Stainless Steel: Surface Cleanliness

by Arthur H. Tuthill, P.E.

This article describes practical procedures for cleaning stainless steel surfaces. A review of the types of contamination and surface defects that may occur; how to prevent defects, and how to remove defects that cannot be prevented will be highlighted. The article also identifies the various options users have to procure clean surfaces originally.

he pharmaceutical and other industries are concerned with purity of product and cleanliness of the process equipment they use. The author is frequently consulted on how to "passivate" stainless steel. Invariably what the client really wants to know is how to "clean" a surface that has become contaminated. Once the somewhat misused term "passivation" has been clarified and the nature of the contamination determined, how to clean and restore the surface becomes straightforward.

Surface Cleanliness

The dictionary gives several definitions of clean. For this article, "clean" will refer to stainless steel surfaces free of oil, grease, embedded iron, impurities and other foreign matter with the normal oxide film intact.

Mills producing stainless steel make a concerted effort to deliver stainless steel with a clean surface free of all forms of contamination. For sheet and strip, the standard 2B surface finish offered for sheet is a "clean" surface. The standard 2B surface finish can be used as a practical reference standard for "clean" and one against which other surface finishes may be compared. The equivalent of a 2B surface would satisfy most of the food and pharmaceutical industry's requirements for cleanliness, if only, it could be maintained through shipping, handling, fabrication, and installation; and if the equivalent of a 2B surface could be obtained for plate, bar, and castings. Figure 1 lists the more common defects that occur in the

DEFECT	ORIGIN	REMEDY
MnS inclusions Slivers	Mill Production	Pickle
Embedded Iron Grease Crayon Scratches	Handling	Degrease & Pickle
Arc Strike Weld Splatter Flux Heat Tint Grind Marks	Welding	Post Weld Cleanup
Sediment Deposits	Process	Scheduled Cleanings

Figure 1. Common defects in the surface of stainless steel; origin and remedy.

surface of stainless steel. The origin and usual remedial measures are also indicated. In order to better understand prevention and removal of surface defects it is useful to have a good understanding of the nature of the surface itself.

The Nature of the Surface on Stainless Steel

When stainless steel is removed from the pickling bath at the steel mill, a thin, adherent oxide film forms almost instantaneously. Cold rolling, which is normal for sheet and strip, produces the bright 2B finish that characterizes stainless steel. The film is thin, about 8-10 Angstroms thick. It is an oxide film, principally chromium oxide with some oxides of iron and nickel.

Much has been written about passivation. 1.2.3 Simply put, the thin chromium oxide film that forms on stainless steels naturally, makes stainless steel "passive" and resistant to corrosion. Pickling at the mill removes most of the manganese sulfide inclusions and other imperfections from the surface. As stainless is removed from the pickling bath at the mill, the passive oxide film forms almost instantaneously. In fact, it is very difficult to prevent the oxide film from forming, although film formation can be prevented under special laboratory controlled conditions. For all practical purposes, however, formation of the film that makes stainless steel, stainless occurs naturally and almost instantaneously in air. Exposure to air is the basic "passivating" treatment.

The film, though thin, is extremely durable and easily maintained in air or other media where oxygen or oxidizing species, such as water or nitric acid, are present. When damaged, for example by scratching, it is self healing in air and other oxidizing media. Healing, like initial film formation is almost instantaneous. The oxide nature of the film is quite similar for all common grades of austenitic stainless steels including grades containing molybdenum. Stainless steels are naturally "passive."

If stainless steel is naturally passive and resistant to corrosion, what then is the purpose of "passivation" treatments? In the author's experience, 99.44 percent of the time, the real need is not so much passivation, as cleaning of impurities and defects from the surface, i. e. restoration or the equivalent of the nice uniform 2B finish that characterizes cold rolled sheet. Passivation treatments will be discussed later in this article. First, it is helpful to understand how a clean 2B finish can become contaminated or "dirty."

