Rust
On Stainless Steel

(Oh my God. . . !)

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Rust on stainless steel is ugly. Rust on stainless steel raises a lot of questions. Is the steel *really* stainless steel? If it's stainless, why is it rusted? Where does the rust come from? Will it continue to rust? Will it spread? Will it cause other forms of attack like pitting or stress-corrosion cracking? See Figure 1 for some ugly rust on stainless steel.

This paper addresses these questions for rust that occurs on a tanks, vessels, piping, etc. that is made from austenitic stainless steel such as Type 304, 304L, 316, 316L, 321, 317, etc. It covers the sources of rusting, the effect of rust on the performance of stainless steel and methods of prevention and removal of rust on those materials. It distinguishes between rust that is found on external surfaces of that are exposed to the atmosphere, including rain, condensation, fog, etc. but are dry most of the time and interior surfaces, particularly those that are wetted, where the consequences of rust depend on service conditions. For continuously wetted surfaces, acceptance criteria should not only address rust but also foreign material contamination, weld oxides, spatter, undercut, surface gouges, and heavy grinding marks.

The following is presented as the opinion of the writer based on common applications of stainless steel. Each application should be evaluated and appropriate cleaning methods should be specified based on the expected service conditions and experience of the purchaser and his engineer with those service conditions.

Background: What Makes Stainless Steel "Stainless?"

Stainless steels are corrosion resistant because there is a high percentage (16 to 36%) of chromium (Cr) is present in these steels. This element is present in sufficient quantity, that, when exposed to oxidizing media (acids, caustics, water, air, etc.), it forms a thin, tightly-adhering and impervious oxide layer (predominantly CrO) that stops further corrosion. In this sense, stainless steels are very much like aluminum in that aluminum also forms an oxide layer that prevents further corrosion of the aluminum. An aluminum oxide layer is different from that which forms on stainless steel because it can become thick enough to form a glassy surface on aluminum that has been exposed to the atmosphere for many years; the oxide layer on stainless steel never gets so thick that it becomes visible to the unaided eye.

While austenitic stainless steels also contain considerable nickel (8 to 25%), it is the chromium that is responsible for formation of the oxide layer that prevents corrosion. The chromium must be dissolved uniformly in the steel's matrix of iron in order for the steel to become "stainless."

What Causes Rust on Stainless Steel Surfaces?

Rust is formed on the surface of stainless steel when a condition develops in which the metal molecules at the surface are not sufficiently alloyed with chromium to create or maintain the required oxide layer. Contrary to popular opinion, surface rusting does not occur when stainless steel is “sensitized” since the bulk of the metal has adequate chromium to prevent surface rusting; sensitized stainless steel only corrodes along the grain boundaries. Rusting phenomenon discussed in this paper is a surface phenomenon only.

The simplest condition under which rusting can occur on stainless steel is when a piece of ordinary carbon or low-alloy steel is rubbed against the surface of an otherwise corrosion-resistant piece of stainless steel. See Figure 1. The iron from the ordinary steel will rub off onto the stainless steel surface as a film of unalloyed steel, and, after exposure to moisture in the atmosphere for a few days, that unalloyed steel film will form ugly rust. This happens because the unalloyed steel film on the stainless steel has little or no chromium, so the film transforms to ordinary “red rust”. Once the shallow film of iron that has “contaminated” the stainless steel surface has oxidized, corrosion stops provided the stainless steel surface remains exposed to the atmosphere and is not wetted on a nearly continuous basis. The rusted surface looks bad, but, the chromium in the stainless steel under the rust film forms a suitable corrosion-resistant oxide layer, and further corrosion does not continue once that film of unalloyed steel turns to rust.

When ordinary steel is rubbed off on stainless steel, the material which is transferred to the stainless steel is generally referred to as “free iron.” This kind of “contamination” of stainless steel is also known by the misnomer of “carbon contamination.” This term is a misnomer because it is not the carbon that causes the corrosion but the unalloyed iron from which the steel is made.

Corrosion of “free iron” on stainless steel is always faster than corrosion of the unalloyed steel itself because the free iron “contamination” is anodic to the stainless steel, so it corrodes to protect the stainless steel, just like zinc corrodes to protect carbon steel when zinc is used as galvanizing.

A second means of forming a rust film on stainless steel occurs during welding when using a process that depends on flux for shielding, such as SAW and GMAW using flux-cored wire. These fluxes tend to be easy-to-remove or self-peeling, and, although the weld surface may look clean, there is a thin residual layer of iron-rich material on the surface. This layer rusts easily if the weld metal surface is not abrasively or chemically cleaned after welding. The nature of this rust is similar to that formed by contact contamination as discussed in the above paragraph.

Effects of Rust on Stainless Steel Surfaces

On surfaces that are constantly wetted by mildly corrosive media, corrosion in the form of pitting can occur under “free iron” deposits which have oxidized. This almost never occurs on the outside surface of piping since the pipe is normally not wet. The writer knows of no occurrence of pitting or other corrosive attack occurring under a rusted area on piping or vessels where the surfaces are generally dry and exposed to the atmosphere. Rust on the external surface of piping or vessels made of stainless steel is, therefore, cosmetic in nature only -- it just *looks* bad!

