FABRICATION & METALLURGICAL EXPERIENCE IN STAINLESS STEEL PROCESS VESSELS EXPOSED TO CORROSIVE AQUEOUS ENVIRONMENTS

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ABSTRACT

Corrosion resistant stainless steel structures, built for service in acidic and neutral, chloride environments can have their inherent corrosion resistant properties destroyed by fabrication and rolling Mill defects. Examples are presented showing degradation by carbon arc gouging, weld attack, grinding, scratching with iron tools, spatter, heat tint, folds, paint, slag, seams and slivers. Conditions are most severe under total immersion. Weld repairing includes spot repairs, weld overlay, use of enriched or overmatched electrodes, patching and sheet liners followed by grinding and pickle paste.

KEY WORDS: Stainless steel, Welding, fabrication, Corrosion, Cleaning, Pickling

INTRODUCTION

Cleaning of stainless steels following weld fabrication is not only necessary but vital in achieving the best performance from the material. Too often stainless steel equipment suffers severe localized attack to the surprise of the owner and fabricator. The proper removal of iron, iron oxides, heat tint, slag, spatter and other contaminates is required on passive-active alloys. Although stainless steels do not necessarily require post fabrication cleaning for high temperature heat resistant applications, in hot oil sulfidation environments, in alkaline kraft liquor or in nitric or sulfuric acids which are self cleaning, it is necessary for aqueous systems in which neutral or acid chlorides are present such as bleachery equipment and sulfite digesters, flue gas desulfurization scrubbers, evaporators, water treating vessels, chemical storage tanks and similar types of equipment.

The Specialty Steel Producers, the Committee of Stainless Steel Producers of the American Iron and Steel Institute, ASTM, ASM International and some trade journals publish guidelines for the descaling, pickling, and cleaning of stainless surfaces for various applications, be they for chemical or for food handling (l, 2, 3, 4). These materials, provide the optional and necessary steps in finishing up a stainless fabrication. But they do not show some of the short falls that arise even when specifying, fabricating and finishing to accepted or recommended practices.

It is the purpose of this paper to show a variety of conditions in fabricated austenitic stainless steel equipment, in both 316L and 904L alloys, that have resulted in unexpected localized attack. Practices for the final shop repair and field repair of these alloys are discussed. The presentation is an illustrated series of field experiences.

EXAMPLES OF FABRICATION DEFECTS

A number of evaporators have been built in water short geographical areas of the world for the purpose of producing boiler feedwater or distilled water from cooling tower blowdown, scrubber blow down and other waste water sources thereby reducing the volume of waste water. They employ a vertical evaporation vessel having a brine flash and storage sump recycle storage tank and an internal calandria type vertically condenser.

The vertical shells enclosing a tubular condenser with sump below, both above and below the liquid level, have been built of 316L stainless steel with a minimum of 2.75 percent molybdenum. Although the chloride level in the recirculating flashing brine has chloride concentrations of 8,000 ppm to 50,000 ppm, depending on the particular installation involved, with pH values controlled generally to 6.5, the majority of the installations have shown no pitting, crevice corrosion or stress corrosion cracking beneath the thick soft layer of sludge comprised of insoluble compounds due primarily to careful deaeration of the feed stream.

Several installations have developed localized pitting and crevice corrosion which has been attributed to incomplete cleanup after fabrication and erection. An intrusion of air or low pH excursions may have been factors too in several cases. Two units have shown stress corrosion cracking which also is most likely a result of inadvertent air intrusion, as the presence of oxygen is generally considered a requirement for chloride induced stress corrosion cracking.

The vertical cylindrical tank portion below the liquid level of one installation is shown in Figure 1 after removal of the settled solids or sludge. Vessels showing attack generally display geometrically arranged reddish-orange rust deposits associated with welds and prior locations of clips and gussets used in assembly where they were welded to the shell. Some of the rust deposits are found associated with random grinding marks.

Figure 2 shows hairline cracking and crevice corrosion in and around a vertical weld as a band, several inches wide, spanning both sides of the weld. It is evident that the attack along the weld is in the zone of weld clean up by grinding. The clean up work introduced surface stresses and contamination by soils picked up from places with iron or carbon from carbon arc gouging.

An area of severe localized attack is shown in Figure 3. In the center of this area, a 316L gusset used for alignment and rigging had been located. The gusset was removed by carbon arc gouging and the area dressed up with a disc grinder. The result is the smearing of the oxides, slag and carbon contaminated metal. These locations some of which could be seen in Figure 1 become active sites for pitting in the concentrated neutral chloride environment.

An elongated carbon arc gouge shown in close up appears in Figure 4. It was not cleaned up and overlayed with virgin weld metal but only ground. Pits have initiated under slag and spatter. In these vessels, no attack is found in the open areas untouched by welding, spatter or grinding.