Surface Defects That Arise During Welded Fabrication

Figure 2 illustrates, in pictorial form, the more common defects that arise during fabrication as listed in Figure 1. Most of these defects are unintentional, but nonetheless, damaging to the film. Once the film is damaged or weakened the substrate

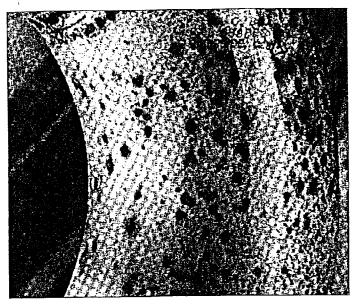


Figure 5. Iron embedded in stainless steel pipe from sandblasting of carbon steel structure overhead.

shops that fabricate steel, as well as, stainless steel vessels. Procurement specifications can not prevent iron embedment, although good shop practice can minimize it.

Procurement specifications can, and should, require a simple water test to detect iron embedded in the surface. The water test consists of wetting down the surface of the vessel or pipe and waiting 12 hours to see if rust spots develop. Any rust spots that develop should be removed with pickle paste or an electropolishing tool as explained later and the test repeated. For critical services, users can specify the ferroxyl test which is even more sensitive in detecting iron contamination. ASTM A380 is an excellent guide for reducing iron contamination in fabricating shops and describes the ferroxyl tests for detection of iron. The ferroxyl test is more sensitive than the water test and is normally specified only where maximum insurance against the presence of iron contamination is required.

The ferroxyl test solution should be made up fresh each day. The solution is applied with a simple laundry type spray bottle. A deep blue color indicates embedded iron. The test is quite sensitive. The surface should be recleaned until there is no, or only a very light blue, color around the edges of the ferroxyl wetted area. A little on-site familiarization with the test is all that is needed in the way of training and establishing acceptance-rejection criteria. The ferroxyl solution should be wiped from the surface after 10-15 minutes, marking those areas that need further cleaning and retesting.

Heat Tint

Welding heats the base metal to temperatures where heavier oxide films (scale) form in the heat affected zones of welds unless the surface is fully protected by inert gas during the welding and cooling period. Heat tint films range in color from light brown to black. Heat tint forms not only on either side of the weld, but also on the inside of vessels where lifting lugs, stiffeners or other attachments are welded to the outside. Such heat tint is generally more damaging than heat tint formed alongside of welds as shielding gas is not normally used on the inside when welding is being done on the outside.

Heat tint is a thicker than normal chromium oxide film. The chromium that is used in forming the heat tint comes from the netal just beneath the heavier film. The surface just below the neat tint is therefore depleted in chromium, reducing the inherent corrosion resistance, Figure 6. The heat tint film itself, being an abnormally thick film with microfissures, tends to retain very small quantities of ionic species and later discharge them into the process stream. Heat tint must be

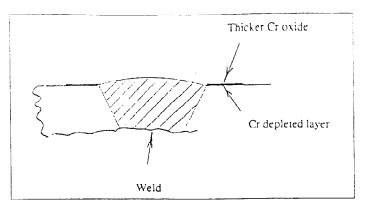


Figure 6. Hint tint: Thicker chromium oxide layer in heat affected zone of weld: Chromium depleted layer beneath.

prevented, or removed, in order to have a clean uniform surface.

Prevention or removal of heat tint is essential to maximum cleanliness. Removal after fabrication is complete, including any repair welds permitted, should be included in procurement specifications for food, pharmaceutical and similar services.

Arc Strikes, Weld Splatter and Welding Flux

When the welder strikes an arc on the base metal, a small X type defect is created in the surface. Arc strikes penetrate the protective film and form sites where corrosion can occur unless the arc strike defect is removed. Prevention is the best procedure. The welder should strike his arc on the weld metal or on the side of the joint ahead of the weld and weld over the arc strike.

Weld splatters are little globs of hot extraneous weld metal which attach themselves to the base metal on either side of the weld. The protective film is broken at each point of attachment, creating sites where corrosion can occur. Prevention is easy. Most experienced fabricating shops paint both sides of the area where the weld is to be made with anti-splatter paint. Antisplatter paint is very effective in preventing adherence of weld splatter to the surface and is easily cleaned off, with little or no damage to the surface, after welding is completed.

