tunnel in Figure 17 is quite unusual and in the authors' experience unique. The different shades of gray indicate that the tunnel varies in height and are somewhat smaller than the thickness of the sheet. Also, the tunnel has different shading indicating that branching has developed and the branches are advancing at different levels through the sheet thickness. Efforts to resolve this nondestructively by X-ray laminography proved fruitless. There are numerous perforations associated with the tunnel. Interestingly, the long tunnel provides a distinction between the two sensitized Type 304 sheets–specimen 56D19's tunnel was long while specimen 56D20's was shorter. The significance of and reason(s) for this difference in attack mode are not known at this time.

The tunneling implies that the sheet specimens were submerged in groundwater at least some part of the year. This is because the tunnel would need to be filled with water for it to propagate. Table 4 reports perforation, tunneling, and pitting after 8 years of burial. These same features were noted on the 33½-year specimens. This shows that the corrosion mechanisms that resulted in the features observed were probably operative at 8 years.[(3)] If this is so, it implies that the water table may have been high enough to cover the specimens for part of the year starting before 1978.

There is a marked difference in the attack mode between sensitized Types 301 and 304 stainless steels. In the former, there are numerous pits, cloud-like formations, and no tunneling. In the latter, there are few pits, no cloud-like formations, and concentrated tunneling attack that originate primarily from the cut edges. Also, there is no grain dropout from the surface of the sensitized Type 301 specimens but grain dropout does occur in the sensitized Type 304 specimens (Figure 19). The reason(s) for these observed differences is not known at this time.

Determining mass loss is the first step in calculating the general corrosion rate and for the sensitized Type 304 specimens after 33½ years of burial the mass loss is relatively low (10 to 24 g for specimen 56D20, and 23 to 36 g for specimen 56D19 [see Table 5]) or about 1.5 to 5% of the estimated original mass. This low a mass loss shows that by assuming general corrosion, the damage from localized corrosion mechanisms such as pitting, tunneling, and intergranular corrosion is drastically underestimated for sensitized 304 stainless steel.

Visual Observations Type 316 (UNS S31600)

Visual observations were performed for the Type 316 sheets and compared with earlier observations document by NIST (Gerhold et al.[4]) in Table 4. Photographs showing the front side of the two annealed Type 316 sheets are on the left sides of Figures 21 and 22, while the sensitized Type 316 sheets are depicted on the left sides of Figures 23 and 24. Surface attack (e.g., staining) was observed primarily on the 33½-year annealed and sensitized specimens although there was very limited dark staining on a sensitized specimen after 4 years and iridescent film on a sensitized specimen after 1 year. Staining was readily removed during the cleaning process. Very minor pitting and etching were observed on the sensitized specimens after 33½ years but the pitting was so shallow as to be almost unmeasurable. The 8-year recovered annealed and sensitized specimens showed no surface staining or invasive attack.

Mass Loss Type 316 (UNS S31600)

The data for the estimated original mass and post-cleaning mass for the Type 316 specimens are in Table 5. The post-clean mass for both the annealed and sensitized Type 316 specimens are within the range of the estimated original mass. This indicates that the Type 316 specimens did not lose much, if any, mass during the 33½-year burial.

X-ray Observations Type 316 (UNS S31600)

X-ray observations for annealed Type 316 samples recovered after 33½ years are found on the right half of Figure 21 and 22. X-ray observations for sensitized Type 316 specimens recovered after 33½ years are found on the right half of Figures 23 and 24. The X-rays show no tunneling or pitting.

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(3) In this study, the perforations in the sensitized Type 304 sheet specimens were associated with tunnels. Where there was no tunneling, no perforations were observed.

Discussion –Type 316 (UNS S31600)

X-ray observations of the annealed and sensitized Type 316 specimens revealed no invasive corrosion indications similar to the visual examination. The post-clean mass for both the annealed and sensitized Type 316 specimens are within the range of the estimated original mass. The observations and measurements indicate no measurable or significant corrosion occurred for the Type 316 specimens buried 33½ years. Therefore, Type 316 stainless steel appears to be superior to Types 301 and 304 stainless steels under the same environmental condition.

The superiority of Type 316 over Types 301 and 304 in this environment is striking. The cleaned Type 316 specimens looked so pristine that they did not appear to have been exposed to a corrosive environment. The reason for this superiority may be found in the composition of Type 316. Molybdenum is well known for its ability to confer pitting corrosion resistance and is present in Type 316 but is absent in Types 301 and 304.

CONCLUSIONS

This research directly applies to environmental management operational corrosion issues and long-term stewardship scientific needs for understanding the behavior of waste forms and their near-field contaminant transport of chemical and radiological contaminants at nuclear disposal sites. As such, the research offers the best comparative study available for DOE waste metals and containers that have been disposed of and have been in the ground for more than 30 years. The uniqueness of the long sampling time allows for further understanding of the actual stainless steel corrosion mechanisms, and when applied back into predictive models, will assist in reduction of the uncertainty in parameters for predicting long-term fate and transport.

The corrosion analysis results described in this paper deals with AISI Type 301(UNS S30100), Type 304 (UNS S30400), and Type 316 (UNS S31600) stainless steel sheet specimens recovered from the partial recovery of the NIST test Site D. The specimens in the research provide good analogies for both containers that have been in use around the DOE complex for radioactive waste disposal (annealed condition) and radioactive metal components exposed to nuclear environments (sensitized condition). For this reason, obtaining long-term corrosion rates from the test is applicable to the fate and transport modeling. Key to the modeling has been corrosion rate applied as general corrosion to determine the amount of mass loss and hence mass available for transport. The actual corrosion mechanisms are not included in the models since the mechanisms are complex and not well understood.

The research results in this paper clearly indicate corrosion mechanisms are dependent on the type and treatment of metal given the same environmental conditions. All three of the metal types may initially start with pit or localized corrosion, but the corrosion propagation mechanism appears to vary from one type to another, and in the same material, with the type of treatment the metal underwent. For each of the material types examined, localized corrosion–not general corrosion–has the greater influence on resulting mass loss and, if further investigations allow, the compositions of the mass loss to the environment.

The definitive turning point during this research was the use of X-radiography as an analytical tool. This technique allowed for visually assessing the extent of the localized corrosion whereas the mass loss measurements did not. The X-ray also allowed the investigators to pinpoint locations of interest for further invasive metallographic evaluation. In turn, the invasive analysis has resulted in developing theories on the corrosion mechanisms allowing comparisons between the treatments and the metal types.

The current modeling methodology uses a single corrosion rate for stainless steel under a given environmental condition. The results of this research can now be used to refine the models by applying first the principle that localized corrosion dominates over general corrosion and that type of localized corrosion attack will vary from one stainless steel type and treatment to another. Further research is needed to continue to understand and apply the complexities of the corrosion mechanisms that have been observed. In turn, this will assist the understanding of potential release of specific long-lived radionuclides from burial sites and the management of disposal facility closure and remedial actions.

SUMMARY

- The corrosion behavior of Type 300 austenitic stainless steels buried for 33½ years varies widely with chemical composition and treatment. However, all forms of corrosive attack are localized; there is very little evidence of general attack. This is probably due to the presence of chromium in the stainless steel.

- Tunneling does not appear to be influenced by gravity as much as the rolling direction.

- Sensitized Types 301 and 304 stainless steels exhibit intergranular corrosion, which, in turn, causes an almost complete loss of ductility in areas subject to invasive attack. This is accompanied by relatively low amounts of mass loss, so considering only mass loss can drastically underestimate the damage to a material's mechanical properties.