Initiation of attack in another evaporator from carbon arc spatter and field welding spatter on the sloping cone from the work on the cylinder above is shown in Figures 5 and 6. There was little apparent attempt of post weld clean up by grinding and pickling in this assembly. Attack shown here occurred within 3-6 months after commissioning.

Localized crevice corrosion has developed in and around crows foot type SCC from the grinding of a fillet weld of a 316L ladder rung (Figure 7). Even though this is a weld executed in a competent fabrication shop known for handling stainless steels and reactive metals, the weld area has been contaminated. Acid cleaning (pickling) is recommended after grinding to dissolve deleterious oxides, iron and carbonaceous matter. A shop made 50mm (2") side branch connection in a 610mm (24") line again illustrates the same condition as found with the ladder rung (Figure 8).

The center of attention now focuses on flue gas desulfurization (FGD) scrubber quencher sumps down stream of the firebox of coal fired utility boilers. The area of discussion is a tank-like compartment called the quencher sump at the bottom of limestone slurry SO_2 acid gas absorbers. The quencher sumps in this installation were fabricated from 904L plate in a rectangular shaped tank to conserve space indoors. They were externally reinforced with carbon steel structural members.

The environment in bottom of these vessels was typically:

Element	Quantity	ppm or value
Ca	460 - 475	ppm
Mg	520 - 540	ppm
Na	10,000 - 13,300	ppm
K	450 - 4,200	ppm
CO_3	85 - 250	ppm
SO_4	21,000 - 29,000	ppm
S =	0 - 1,700	ppm
C1 −	4,200 - 5,000	ppm
pH	3.0 - 5.0 4.5-5.0 normal	
TSS	13 - 15	

Localized corrosion and perforation of the 6.4 mm (0.25 inch) thick plate occured in three months. The leaks in the tanks were found to be from attack immediately next to vertical welds at transitions from flat sides to curved corners, right at the toe of the weld pass (Figure 9) or next to it in the HAZ at locations of grinding (Figure 10). The longitudinal orientation of the corrosion pit is felt to be due to gravity and streaming ferrous chloride from the active pit. Just as with the evaporators, it was quite common in the FGD scrubber sumps to encounter attack brought about by grinding. Figure 11 is an illustration.

When inspecting surfaces covered in inorganic scale, found both in FGD modules and evaporator sumps, prior to scale or sludge removal, the active corrosion site could be found by a dark (brown or black) spot showing in the surface deposits (Figure 12).

Active attack is frequently initiated by scratches, particularly scratching with ordinary carbon steel tools. Iron is embedded in the surface and reacts with chloride to initiate pitting (Figure 13).

Figure 14 illustrates graphically activation of 904L by grinding in close contrast to the normal shot blasted and pickled mill finish of plate. In some instances, it was found microscopically that the groove type pitting from grinding activation would penetrate part way through the thickness of the plate at the active spot and spread out at an internal banded structure. This condition was found by a cross sectional microscopic examination of the corrosion.

Paint films or identification marks lead to crevice corrosion. Figure 15 shows paint identifications on 904L piping which resulted in crevice corrosion.

It was previously mentioned that the rectangular tanks, were supported externally by steel members to contain the hydraulic load. The members were tack welded with stainless welding filler to the 904L plate. The result was a countless number of heat tint spots on the inside. Some of these spots as shown in Figure 16 became active, under conditions of total immersion, but not above it, and showed localized attack. The reduced corrosion resistance from heat tint has been discussed by Wilson, et al (5), Kearns (6) and other investigators.

Figure 17 shows an example of localized attack where the weld bead and a place in the plate immediately above it has corroded. This example is from an evaporator but weld attack was prevalent in the matching filler weldments of the FGD units also. Figure 17 was a shop made weld. Garner (7) discusses the attack of matching welds in oxidizing acid chloride environments and discusses the advisability for the use of enriched filler metal. Figure 18 shows attack of shop executed circumferential butt weld in large diameter prefabricated pipe made under good shop conditions. This example is further evidence that matching welds generally have lower corrosion resistance than the parent metal, hence the need for enriched filler. Test work done by one of the authors in hydrometallurgical solvent extraction for copper and uranium production both operations of which are done in oxidizing chloride environments with a background of dilute sulfuric acid has shown similar results with matching welds.

Repairs of pitted areas in welds and carbon arc gouges in both the evaporators and the FGD modules were made with ENiCrMo-3 (alloy 625 coated electrode) composition (7) after careful removal of corroded metal by grinding. A repaired weld is illustrated in Figure 19.

Locations of active corrosion, as indicated by oxide stains and around repair welds, were scrubbed with a nitric-hydrofluoric pickle paste and then subsequently washed and neutralized with slaked lime. This treatment has been successful in arresting corrosion in three evaporators.