It is difficult to completely remove arc strike and weld splatter defects as the defects often extend through the surface layer into the substrate steel. Prevention is easy and should be enforced.

Welding with flux coated (stick) electrodes was the only practical method of welding until inert gas shielding was developed and came into widespread use. The flux protected the hot weld metal from oxidation but was difficult to remove completely from the edge of the weld. Small particles of flux tended to survive the flux removal operation and create sites where crevice corrosion could initiate. Flux coated electrodes should be avoided for food, pharmaceutical and similar services. They are mentioned here, so that users will be familiar with the flux removal problem, should contractors occasionally request their use in special situations.

Crayon Marks, Paint, Oil, Grease and Fingerprints

Organic material on the surface creates sites where crevice corrosion may occur. Figure 7 shows crevice corrosion initiating from crayon marked fabrication instructions left on the surface. All organic material must be removed from the surface by degreasing. This must be done prior to pickling or electropolishing operations. Oil, grease, paint or other organic matter remaining tend to shield the surface from pickling or electropolishing. ASTM A380 includes a very simple "water break" test to detect organic surface contamination. A sheet of water directed to the top of a vertical surface tends to "break" around those areas where organic contamination may remain on the surface.

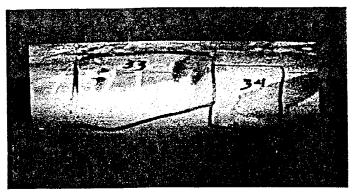


Figure 7. Crevice corrosion originating under crayon instructions to DRILL.

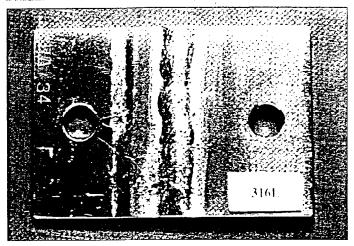


Figure 8A. Corrosion in smeared surface layer formed by power wire brushing 316L welded specimen with stainless steel wire brush.

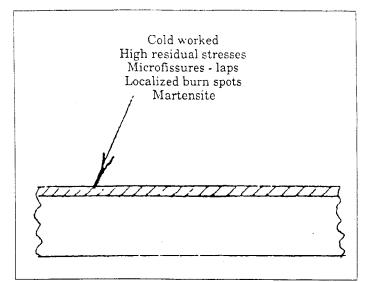


Figure 8B. Smeared surface layer produced by light grinding, machining or glass bead blasting.

Removal of Surface Contamination - Mechanical Cleaning

Mechanical cleaning is the primary clean-up method employed by fabrication shops. Blasting, wire brushing and grinding are the principal mechanical cleaning methods normally employed by fabricators. Blasting with shot, grit, and sand is likely to do more harm than good and should be prohibited. Blasting with clean glass beads is very effective in removing heat tint. Blasting with walnut shells and similar media is acceptable. Glass bead and walnut shell blasting do not roughen and cold work the surface to the extent that shot, grit and sand-blasting do. Blasting can be followed by further cleaning.

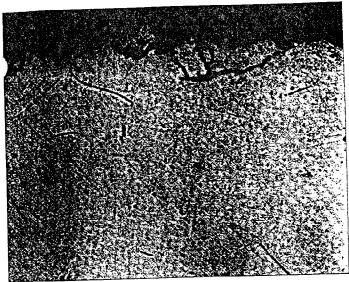


Figure 8C. Hand ground surface - type 304 - 500X. (EPRI - Danko, Smith & Gandy).

Wire brushing is the next most common method of cleaning. The damage resulting from use of carbon steel wire was illustrated in Figure 4. Even when clean stainless steel wire brushes are used, a smeared layer of lower corrosion resistance (type 302 smeared on 316L) is left on the surface as shown in Figure 8A. Such smeared layers left by stainless steel wire brushing are potential sources of "rouging" material.