- Sensitized and annealed Type 316 stainless steel exhibits almost no mass loss after 33½ years of burial. This is probably due to the molybdenum content.

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This work was originally started by the National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards – NBS) by a team of dedicated corrosion scientist including Edward Escalante and the late Jim Fink who have continued to have interest and have provided invaluable support in the continuation of this research. The research done since 2002 has been carried out with funding provided by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy (project number 86803) through contract DE-AC07-05ID14517. The support necessary to successfully pursue the objectives of this research has been vast, and the authors wish to thank the many Idaho National Laboratory personnel who have made significant contributions, the continued interest and support from NIST, and especially those of the U.S. Coast Guard Station at Wildwood, NJ, who have made this project both safe and successful.

TABLE 1

TREATMENT AND PASSIVATION PROCEDURES FOR NIST STAINLESS STEELS[4]

Stainless Steel Type	Treatment	Passivation Procedure
301	Annealed	I
301	Sensitized	I a
304	Annealed	I
304	Sensitized	I a
316	Annealed	I
316	Sensitized	I
Sensitized: by heating at 1200 ˚F for 2 hrs, followed by air cooling and descaling in sodium hydroxide.		
I – Passivation: 20 to 40% by volume of 67% nitric acid at 120-160 ˚F for 20-30 minutes.		
a. Minimum specified concentration of acid, temperature at the time for sensitized material.		

TABLE 2

CHEMICAL ANALYSIS FOR EACH NIST ALLOY[4]

	C	Mn	Si	S	P	Cr	Ni	Mo	N	Cu	Ti	Others
Type 301	0.092	1.1	0.49	0.006	0.015	16.1	7.1	0	0	0	0	0
Type 304	0.048	1.46	0.5	0.012	0.03	18.2	9.8	0.17	0.042	0.19	0	0
Type 316	0.049	1.62	0.53	0.09	0.02	17.48	13.53	2.28	0	0.11	0	0

TABLE 3

CHEMICAL ANALYSIS FOR INL CONTROL SPECIMENS

	C	Mn	Si	S	P	Cr	Ni	Mo	N	Cu	Ti	Other
UNS S30100	0.088	0.91	.5	0.012	0.025	17.41	7.29	0.22	0.053	0.46	0	0
UNS S30400	0.8	2	1	0.01	0	20	10.51	0	0	0	0	0
UNS S31600	0.29	1.652	0.298	0.001	0.028	16.92	10.332	2.174	0.044	0.373	0	0

TABLE 4

VISUAL EXAMINATION RESULTS OF AISI TYPE 300 SERIES STAINLESS STEEL SHEET SPECIMENS BURIED AT NBS SOIL CORROSION TEST SITE D. (1, 2, 4, AND 8-YEAR NBS EXPOSURE DATA [4])

Material		Year(s) buried	Visual Observation - Invasive						Visual Observation - Surface				
			Perforation	Pitting	Tunneling	Etched	Cracking	Blister	Rust Stain	Black Stain	Dark Stain	Iridescent Film	Adhering Product
Type 301	UNS S30100	33½	x	o x	o			o x	o x	o x	o x	o x	x
		8	-	x	-		x	x	x	-	-	-	-
		4	-	x	-	x	-	x	o	-	o	-	-
		2	-	o x	-	-	-	x	-	-	-	-	-
		1	-	o x	-	-	-	-	-	-	-	-	-
Type 304	UNS S30400	33½	x	o x	o x	-	-	x	o x	o x	o x	o x	o x
		8	x	o x	o x	-	-	-	-	-	-	-	-
		4	-	x	x	-	x	x	-	-	o	-	-
		2	-	x	-	-	-	x	-	-	-	-	-
		1	-	-	-	-	-	-	-	-	-	o x	-
Type 316	UNS S31600	33½	-	x	-	-	-	-	o	o x	o x	-	-
		8	-	-	-	-	-	-	-	-	-	-	-
		4	-	x	-	x	-	-	-	-	x	-	-
		2	-	-	-	-	-	-	-	-	-	-	-
		1	-	-	-	-	-	-	-	-	-	x	-

Key: o present in annealed x present in sensitized – not present

TABLE 5
MASS MEASUREMENTS AFTER CLEANING AND ESTIMATED ORIGINAL MASS CALCULATION RESULTS FOR AISI TYPE 300 SERIES STAINLESS STEEL SHEET SPECIMENS BURIED AT NBS SOIL CORROSION TEST SITE D. (33½YEAR EXPOSURE DATA\)

Specimen Identification	Post-Clean Mass (g)	Estimated Original Mass (g)
Type 301 (52D19) annealed	782.107	767.10 - 796.08
Type 301 (52D20) annealed	785.194	780.00 - 802.99
Type 301 (53D19) sensitized	768.404	777.17 - 800.09
Type 301 (53D20) sensitized	764.424	784.37 - 807.50
Type 304 (55D19) annealed	796.537	799.41 - 812.57
Type 304 (55D20) annealed	784.655	786.70 - 799.65
Type 304 (56D19) sensitized	782.916	806.27 -819.54
Type 304 (56D20) sensitized	812.743	823.31 - 836.85
Type 316 (58D19) annealed	---	798.45 - 811.59
Type 316 (58D20) annealed	796.259	788.46 - 801.44
Type 316 (59D19) sensitized	791.890	785.10 - 798.02
Type 316 (59D20) sensitized	798.364	791.81 - 804.84

FIGURE 1. Type 301 SS annealed (front of 52D19). Cleaned specimen (left) and X-ray (right).

FIGURE 2. Type 301 SS annealed (front of 52D20). Cleaned specimen (left) and X-ray (right).

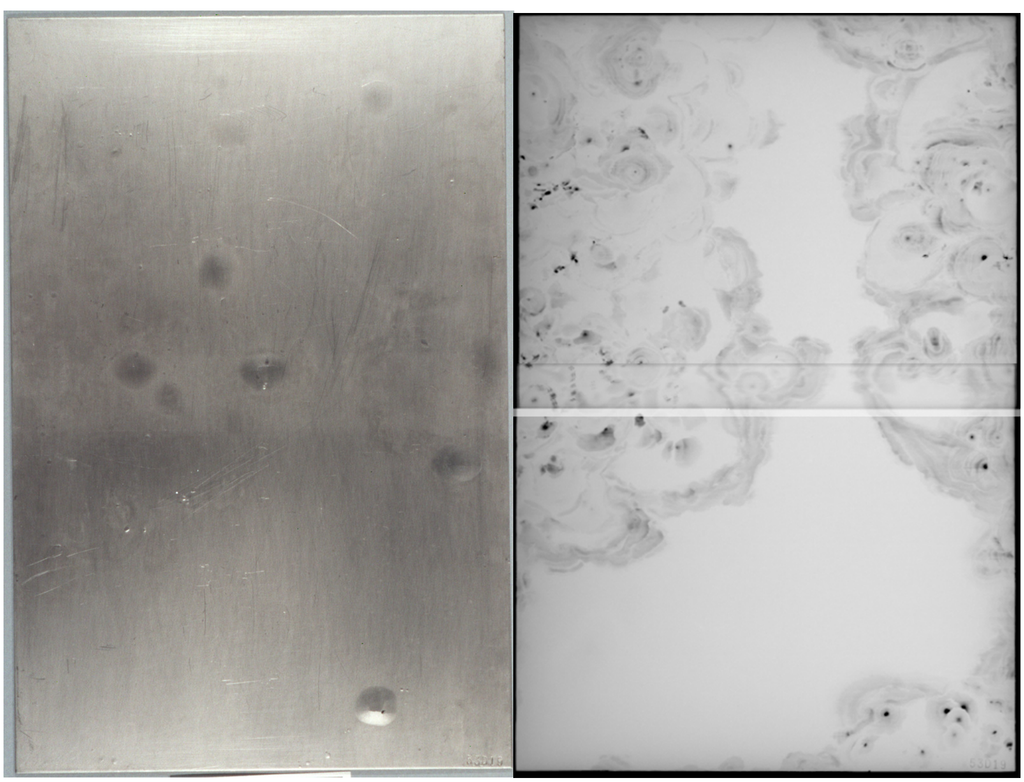

FIGURE 3. Type 301 SS sensitized (front of 53D19). Cleaned specimen (left) and X-ray (right).