Although, it is not altogether clear in a black and white illustration, the area shown in Figure 20 had been treated with pickle paste with no recurrence of rusting or corrosion activity.

These experiences with stainless steel structures destined for service in neutral, acid and oxidizing chloride environments indicate that the equipment should be pickled with nitric-hydrofluoric or phosphoric acid pickle paste along the guidelines of ASTM A 380 to remove the smeared and transferred soils from grinding, wire brushing and spatter. Furthermore, consideration should be given to the use of an anti-spatter tape or paste (8) in fabrication.

OTHER METALLURGICAL AND CORROSION CONDITIONS

FGDscrubbers for one Western installation were specified and built from a special grade of 317L stainless steel with high nickel, high molybdenum and high nitrogen contents. The stainless plate was found to have surface blemishes called "seams" in the steel industry. They are in fact oxide filled crevices. Two examples are shown in Figures 21 and 22. This condition was found in plate produced by three rolling mills. The condition is the result of a very narrow hot working or forging range. As the undesirable condition was found on one face only of each plate, it was decided to turn the good side to the corrosive environment, and seamed or blemished side to the atmosphere or outside.

The manways of some FGD scrubbers and other equipment were found to be sealed with black rubber gaskets or graphite impregnated asbestos. The carbon black in the rubber and graphite in the fiber creates a galvanic couple with 904L or 316L resulting in pitting (Figure 23). Red rubber, white rubber or Teflon (R) has been substituted.

CONTROL OF FABRICATION DEFECTS

Again it should be emphasized that fabrication defects in this discussion are those imperfections that impair the service of the stainless steel equipment in acidic and neutral, chloride environments. For example, the presence of free iron on surface of stainless in this environment can initiate pitting or crevice corrosion while the same surface condition in a vessel for 10% nitric acid service is probably of no consequence. Therefore the fabricator should be aware of service conditions and the type of defects that influence service performance, otherwise needed precautions may be omitted or unnecessary measures imposed. Also it can not be over emphasized that the individual with the greatest influence on fabrication defects is the worker directly involved in making the equipment. Fabrication specifications are of little use if the worker is not knowledgeable of the requirements and observes them on the shop floor.

Preventive Measures

Precautions to prevent shop induced defects are usually the most economical approach. Some of these practices are discussed.

Surface protection. Stainless steel mill products are usually shipped from the mill in either the acid cleaned, ground or cold rolled condition with an absence of oxides, free iron and other foreign material. In handling sheets and plates, the fabricator should protect the surface with paper or other suitable covering, leaving only the weld area exposed. This will minimize embedding free iron, weld spatter and tool gouge marks. When covering is impractical, applying anti-spatter compound to the weld area is useful particularly when welding is done with spatter prone processes such as shielded metal arc or gas metal arc.

Shop tools. Where ever practical, carbon steel tools should not be used in the fabrication of stainless steel equipment. Precautions such as facing handling tools with stainless steel is good practice. The often cited example of embedded iron from the nails in workers shoes occurs all to often. Only austenitic stainless steel wire brushes (power or manual) should be allowed.

Grinding and abrasive materials. Examples of corrosion by contamination from grinding was shown in Figures 2 and 8. Very often iron contaminated grinding abrasives are to blame but other contaminates can be picked up and smeared to new locations. Abrasive blasting materials used on steel should never be used to clean stainless steel surfaces, however even "new, unused" abrasive materials may contain iron particles from crushing and screening operations. To be safe, both ground and abrasive blasted surfaces should be acid cleaned as the final step in removing free iron and other contaminates.

Heat tint and oxides from welding. While heat tint, such as results from welding on the opposite side of a stainless steel plate, is innocuous for many service environments, pitting corrosion may occur in neutral or acid chloride environments. Heat tint is removed with acids such as nitric-hydrofluoric or phosphoric acid solutions, however, where extensive reverse side welding is done, the service side can be protected from oxidation by inert gases (argon or nitrogen) or water spray cooling.

Final Shop Inspection

Preventive measures eliminate many surface type defects but for equipment destined for chloride environment services, a critical visual final inspection should be performed and defects corrected. Most of the commonly encountered defects are shown in Figure 24. Figure 4 shows corrosion in modified 316 as a result of an improperly ground carbon arc surface. Comments on repair practices for such defects follows.

Solvent cleaning. Paint, marking crayons or any type of organic coating should be removed by solvent cleaning to prevent crevice corrosion in service. Solvent cleaning should also be used to remove any oily or greasy film as might be indicated by a water-break test. An oily film can mask the detection of free iron or prevent the removal during the acid treatment.