Clean abrasive disc and clean flapper wheel grinding are common methods used to remove heat tint and other surface contamination. These light grinding methods also leave a smeared layer of lower corrosion resistance on the surface.

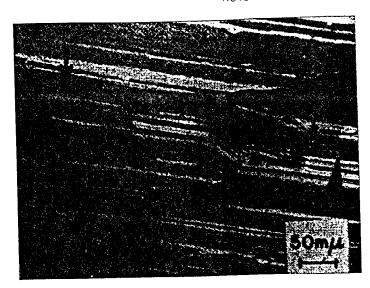


Figure 8D. Ground inside surface of type 304 pipe showing crack initiation (EPRI - Danko, Smith & Gandy).

Figure 8B identifies the problems with the smeared layer left by light grinding operations. Figure 8C shows an actual microfissure in a lightly ground surface. Figure 8D is a SEM picture of a micro-crack which has initiated in a cold worked surface. Smeared surface layers have lower corrosion resistance and are a potential source of rouging problems in later service. Figure 9 shows the improvement in corrosion resistance that occurs when the smeared surface layer is removed by pickling.

Grinding with grinding wheels overheats and deforms the surface to considerable depth as illustrated in Figure 10.

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Instructions to Publishers

Figure 11 shows the "Happy Grinder" enjoying his work but doing more damage to the surface than can be removed by pickling, electropolishing or blasting. Grinding, even with ean grinding wheels, should be limited to grinding out detects prior to rewelding; and to removal of weld reinforcement, when removal is absolutely necessary for process reasons. The heat from grinding disturbs the surface to a depth that cannot easily be removed by later pickling or electropolishing.

Chipping, if limited to areas that are to be welded over, is

generally acceptable.

The surface layer left by these common mechanical cleaning operations is heavily cold worked and highly stressed. It is full of microfissures and often contains martensite, an austenite transformation product of considerably lower corrosion resistance. Although tolerable in many applications, in food, pharmaceutical and other high purity services the mechanically smeared surface layer is a potential source of both rouging and batch to batch contamination of species that may be adsorbed in, and discharged from, the smeared surface layer.

Removal of Surface Contamination: Chemical Cleaning

Embedded iron, heat tint and the smeared layer left by mechanical cleaning operations can easily be removed by either pickling or electropolishing. Pickling and electropolishing are processes that corrode away, in a controlled manner, the thin oxide layer and 0.0002-0.0005" of the surface beneath. By corroding away this thin surface layer, embedded iron; heat tint; the chromium depleted layer beneath heat tint; the smeared layer left by mechanical cleaning and any manganese sulfide inclusions in the surface are removed. Both treatments are designed to thoroughly clean a "dirty" surface and reform a uniform, defect free, protective oxide film.

Two nitric acid-hydrofluoric acid pickling solutions are escribed in A380. A common pickling bath contains 10 percent itric acid 2 percent hydrofluoric. The hydrofluoric acid addi-

tion is made so that the solution will corrode, in a controlled manner, a small amount of the surface of stainless steel. For equipment that will not fit in the pickling vat, pickle paste is used. Pickle paste is applied with a roller along welds where heat tint is to be removed or to the whole surface. Pickle paste should be washed off with water within 30 minutes so that corrosion will not etch the surface too deeply. Protective equipment is required for handling pickle paste. The surface is roughened by pickling.

Electrocleaning, or electropolishing, which is not described in ASTM A380, uses an electric current to corrode the surface. This process is also termed "chemical machining" and "reverse plating" in some quarters. Stainless steel to be cleaned is made the anode in a low amperage, dc circuit in a good electrolyte. The surface layer is corroded away in a controlled manner. Electrocleaning may be done by immersion in a plating type bath or locally using a hand held electropolishing tool. A hand

held electropolishing tool is shown in Figure 12.

Unlike pickling, which roughens the surface, electropolishing tends to smooth the surface as the process tends to corrode the minute surface projections, or ridges, more rapidly than the valleys. There are limits as to how much "smoothing" can be achieved by electropolishing. A "rule-of-thumb" is that electropolishing can improve an RMS finish by about 1/2, i. e. smooth a 32 RMS finish to 16 or an 8 RMS to 4, but can not convert a 32 RMS finish to 8, or an 8 RMS finish to 2.