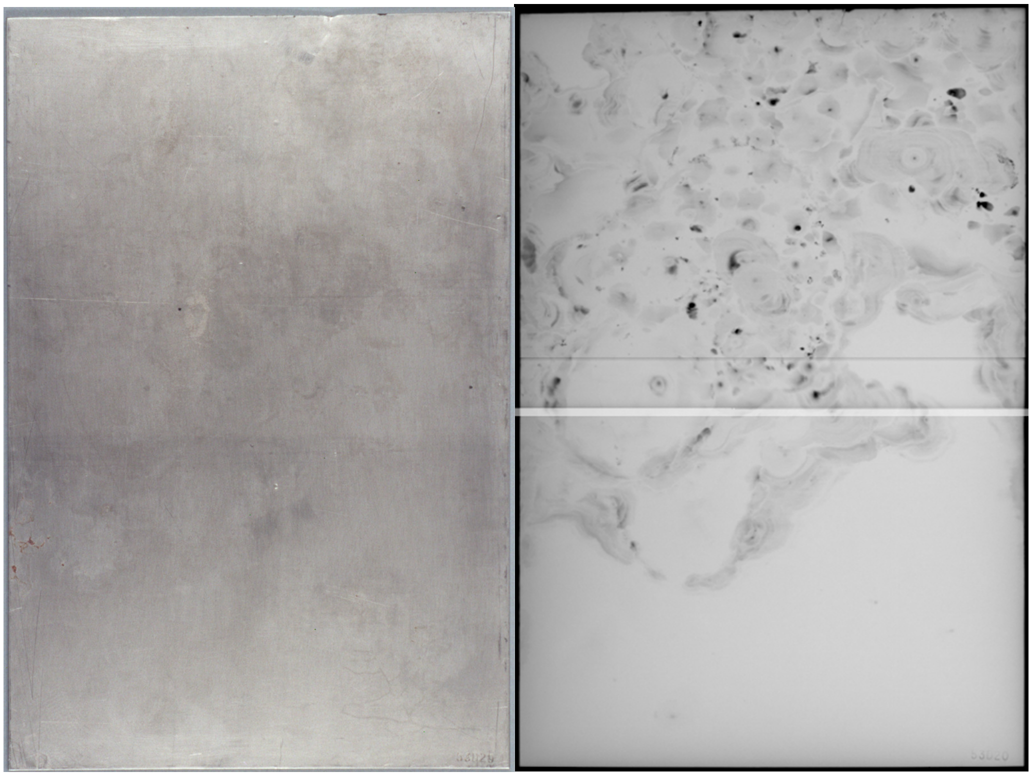

FIGURE 4. Type 301 SS sensitized (front of 53D20). Cleaned specimen (left) and X-ray (right).

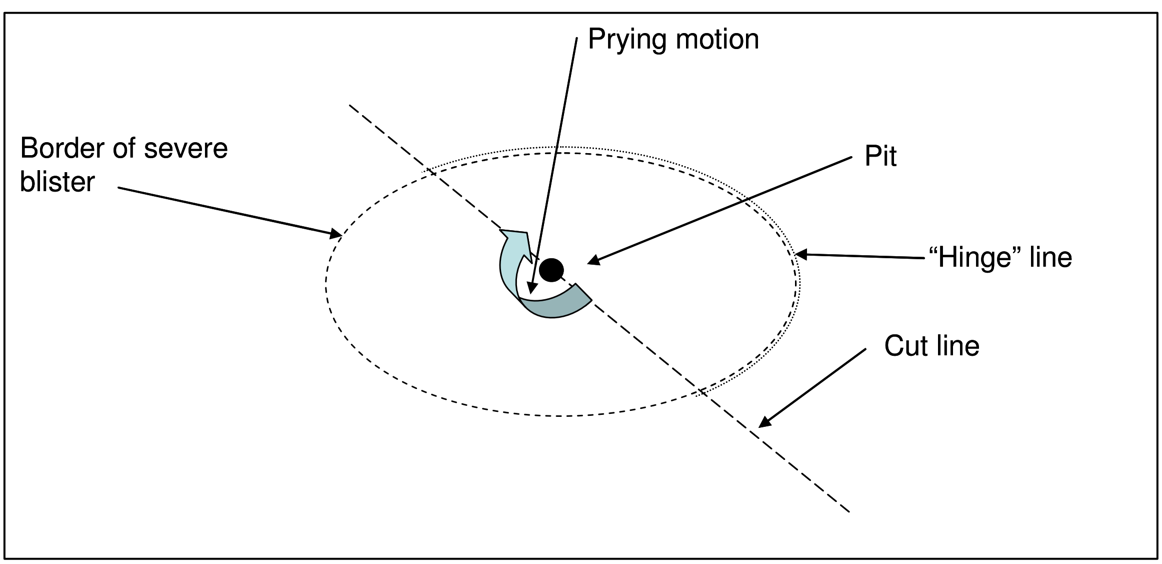

FIGURE 5. Sectioning of severe blister in sensitized Type 301 stainless steel (53D19).

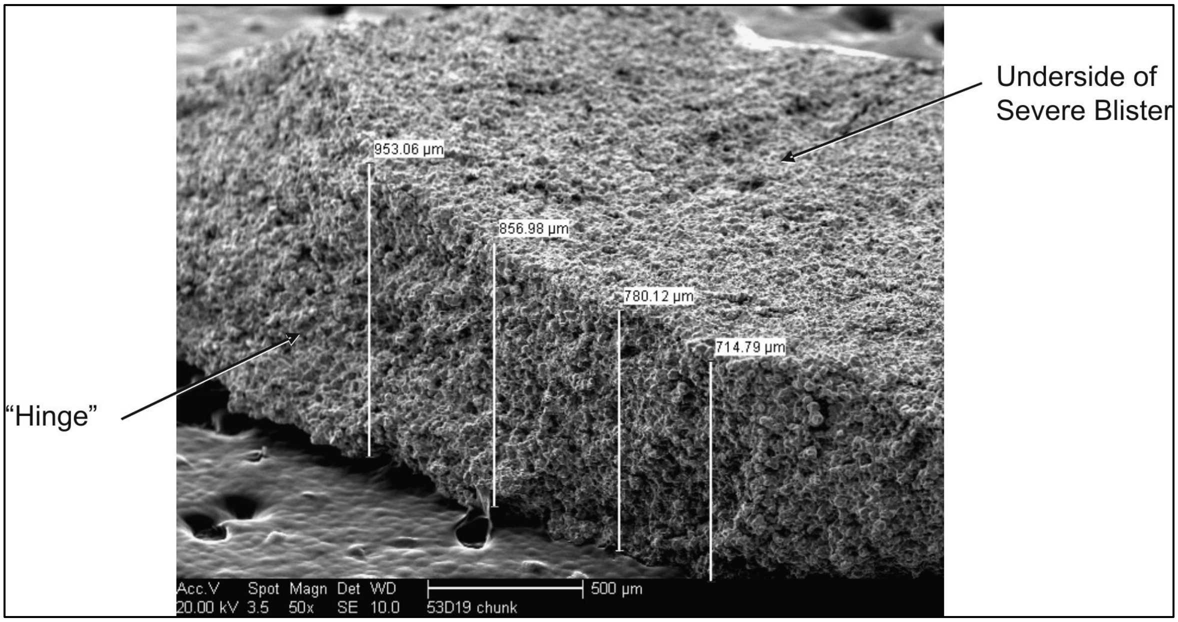

FIGURE 6. SEM photomicrograph of pried-open sever blister in Type 301 stainless steel (53D19).