Grinding and abrasive blasting. Abrasive grinding is standard practice to remove defects such as shallow surface marks, weld spatter, arc strikes, weld undercut, dressing arc air surfaces and similar conditions. The grinding operation can also create a condition conducive to corrosion as cited earlier but can be minimized by a using fine to moderate sized abrasive products, keeping the wheels clean and free of contamination. (Periodic dressing such as on a waste piece of stainless steel will help clean out contaminates). Acid cleaning of ground or abrasive blasted surfaces is good practice and is mandatory when free iron is detected.

Weld repair. Repair welding may be necessary for filling pits or other defects which are too deep to remove by grinding. Repair welding deserves as much or more attention than the original structural welds. Good welding practice includes:

- use of comparable or higher alloy filler metal, e.g. ENiCrMo-3 covered electrode or ERNi CrMo-3 filler metal in repair of 904L alloy.
- always add filler metal and never "blend in" defects such as weld undercut by a gas tungsten arc fusion weld without adding filler. A "blend weld" is prone to cracking and reduced corrosion resistance.
- use a technique or current control equipment to prevent crater cracking. Crater cracks are best detected by dye penetrant inspection and can lead to crevice or pitting corrosion.

Free iron test. Two commonly used tests for free iron are the water-wetting and drying test and the ferroxyl test(2), the later being much more sensitive than the former. A free iron test, at least on a spot check bases,is good practice for equipment destined for services were pitting is a possibility. As noted earlier, oily films may mask the free iron and negate test results.

Acid cleaning. Acid cleaning of fabricated stainless steel equipment is the most effective means of removing free iron, free iron plus rust stains or heat tint. There are a number of solutions prepared from commercially available acids and chemicals and proprietary components,(1)(2)(3)(4) Often some experimentation is needed to obtain the most effective solution or concentration for the particular condition. Typical solutions and comments follows.

- 5 to 25 percent nitric acid and 1 to 3 percent hydrofluoric acid is very effect in removing free iron, rust stains, heat tint etc. but solutions must be handled with great care.
- 10 to 50 percent nitric acid is effective in removing free iron but not rust stains.
- phosphoric acid solutions remove both free iron and iron oxide but are much slower acting on free iron than nitric-hydrofluoric solutions.

Hydrostatic testing. The hydrostatic test performed on many vessels and piping systems may reveal embedded free iron by rust formation. On the other hand, the test water could also be a source of iron or rust contamination. When test water is reused for both stainless steel and low alloy steel, treatment with an inhibitor such as sodium nitrate may be used. Following the hydostatic test, the water should be completely drained and the surface dried by circulating air or wiping. At this point, the surface should be checked for rusting.

Figure 25 shows an unusual occurrence where well water was left in a stainless steel tank for 30 days after the test, at which point rust colored streaks were found normal to a horizontal weld. One or more pits were found at the edge the weld and associated with the rust streaks.(9) Iron and manganese bacteria in the well water apparently concentrated iron and manganese compounds containing chlorides in the stainless steel surface. The bacteria oxided iron and manganese to ferric and manganic ions which created ferric and manganic chlorides and in turn caused the stainless steel to pit. In geographic areas where corrosion by microbes in natural water is likely, it is good practice in hydrostatic testing to use demineralized water, high purity steam condensate or as a last choice natural fresh water. Whatever water is used, it should be removed as soon as possible after the test and the surface dried.

Field repairs. Field repairs of corroded stainless steel may require precautions in the construction of new equipment before exposure to service environments. A most important consideration is rigid cleaning prior to any weld repair. The safest practice is to remove all foreign material from the surface and grind the weld and heat affected area to clean metal, taking care that contaminates are not smeared to another area. It is not feasible to list likely contaminates but one frequently encountered is caustic which could lead to weld cracking if not removed. In this case it may be advisable to neutralize the area with an acid solution as a final step.

Weld repairs. Field repairs usually are made by spot weld repair, weld overlaying or sheet lining. Selection is based on factors such as extent of area to be repaired, accessibility and cost to name a few. Comments on these techniques follows.

- **Spot Weld Repair.** The same comments on shop repair welds plus preweld cleaning apply. If the repair is to a corroded original weld, a filler metal of higher alloy content, particularly higher molybdenum, should be considered.

- **Weld Overlay.** Weld overlays may be used to repair areas of a couple of square inches to complete vessel coverage but are usually limited to areas of up to a couple of square feet. In overlaying 316L or 904L alloys matching composition fillers may be used, although a higher alloy filler such as ENiCrMo-3 or ERNiCrMo-3 should be considered if improved corrosion resistance is indicated. For field work either the shielded metal arc or gas metal arc welding process is most widely used although other arc processes may be acceptable. After welding, the surface may require grinding or dressing to remove crevices or rough contours.