Prevention of Contamination by "Free Iron"

Good fabrication practice avoids allowing stainless steels to come in contact with ordinary iron or steel, such as work tables, lifting tools, storage racks, steel turning rolls, steel truck beds and chains, steel fork lifts, etc. Iron and steel dust, such as may be created by grinding, cutting, blast cleaning, etc., should be kept away from areas where stainless steel is being fabricated, since that dust may settle on otherwise non-contaminating surfaces where they will be picked up by the stainless steel.

Cleaning and grinding tools, such as grinding wheels and wire brushes that have been used on carbon or low alloy steel should not be used subsequently on stainless steels. Only stainless steel wire brushes should be used on stainless steel.

Weld Oxidation

Welds will frequently exhibit rusting along the edges as shown in Figures 1 and 2. For welds that have not been properly cleaned after completion, this is normal, particularly when the weld was made using a gas shielded welding process. While ugly, this rusting is not an indication of bad welding practices, excessive heat input or excessive interpass temperature; rather, it is the natural result of the high temperature that the heat-affected zone reaches during welding combined with exposure of the hot metal to the oxygen in the atmosphere. Oxides can vary from straw to dark brown when initially formed, and they eventually they turn rust red as the available free iron oxidizes them to a lower free-energy state and the oxides hydrate.

Under normal atmospheric conditions rusting associated with welding stops once the free iron is oxidized; no further damage occurs – it just looks ugly. To eliminate rusting associated with welding, welds should be cleaned as described below within one or two days of being completed. If the service conditions are nearly continuously water-wetted, any discoloration associated with welding and any free iron should be removed by mechanical or chemical means. Further, any coarse or rough surfaces should be smoothed, and mechanical marks or scratches should be removed and all foreign matter should be removed, including paint, slag and spatter to optimize corrosion resistance. Engineers who purchase stainless steel piping should refer to Pipe Fabrication Institute Standard ES-50 (www.PFI-institute.org) for guidance on specifying discoloration on the inside surfaces of piping welds.

Removal of "Free Iron" and Welding Oxidation from Stainless Steel

Free iron, welding oxidation and embedded materials, such as dirt, sand, flux, metals other than steel or iron, etc. may be removed by either chemical cleaning or by abrasive cleaning.

Chemical cleaning agents that will successfully remove free iron and most other contaminants are commercially available. These cleaning agents are acids which typically remove a little of the material (about 0.001 inches) from the surface to which they are applied. They need to be left on the surface long enough to remove any free iron and any visible oxides. Most contain nitric and hydrofluoric acids, so they must be handled using rubber gloves and other personal protective equipment, and they must be thoroughly rinsed off the surface, and the rinse water should be neutralized with baking soda, baking powder, limestone or other basic material. Some commonly available commercial solutions are:

Derustit SS-3, Bradford Derustit, 21660 Waterford Drive, Yorba Linda, CA 92887 877-899-5315. http://www.derustit.com/products/derustit_ss3.php

Avesta Pickling Paste. https://weldingshop.voestalpine.com/US/en_US/voestalpine-Böhler-Welding/5-Finishing-Chemicals/Chemicals/Finishing-Chemicals/Pickling-Pastes//p/69950

Oakite 33, Berkeley Heights, NJ, 201-464-6900. https://www.chemetallna.com/products/by_app/generalMaint.aspx

Compound 302, Arcal Chemicals, Seat Pleasant, MD 800-638-2672, 301-336-9300. https://www.arcalchem.com/metal-treatments

Ox-Out 536, ChemClean Corporation, 130-45 180th Street, Jamaica, NY 11434, 718-525-4500. ChemClean also sells a power supply and wiping pads (Product #85) that electrolytically clean the surface, accelerating to process. Uses less wet solution and is great for small cleanup and welds. www.chemclean.com

Blue Away, Competition Chemicals, Iowa Falls, IA, 515-648-5121 (abrasive paste, not an acid cleaner.) https://www.speedwaymotors.com/Blue-Away-Chrome-Polish-2-5-Oz-,2593.html

Metinox 71E (paste) or 73E (spray), http://www.elmerwallace.co.uk/Stainless-steel-cleaning-and-maintenance/C15-1-0.htm

A rapid and foolproof way to clean the rust off stainless steel is electrochemically. This is very similar to electropolishing in that is removes the surface rust and passivates the surface in seconds. See: http://www.capitalweldcleaners.com

A 20 to 30% nitric acid solution works really well for cleaning welds. It works best if the weld has been power wire brushed to remove heavy oxides. Use in a well-ventilated area, neutralize any runoff with baking soda or wash into a bed of marble chips, rinse with potable water and wear the proper protective equipment.