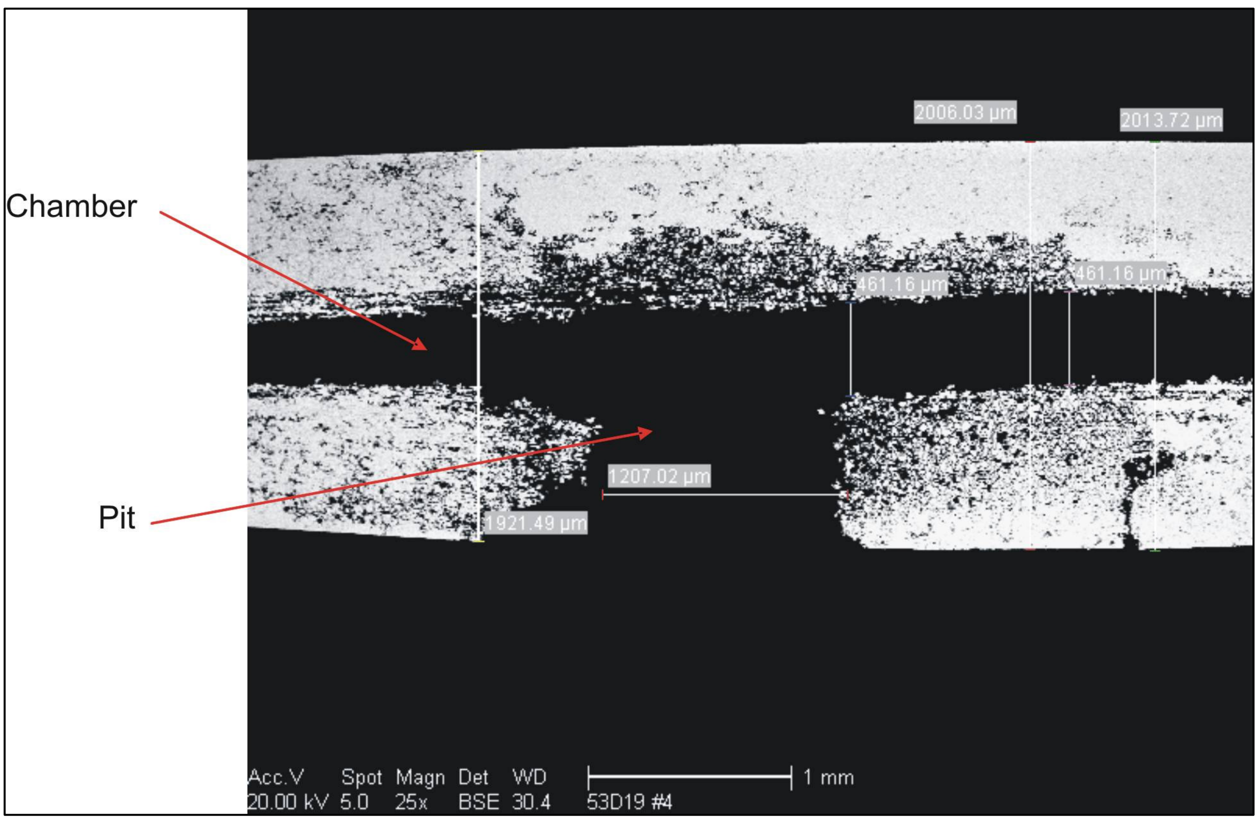

FIGURE 7. Photomicrograph of a section of a severe blister, sensitized Type 301 stainless steel (53D19).

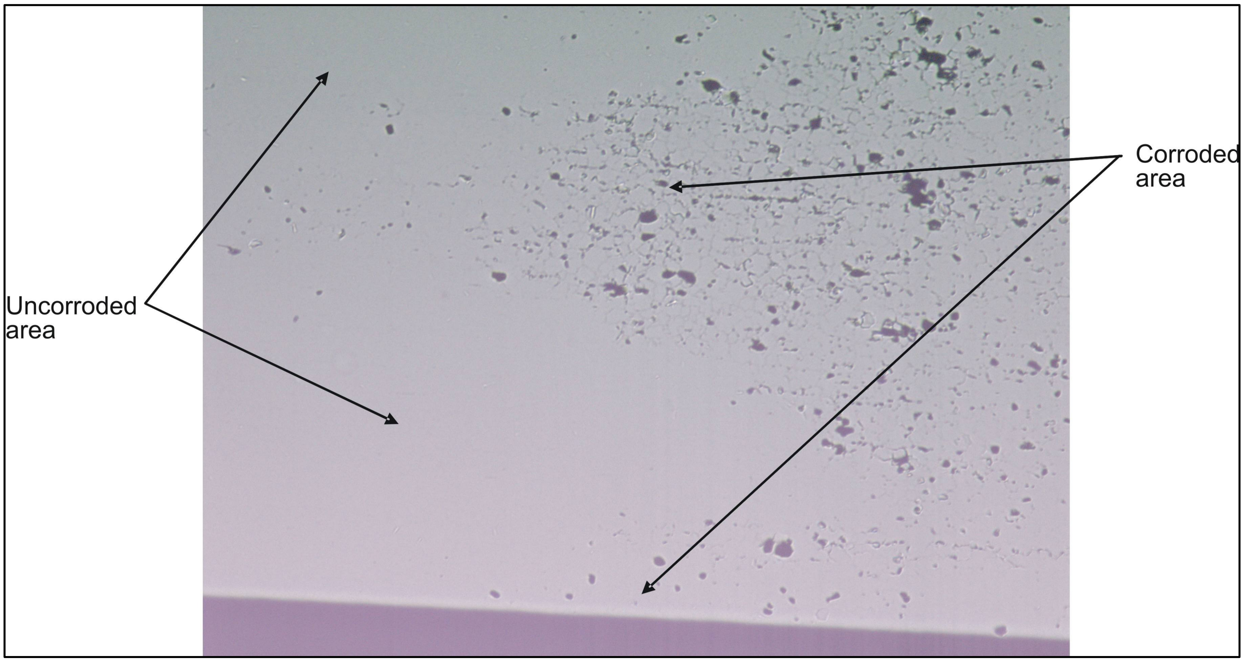

FIGURE 8. Photomicrograph of sensitized Type 301 stainless steel (53D19) showing corroded and uncorroded areas, 50×.