- **Sheet Lining.** Sheet lining (sometimes called wallpaper lining) allows an alloy up grade to the corroded area, usually at a lower cost than replacement with solid material. In cases of severe corrosion to the backing material, weld repair or replacement of solid sections is needed before the cladding is begun. Fabrication details of sheet lining is discussed elsewhere. (10)

CONCLUSIONS

The inherent corrosion resistance of a specific grade of stainless steel can be degraded by substandard fabrication practice or even accepted fabrication practices. The area of post fabrication clean up of stainless steels destined for use in acidic, neutral and oxidizing chloride environments appears to deserve renewed attention and further study. One serious, unknown or little discussed deleterious condition, is created by cleanup grinding, even with new clean silicon carbide or aluminum oxide discs. Contaminants are picked up and transferred to other positions.

Special conditions contributing to degradation are:

- Grinding
- Spatter
- Laps and Crevices
- Slag
- Heat tint
- Matching but segregated welds
- Scratches
- Paint films
- Carbon-arc gouging
- Seams and slivers
- Galvanic attack

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Figure 1
A perspective view of a 316L vessel wall showing evidence of localized corrosion.

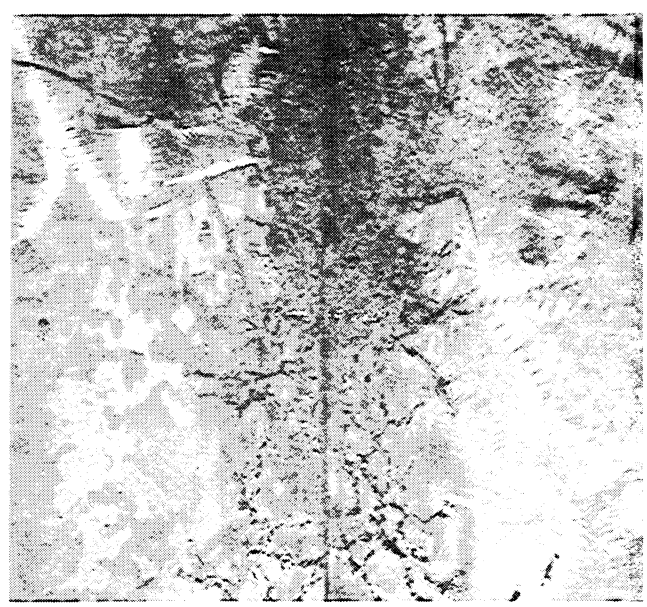

Figure 2
Corrosion on both sides of a weld seam showing attack as a result of grinding or brushing.

Figure 3
The location of a prior construction gusset cut off by carbon arc with irregular disc grinding.

Figure 4
A groove left after carbon arc gouging without proper final dressing.

Figure 5
Corrosion initiated from carbon arc spatter from overhead construction work.

Figure 6
Spatter alongside a vertical weld with the initiation of attack.

Figure 7
Corrosion around the fillet weld of a ladder rung.

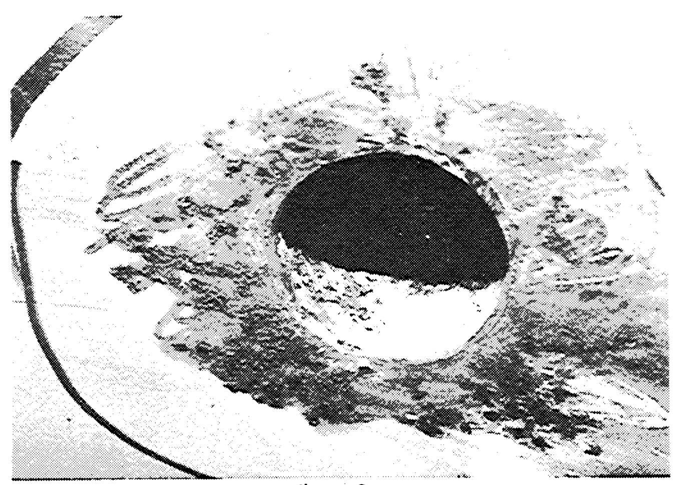

Figure 8
Corrosion around a side branch connection. Attack was initiated by clean-up grinding.

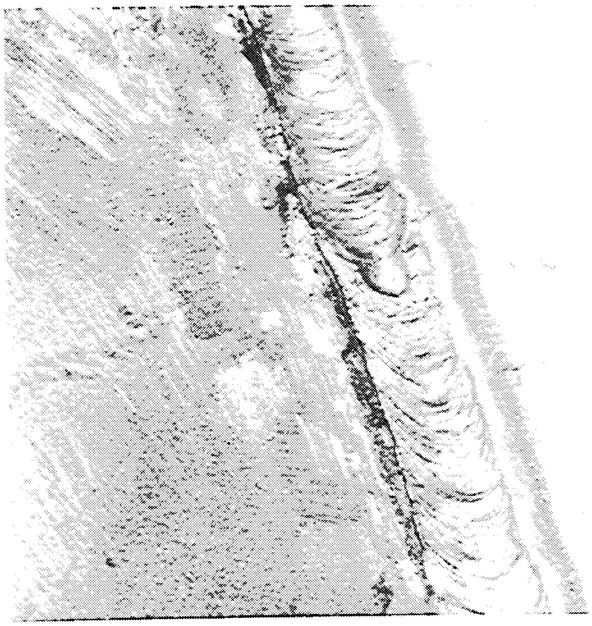

Figure 9
Corrosion at the toe of a vertical weld, probably from residual slag.