Since pickling and electropolishing remove metal, both processes will change dimensions slightly, which may be a consideration on parts machined to close tolerances. Such parts should be pickled or electropolished before final machining. Passivation, which is described below, does not alter dimensions. Pickling and electropolishing will also alter surface finish. Passivation has little effect on surface finish.

When pickling, it is important to avoid over pickling by leaving stainless steel in the pickling vat too long, or by leaving

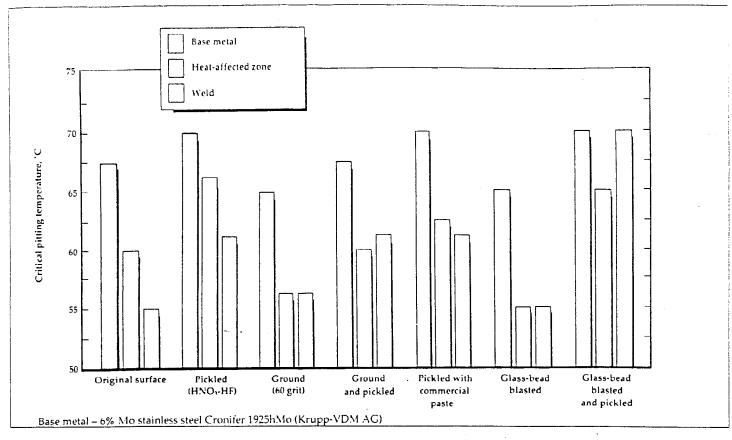


Figure 9. Pickling of stainless steel removes the smeared surface layer and improves corrosion resistance of stainess steel.

pickle paste on overnight. Pickle liquor should be washed off promptly as soon as removed from the pickling bath. Pickle paste should be washed off within 30 minutes of application.

As soon as the pickle liquor or electropolishing fluids are washed away, the oxide film that makes stainless steel passive reforms uniformly and instantaneously over the freshly cleaned surface. Some prefer to require a "passivation" treatment after pickling or electropolishing. Passivation after pickling or electropolishing does no harm, but whether it does any good or not is a point on which there are wide differences of opinion and very little data.

Disposal of spent pickle liquor is a growing problem that tends to limit pickling by immersion to those fabricators that have pickle tanks and to chemical cleaning contractors who have approved arrangements for disposal. Electropolishing, because it can be done with milder acids, such as phosphoric, presents less of a disposal problem.

Passivation

ASTM A 380 describes several nitric acid based, and four other chemical solutions that may be used for what is termed "cleaning- passivation or nitric acid solution or other chemical solutions" for stainless steel. Nitric acid and the other "passivation" treatments do not remove the thin oxide film or any significant amount of contaminants that may be embedded therein. These treatments are designed to do "light" cleaning, to remove metallic and soluble matter laying on or lightly adhered to the surface. These "passivation treatments" are not designed to do the "heavy cleaning" required to remove contamination embedded in the surface or heat tint since they do not remove metal, as does pickling or electropolishing.

Nitric acid passivation is reported to be quite effective in enhancing the corrosion resistance of machined parts. The corrosion resistance of raw machined surfaces, especially when the cut is "across the grain" is enhanced by nitric acid passivation according to DeBold.⁵

Procurement of Clean Stainless Steel Equipment

For equipment that is to be fabricated, surface degradation must be addressed in procurement documents. A major aid is ASTM A380 which describes a number of ways fabricating shops can reduce surface contamination during fabrication. Industry procurement documents should include, at least, the following requirements.

- All surfaces that will be wetted by process fluids should be free of oil, grease, fingerprints, crayon marks, paint, tape and other organic material. To insure that vessel walls are free of organic contamination, the water break test described in ASTM A380 should be specified.
- 2. All surfaces should be free of iron contamination. There are two tests.