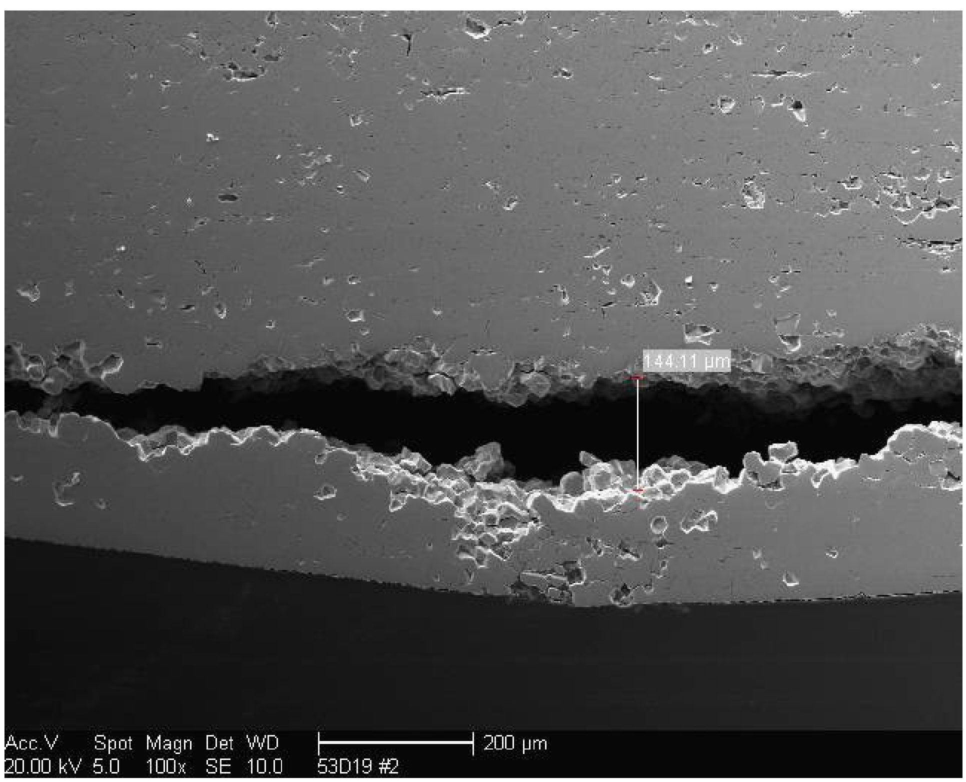

FIGURE 9. SEM photomicrograph of a section of a small blister in sensitized Type 301 stainless steel (53D19).

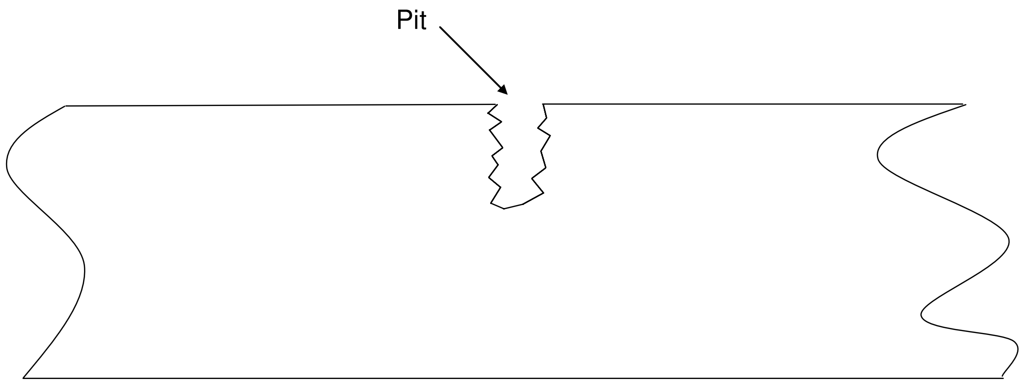

FIGURE 10. Pit forms on surface and propagates to center of sensitized Type 301 stainless steel sheet.

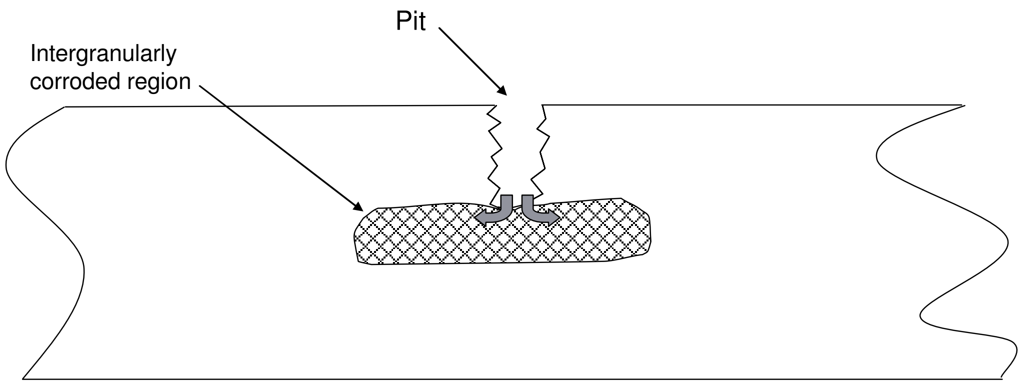

FIGURE 11. Intergranular corrosion starts to spread laterally from pit in sensitized Type 301 stainless steel.

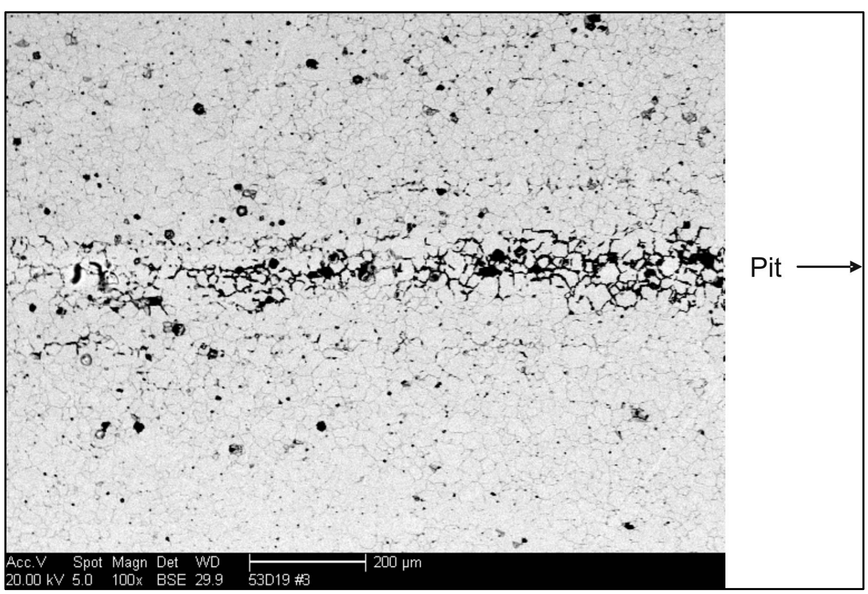

FIGURE 12. SEM photomicrograph of metallographically polished sensitized Type 301 stainless steel (53D19) showing intergranular attack in the center of the sheet (unetched).

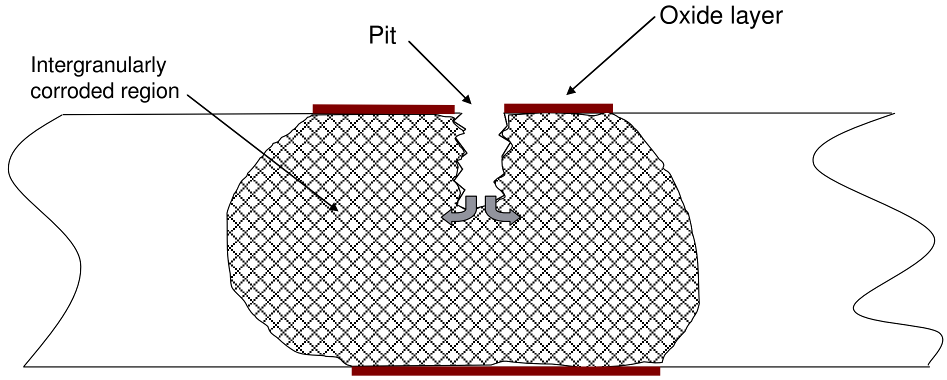

FIGURE 13. Intergranular corrosion spreads laterally and toward surfaces from pit in sensitized Type 301 stainless steel.