Figure 10
Corrosion along a vertical weld from either grinding or slag. The vertical nature of a pit may be from gravitational effects.

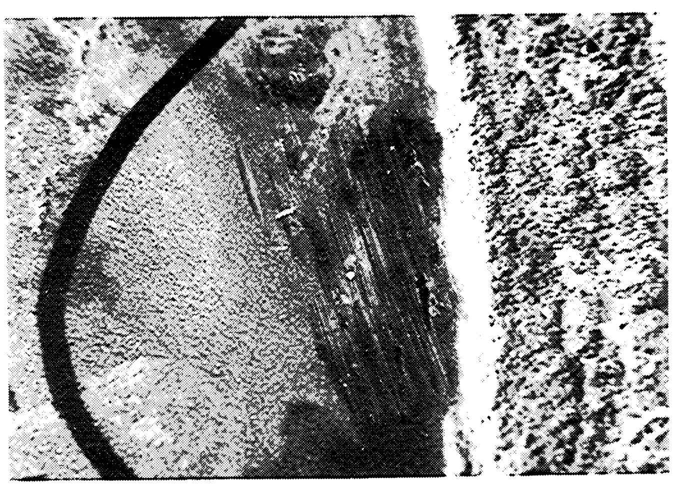

Figure 11
Corrosion as a result of clean up grinding.

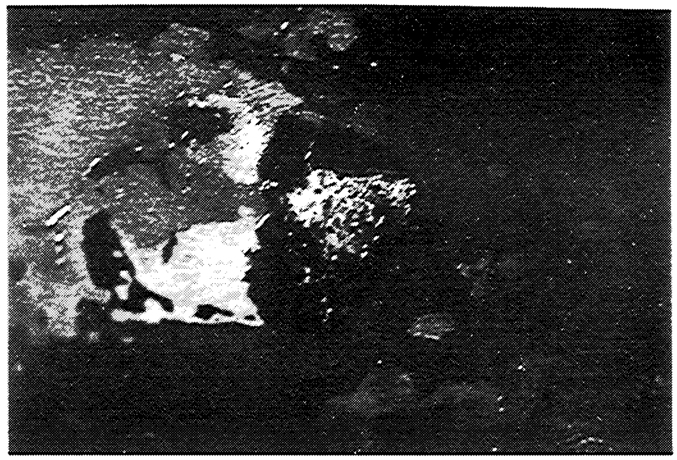

Figure 12
Active corrosion of stainless steel can be indetified by dark spots in the scale.

Figure 13
Corrosion initiated by scratches.

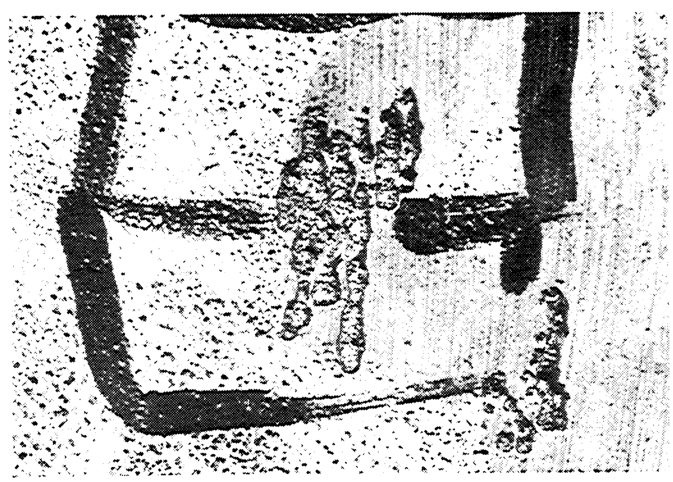

Figure 14
Attack in a ground zone.

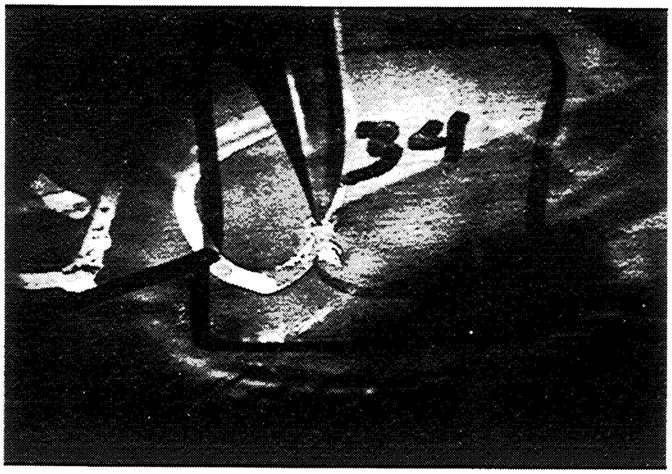

Figure 15
Attack caused by paint markings.