For less critical services, wet down the surface with water. Wait overnight. Remove any rust spots or streaks found and repeat the water test until clean.

For critical surfaces, require the ferroxyl test described in A380. A deep blue color indicates iron contamination. Remove any contamination indicated, with pickle paste or an electropolishing tool and retest until clean. The ferroxyl test is very sensitive, but a little on-site practice will enable users and fabricators to agree on acceptance-rejection criteria.

- Require secure closure of all openings after cleanliness has been achieved. Require closures to remain in place until final assembly.
- 4. Require welds to be free of heat tint, weld splatter, and smeared layers from brushing, and other light grinding operations, i. e. pickled or electropolished. There are no good tests, other than visual inspection, for compliance.

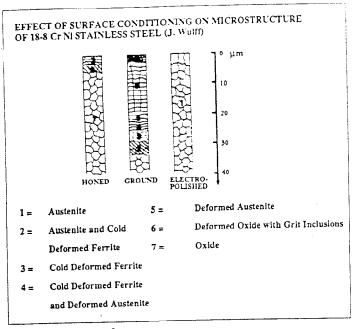


Figure 10.

5. Inspect on-site, for compliance with 1, 2, 3 and 4, above.

Failure to incorporate, at least, items 1 through 4 in procurement specifications can be the source of serious misunderstandings as to fabrication requirements and problems with cleanliness and rouging in later service.

Plate, Pipe, Bar and Castings

Plate, pipe, bar and castings present special problems insofar as surface quality is concerned. Comments on each follow.

Plate: The good 2B finish available for sheet is not available for plate. Mills define plate as material 3/16" and thicker. ASTM A480 describes 5 finishes available for plate. Only the polished, No. 4 finish, is really suitable for food and pharmaceutical service. The other plate finishes described in A480 are normally too rough, and may contain slivers, and other defects, unless special arrangements can be made for mills to produce



Figure 11. The "Happy Grinder.

the surface finish needed without incurring the extra for polishing.

Bar: Manganese sulfide inclusions were identified in Figure 1 as surface imperfections found in mill products. Manganese sulfide inclusions in the surface are believed to form sites where pits initiate. Inclusions in sheet and strip products are normally removed from the surface layer in the pickling operation and are of little concern in these cold rolled products.

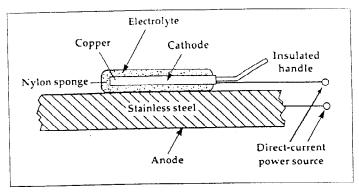


Figure 12. Hand held electropolishing tool.

Inclusions are of greater concern in bar. Sulfur is sometimes added for machinability, especially for bar stock, increasing the inclusion count. Inclusions are drawn out in the direction of rolling forming a banded structure as illustrated in Figure 13. When bar stock is cut across, the ends of the inclusion-stringers are quite vulnerable to corrosion and are difficult to electropolish successfully. The exposed cross section of components made from bar also forms potential sites for rouging.

Removal of inclusions from bar stock must be done at the mill, if it is to be done at all. Stainless steel production technology has improved to the point where low-sulfur, low inclusion bar stock is quite feasible. Car-Tech has recognized the need for minimum inclusion count, bar stock to facilitate electropolishing of valve components made from bar and now offers SCQ[™] bar to meet this need.⁶

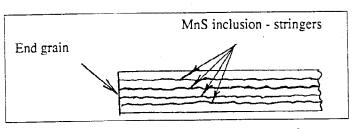


Figure 13. Manganese sulfide inclusion stringers elongated in direction of rolling.

Pipe: Welded pipe producers generally supply pipe with a smooth ID weld approximating the 2B finish on strip or sheet from which the pipe is made. However, if the wall thickness is 3/16" or greater, the starting mill product is plate and must be polished unless special arrangements for a smooth defect free surface can be made.

Trent Tube Division of Crucible Steel Corp. offers welded, stainless steel pipe in 1/2" to 4" diameters with electropolished finish. Other producers can furnish electropolished pipe on special order.