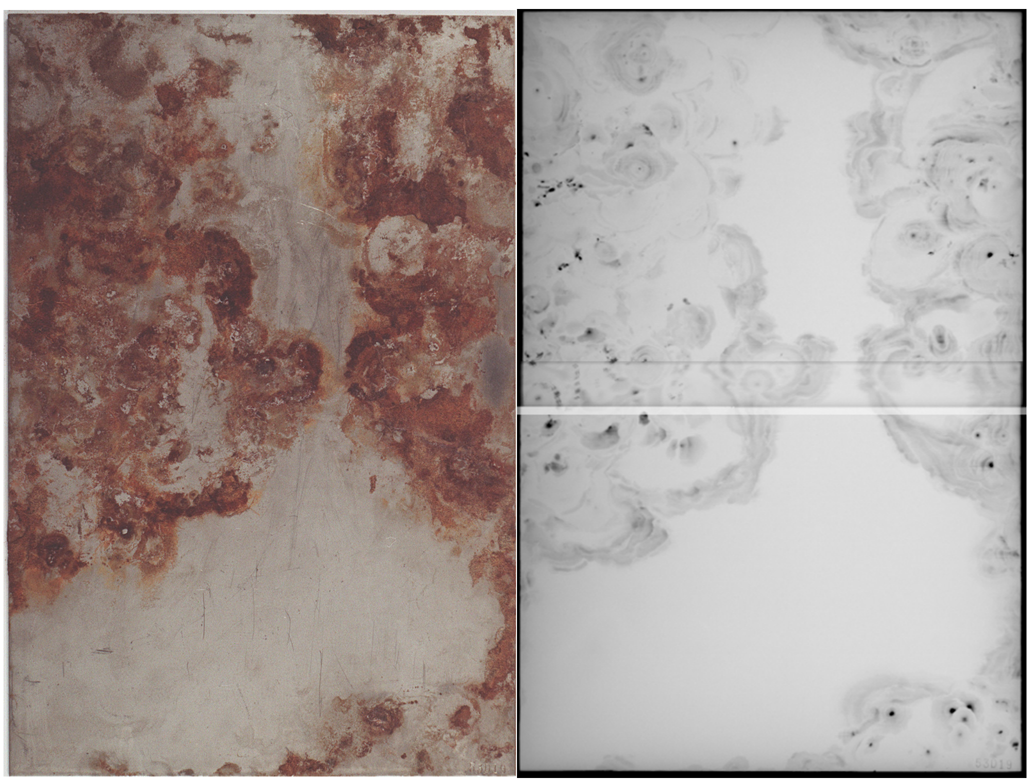

FIGURE 14. Pre-cleaned sensitized Type 301 SS (front of 53D19) on left and X-ray (52D19) after cleaning on right.

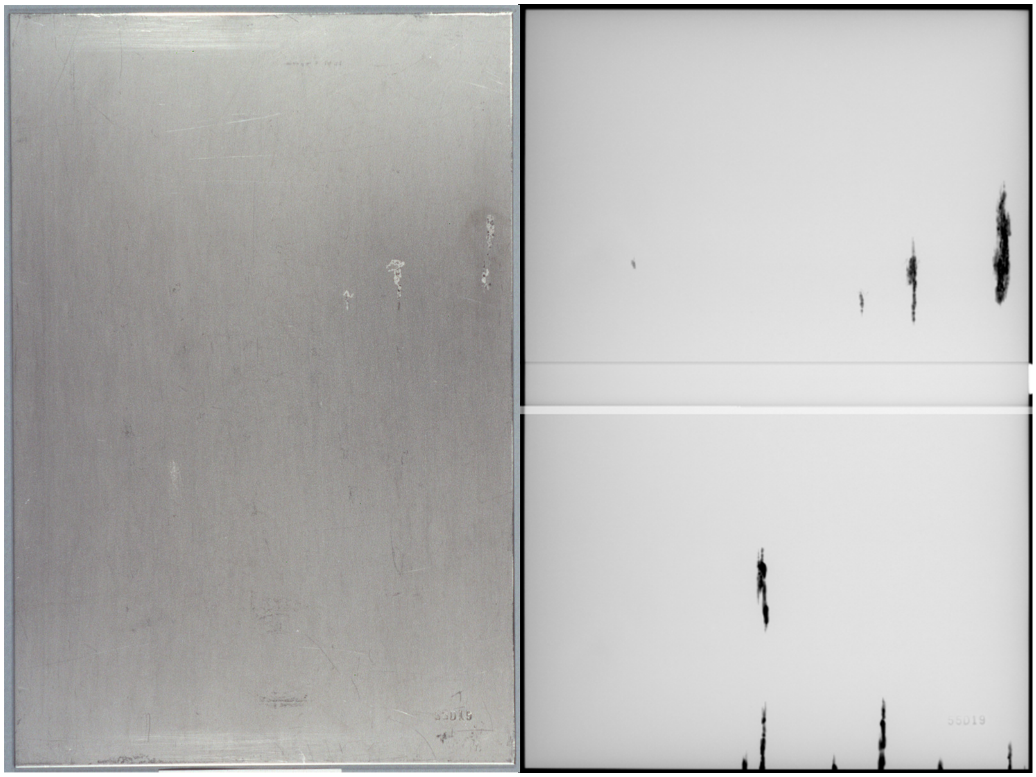

FIGURE 15. Type 304 SS annealed (front of 55D19). Cleaned specimen (left) and X-ray (right).