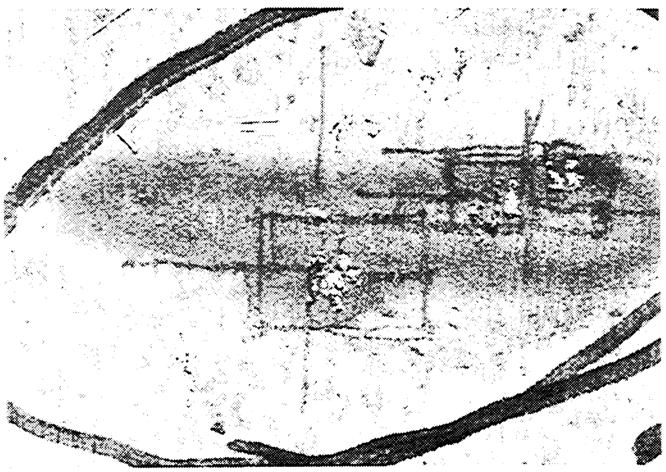

Figure 16
Pitting of 904L at a point of internal heat tint from external welding.

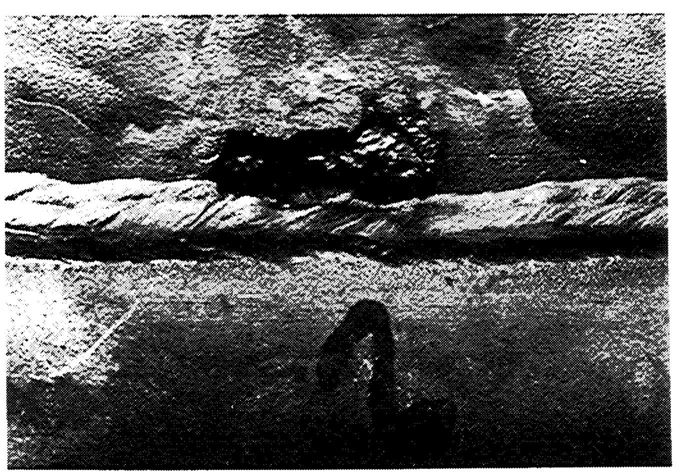

Figure 17
Attack in a field seam and immediately above it.

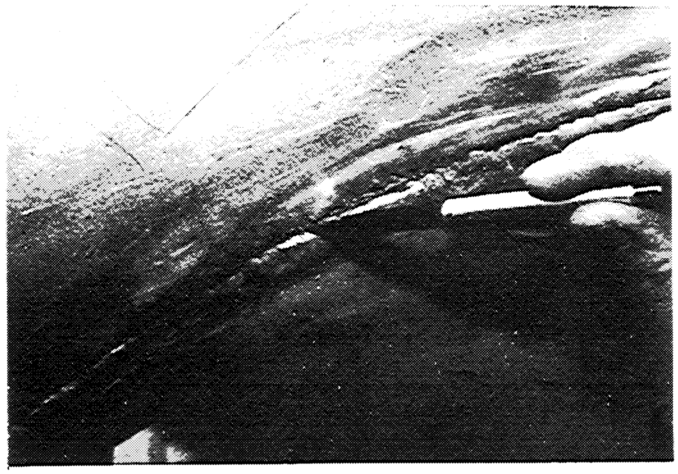

Figure 18
Attack of a shop weld.

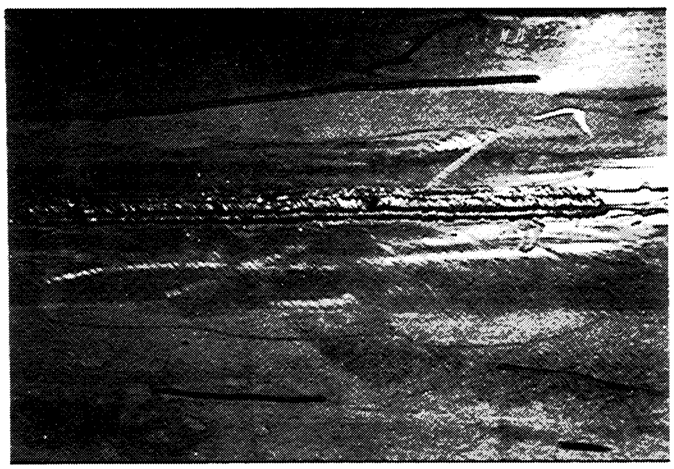

Figure 19
Repair of a pitted zone of an E 316L weld made with an ENiCrMo-3 electrode.