Orbital, machine made circumferential welds, can be produced with a good surface finish, which is a primary reason orbital welding is preferred especially for smaller diameter pipe.

These relatively new products, SCQ™ bar, electropolished pipe and orbital welding, are indicative of suppliers recognition of the growing needs of the food, pharmaceutical, semiconductor and other industries for products with clean, smooth surfaces and of suppliers willingness to offer new products to meet those needs.

There are two other products these industries should be aware of that are not widely known, but may be useful for some

applications.

Type 316L with 2.75 percent Mo is available. This product is being increasingly specified by users concerned with corrosion resistance. The same improvement in steel making technology that has allowed production of low sulfur, low inclusion content stainless steel bar has also allowed routine production

of 316L with Mo close to the 2.0 percent minimum of the 2-3 percent specified range. Specifying 2.75 percent minimum Mo ensures the user that he will obtain the full corrosion resistance of 316L.

Type 316L ESR strip, sheet and plate is also available. ESR refers to electro slag remelt. This product allows the user to obtain sheet, strip and plate to the same low sulfur, low inclusion content as SCQ™ bar discussed above. Although most inclusions are removed from the surface in the pickling operation, there is an advantage in some critical electropolishing operations to start with the cleaner ESR material.

Castings: Although many valves are made from bar stock for these industries, many pumps and valves are still made from castings. Each wrought stainless steel has a cast counterpart of slightly different composition to insure good castability, good weldability and avoid "hot shortness" i. e. microcracking during cooling through the mid-temperature range. There is no significant difference in the corrosion resistance of the cast and wrought stainless steel compositions. The cast counterpart of 304 is CF8; of 304Lis CF3; of 316 is CF8M and of 316L is CF3M. The 3 and 8 refer to carbon content.

Coleman and Evans' article, "Fundamentals of Passivation and Passivity" led to a concern about the need for non magnetic valves through a misinterpretation of their comments on the magnetism the valves exhibited. Cast austenitic stainless steels are designed with 12-15 percent ferrite, the magnetic phase, and exhibit varying degrees of magnetism depending upon the actual percentage of ferrite. Weld filler metal for austenitic stainless steels is also designed with a small amount of ferrite. The ferrite in cast austenitic stainless steels and weld metal is designed to insure good weldability and prevent microfissuring. Corrosion resistance of the cast and wrought grades are comparable in most environments. Magnetic re-

sponse of cast stainless steels measures the amount of ferrite present, but does not measure corrosion resistance.

The author's experience has been that staining (rouging) of CF3M and CF8M cast stainless steel surfaces may occur unless care is taken to ensure that 1) the surface chemistry of the casting is within the specified ranges; 2) the castings are pickled after mechanical cleaning; 3) annealing is done at 100°F min. above the 1900°F allowed by the ASTM specifications. Many foundries routinely observe these precautions, but others do not. The higher annealing temperature is required to homogenize Mo, which is the element that contributes so much to the pitting resistance of 316L.

Cleaning in Place (CIP)

Equipment that has been contaminated during fabrication and not thoroughly cleaned as above, is a potential source of rouging and cleaning problems throughout its service. Cleaning of contamination incurred during fabrication, if deferred until after equipment has been placed in service, is seldom as effective as cleaning before being placed in service. Such deferred cleaning requires special consideration for each case.

Cleaning in place (CIP) refers to removal of precipitates, deposits or other matter adhering to the surface, not to the initial cleaning after fabrication. The usual sequence is:

- 1. Draining and rinsing with water
- 2. Water lancing with high pressure water.
- 3. Steaming with low pressure or high pressure steam

These are beneficial to stainless steel and not harmful. However, steaming out may introduce particles of iron from the carbon steel piping in which steam is carried. These particles are a common source of rouging material, unless filtered out.

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"Equipment that has been contaminated during fabrication and not thoroughly cleaned is a potential source of rouging and cleaning problems throughout its service..."

4. Chemical cleaning with solvents and alkali.

These are seldom harmful to stainless steel. Consult corrosion references to be certain.