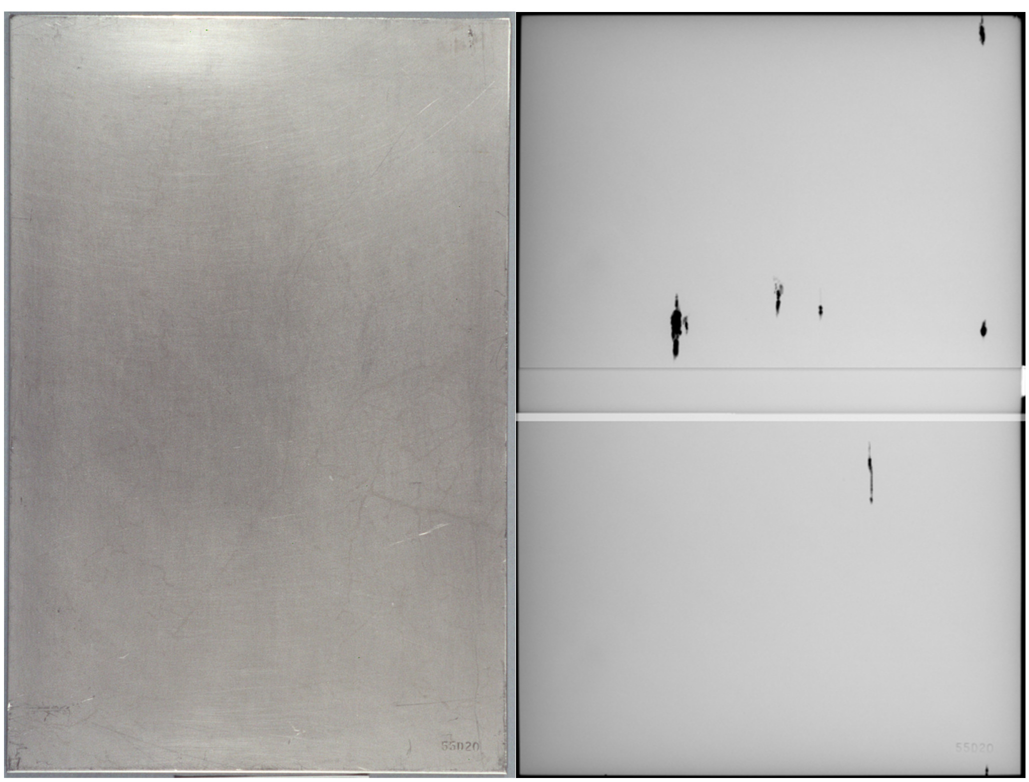

FIGURE 16. Type 304 SS annealed (front of 55D20). Cleaned specimen (left) and X-ray (right).

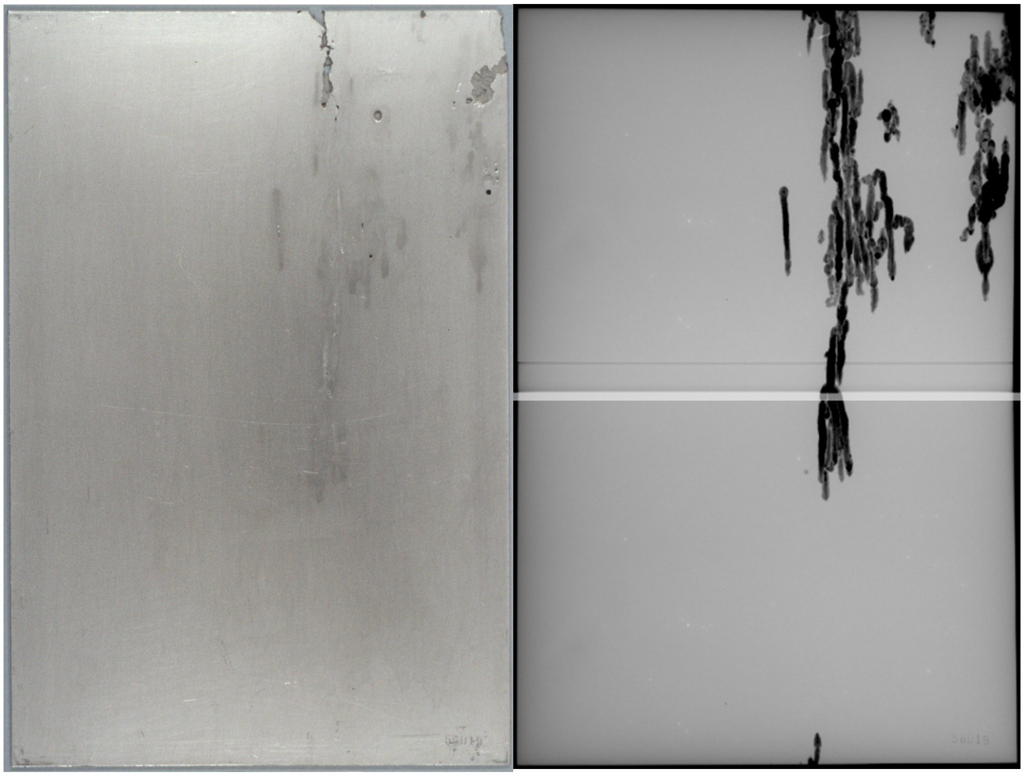

FIGURE 17. Type 304 SS sensitized (front of 56D19). Cleaned specimen (left) and X-ray (right).

FIGURE 18. Type 304 SS sensitized (front of 56D20)). Cleaned specimen (left) and X-ray (right).

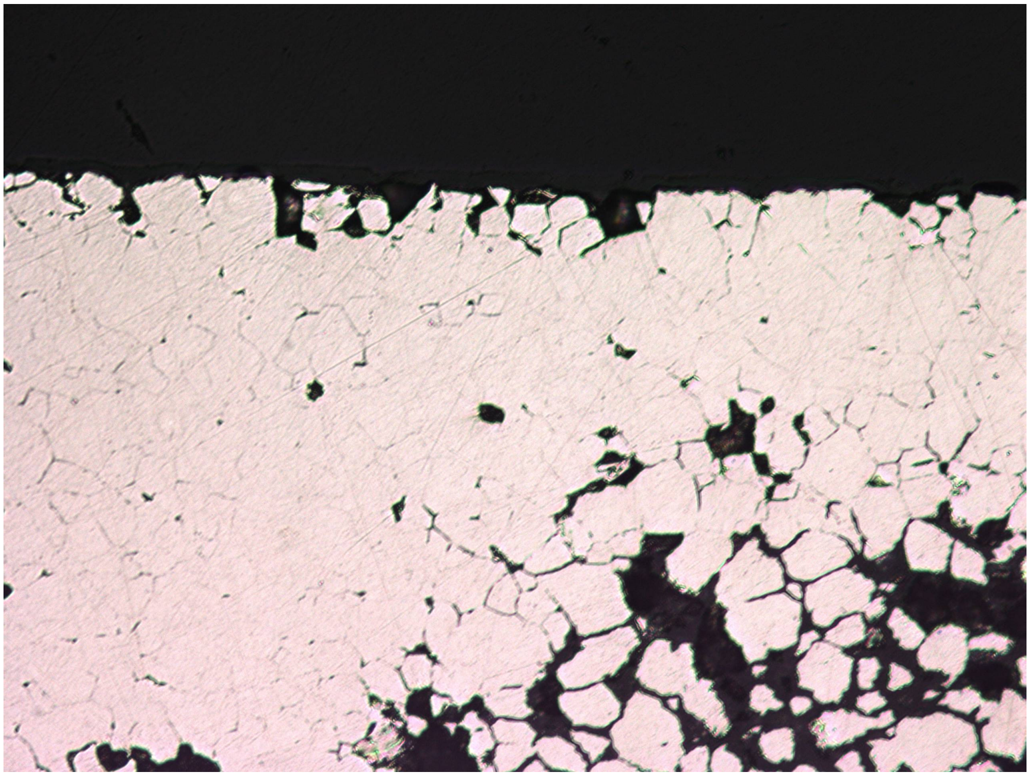

FIGURE 19. Metallographic section of sensitized Type 304 stainless steel (Specimen 56D19).