Mechanical cleaning should only be done using grinding wheels, flapper wheels, and stainless steel wire brushes which have not been previously used on carbon or low alloy steel. *Final cleaning by power wire brushing is not recommended*; wire brushes – even stainless steel wire brushes – will microscopically deform the surface, drive contaminants into the surface, smear the metal and form crevices – none of which are particularly good for the corrosion resistance of stainless steel. Wire brushing between weld passes to remove slag is OK since the brushed surface will be remelted during subsequent welding. If wire brushing is used for finish cleaning, it should either be hand brushing or the bristles should be soft and flexible and the pressure light.

Free iron that has already rusted cannot be successfully removed using grinders or wire brushes. Also, wire brushes will not remove free iron that has deposited as a vapor such as that formed on the heat-affected zone during GTA welding. If cleaning with grinder or wire brush is attempted in these cases, the rust and free iron are dehydrated by the heat generated during cleaning, turning the oxide white, making it look like it's gone. The oxides are then smeared over the stainless steel surfaces that were not previously rusted, and, although the rust will have appeared to have been vanquished, after exposure to moisture in the atmosphere for a few days, those previously rusted surfaces and any new surfaces on which the oxide has been smeared will turn red as the oxides rehydrate.

In these cases, cleaning using either chemical cleaners described above or an abrasive cleaner that has a sufficiently high wear rate that new, uncontaminated abrasive is always being exposed is required. "Flapper wheels" consisting of sandpaper sheets on a hub are OK for this cleaning, but the best product is 3M Unitized™ wheels (compressed Scotch-Brite™ in grinding wheel form) or equivalent. Search Amazon for 3M Scotch-Brite XL-UW Unitized Silicon Carbide Soft Deburring Wheel. Both can be used on a standard shop grinder. When the writer worked at ITT Grinnell back in the dark ages (1970s), we used 3M's unitized wheels for cleaning stainless piping spools and never had a complaint about rusting that was not clearly attributable to handling during unloading and storage at the construction site.

Verification of Removal of "Free Iron" from Stainless Steel

The presence of free iron on stainless steel is readily detected by spraying the steel with water and letting it set overnight. This test is described in ASTM A-380, *Standard Practice for Cleaning, Descaling, and Passivation of Stainless Steel Parts, Equipment, and Systems*. Spraying should be done in the shade and it should be done late in the day to maximize the time that the surfaces stay wet. The surface should wet completely without breaks in the water film; breaks in the film indicate surface contamination, and further cleaning is required. Any areas of free iron will rust overnight, staining the surface. In humid or rainy weather, stainless steel only needs to left boldly exposed outdoors for a day and any free iron will turn to ugly rust. Only those areas exhibiting rust need to be cleaned as described above.

A much faster way of identifying free iron is to brush (not spray) the ferroxyl solution described below over the stainless steel to be checked. Personal protective clothing is required when doing this since the solution is acidic and contains cyanides. Iron contaminated areas will turn blue within a few minutes; if the solution is left on the surface too long, the entire surface will eventually turn blue even if no free iron is present (stainless steel is, after all, mostly iron. . .). This solution should be removed after a few more minutes using water, and the rinse solution should be neutralized. A baking soda solution works fine for this.

Ferroxyl Solution for Finding Free Iron on Stainless Steel

Distilled Water 1 liter
Nitric Acid 30 milliliters
Potassium Ferrocyanide 30 grams

This solution should not be used on surfaces that will come in contact with food or liquids that will be consumed without extreme care to thoroughly remove it since it contains cyanide compounds. The wash effluent should be verified as being cyanide-free.

Summary and Conclusions

Although rust on the exterior surfaces of stainless steel piping is generally innocuous, its ugly presence causes concern on the part of purchasers. Cleaning of stainless steel after welding, proper care to avoid contact with iron and steel during fabrication and verification of the absence of iron contamination prior to shipment will ensure that your product arrives on site free of unsightly rust. If purchasers want to be sure that no ugly rust forms on stainless steel surfaces, they should specify the cleaning described above, and fabricators and contractors should apply those methods liberally. Purchasers, of course, should have proper handling and storage procedures in place to avoid contaminating the stainless steel themselves.

Figure 1

The photograph shows rust on a stainless steel pipe spool piece.

Note the rust on each side of the butt welds. This rust is caused by iron vapors created by a GTAW arc that condense on the base metal next to the weld metal. The vapors are carried out to the base metal by the shielding gas. Welds at the bottom of the photograph where there is an attachment were made using SMAW and do not exhibit this phenomenon. The fitting also exhibits some rust caused by contamination of the surface by contact with ordinary steel (blue arrows).

Figure 2

The photograph shows rust on a stainless steel plate.

Note the rust on each side of the butt weld. This rust is caused by iron vapors created by a GMAW arc; those vapors condensed on the base metal next to the weld metal and rusted after exposure to the atmosphere. Welds were also made on the opposite surface from that shown in the photo; that welding resulted in heat tint (blue arrows) on the side visible in the photo. If service conditions are such that this surface will be boldly exposed to an ordinary atmosphere, further significant attack will *not* occur, but these oxides should be removed by mechanical or chemical means for optimum appearance and to preclude further suspicion. If these surfaces are to be used in continuously or near-continuously water-wetted service, the oxides around the welds and the oxides at the blue arrows, should be removed by mechanical or chemical means because they can lead to pitting attack.