5. Chemical cleaning with acids.

Prohibit inhibited HCL, a favorite with chemical cleaning concerns and usually their first recommendation. Chlorides are able to "hide out" in crevices and become the active agent in crevice corrosion, stress corrosion cracking and even rouging when the equipment is returned to service.

Nitric acid does not corrode stainless steels. Repeated treatment with nitric acid, as described in ASTM A380 does no harm. There are those who feel repeated nitric acid "passivation" treatments are necessary. The author's experience would indicate that once stainless steel is clean repeated nitric acid passivation treatments are unnecessary unless required to remove process deposits, but they do little or no harm.

Water for Injection (WFI)

High purity water is normally contained in clean stainless steel. Non-metallics are sometimes substituted for stainless steel based on lower cost. Non-metallics adsorb water in small amounts. Some non-metallics adsorb more water than others. The adsorbed water tends to leach out into the process stream. Systems where such adsorption and leaching can be tolerated tend to use non-metallics. Stainless steel is generally preferred for systems which must maintain the highest degree of cleanliness, i. e. the least adsorption, and the least leaching. Figure 13 shows an electronic chip washing system of stainless steel where zero total dissolved solids can be tolerated, the absolute ultimate in purity and cleanliness.

Summary

- 1. The basic passivation treatment for stainless steel is exposure to air. The as delivered, standard 2B finish on stainless steel sheet is a uniform, clean, durable finish that would meet most of the needs for cleanliness, if only, it could be maintained through, shipping, handling, fabrication, construction and service.
- 2. Nitric acid does not corrode stainless steel. Hence, nitric acid passivation and other passivation treatments are designed only for light cleaning of deposits and other loosely adherent contamination.
- 3. Pickling and electrocleaning/electropolishing corrode, in a controlled manner, and remove the surface layer including any contaminants embedded therein.
- 4. Mechanical cleaning methods leave a smeared surface layer of lower corrosion resistance which is a potential source of rouging in service unless mechanical cleaning is followed by pickling or electrocleaning.

- 5. Pickling differs from electrocleaning in surface roughness/ smoothness. Pickling leaves the surface rougher. Electrocleaning leaves the surface smoother.
- 6. Pickling and electrocleaning may be done by immersion or locally using pickle paste or a hand held electropolishing
- 7. Heat tint is a potential source of rouging and batch to batch contamination unless removed.
- 8. Procurement documents must be carefully drawn. Equipment must be carefully inspected in order to eliminate sites that are potential sites of rouging in service.
- 9. Special attention must be given to procurement of plate and to heavier wall pipe made from plate to ensure the surface is smooth enough for intended service.
- 10. New products with improved surface finish are becoming available: electropolished pipe, low inclusion count bar and orbital welding.
- 11. Castings are designed with small percentages of ferrite, which is magnetic, to ensure good castability, good weldability and to achieve the strength-desired. Magnetism is measured to ensure sufficient ferrite is present and is not a measure of corrosion resistance.
- 12. Repeated passivation in nitric acid does little harm, but may not be necessary unless it is part of the procedure used to remove process deposits from the surface.

References

- 1. Banes, P. H., "Passivation: Understanding and Performing Procedures on Austenitic Stainless Steel Systems," Pharmaceutical Engineering, Nov./Dec. 1990 Vol. 10, No. 6 pg
- 2. Coleman, D. C., and Evans, R. W., "Fundamentals of Passivation and Passivity in the Pharmaceutical Industry,"Pharmaceutical Engineering, March/April 1990, Vol. No. 2,
- 3. Tuthill, A. H. and Avery, R. E., "Specifying Stainless Steel Surface Treatments," Advanced Materials and Processes, Dec. 1992.
- 4. "Cleaning and Descaling Stainless Steel Parts, Equipment and Systems," ASTM A380-88, American Society for Testing Materials, Philadelphia, PA.
- 5. DeBold, T., "Passivation of Stainless Steel Parts," TAPPI Journal, Jan. 1988, pgs 196-198.
- 6. Registered trademark, Carpenter Technology Inc. Reading, PA.