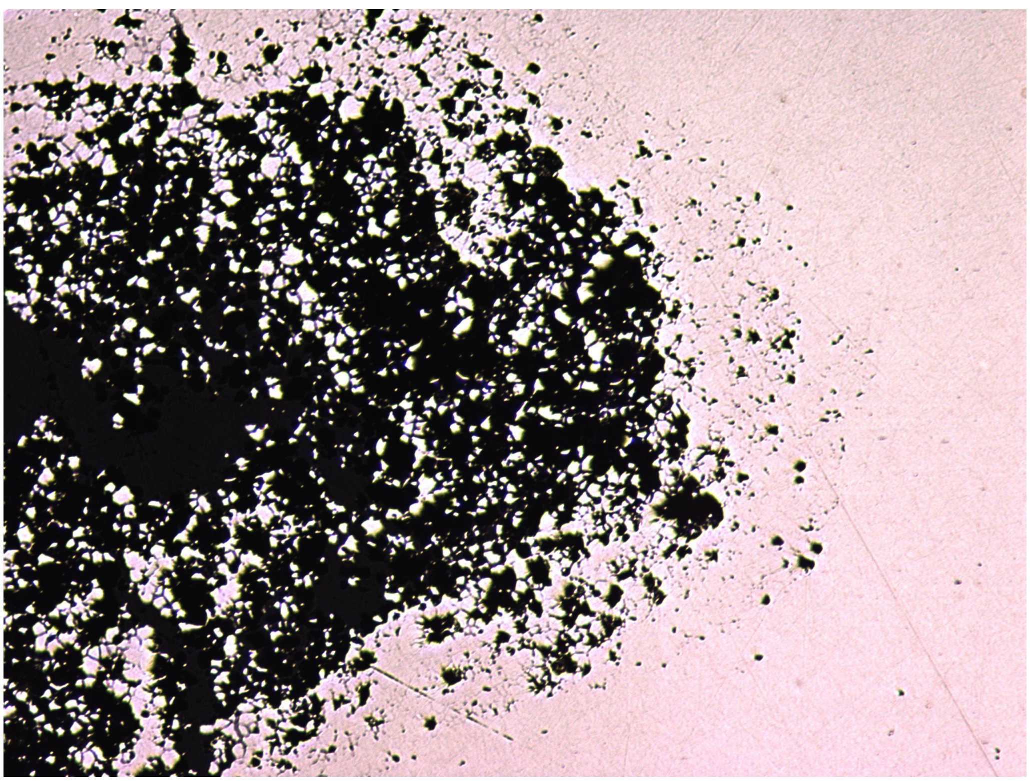

FIGURE 20. Metallographic section of sensitized Type 304 stainless steel (Specimen 56D19).

FIGURE 21. Type 316 SS annealed (front of 58D19). Cleaned specimen (left) and X-ray (right).

FIGURE 22. Type 316 SS annealed (front of 58D20). Cleaned specimen (left) and X-ray (right).

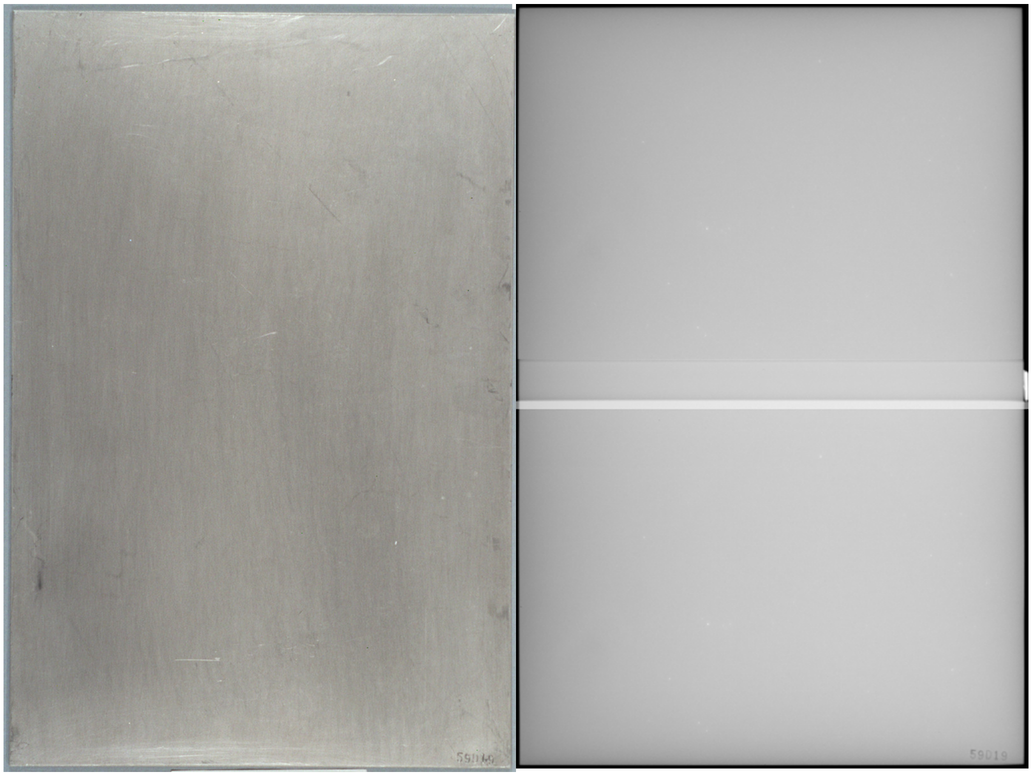

FIGURE 23. Type 316 SS sensitized (front of 59D19). Cleaned specimen (left) and X-ray (right).

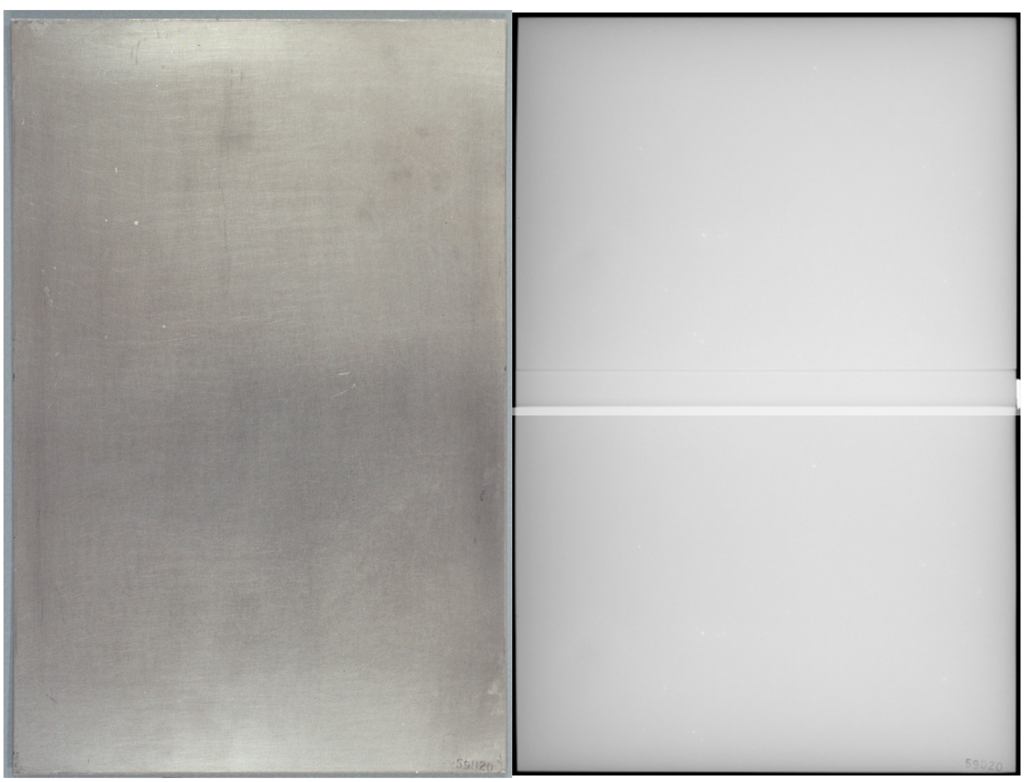

FIGURE 24. Type 316 SS sensitized (front of 59D20). Cleaned specimen (left) and X-ray (right).

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