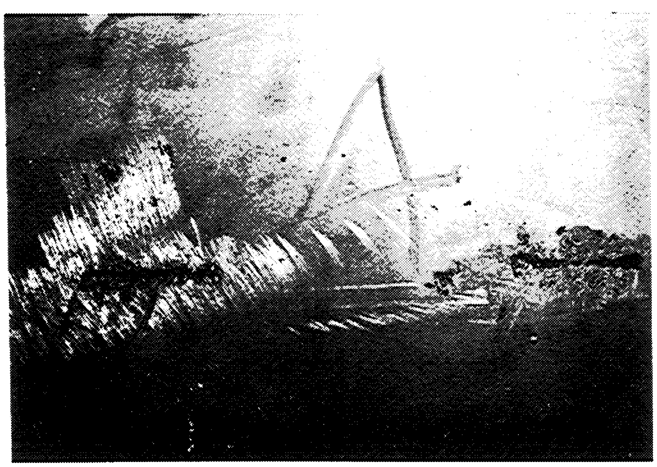

Figure 20
A passive surface as a result of treating with pickle paste. This area had been active.

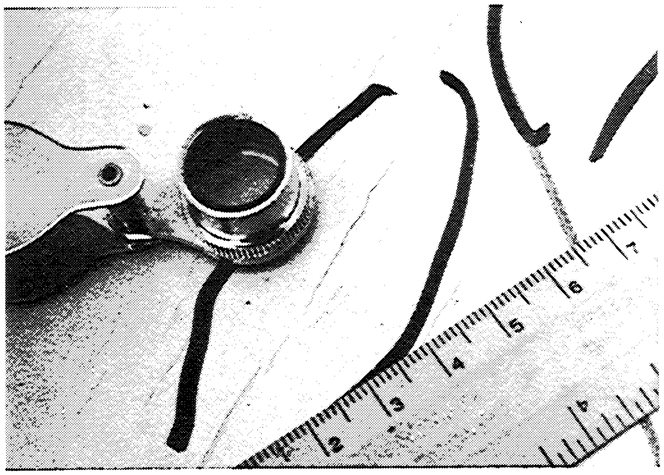

Figure 21
Seams in a high Mo, high Ni, high N special grade of 317L created during hot working.

Figure 23
Pitting from the galvanic action of 904L by a black rubber gasket.

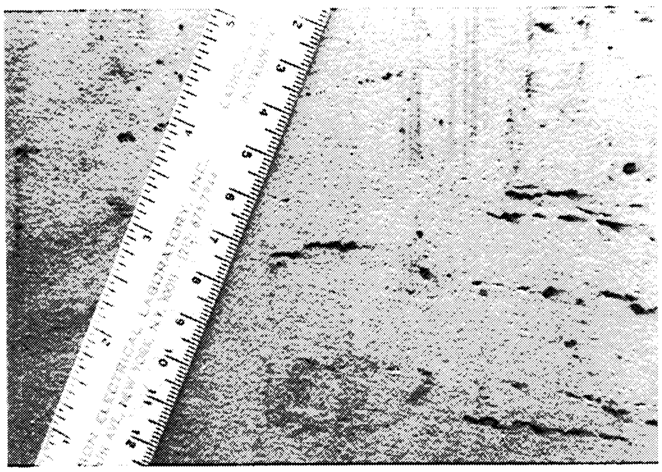

Figure 22
Oxide-filled seams and slivers which result in surface crevices.

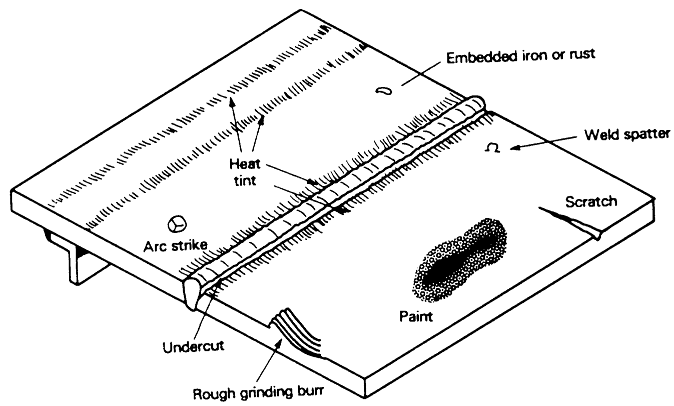

Figure 24
Typical fabrication defects or surface conditions commonly encountered.

Figure 25
Corrosion to a horizontal weld by microbiological organisms following hydrostatic testing.

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