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Stainless steels
for bioprocessing

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NiDI Technical Series Nº 10 077

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Stainless steel equipment has a long history of successful use in bioprocessing operations for which high-quality surface finishes, cleanliness, and maintenance of sanitary conditions are essential. Stainless steels are widely available, corrosion resistant, economical, and easy to fabricate; they are uniquely qualified as construction materials for equipment and systems in the bioprocessing industries.

A knowledge of the many available stainless steel options and an understanding of what makes stainless steel "stainless" and what makes it corrode may help equipment specifiers and procurers for the bioprocessing industries to select the best material for a particular application and obtain the best possible service from it.

This article by the Nickel Development Institute describes the characteristics of stainless steels, some criteria for the selection of materials for process equipment, the basics of corrosion and corrosion control, and some principles of quality assurance for the procurement of stainless steel equipment. It is based on a 4-part serial article by C. P. Dillon, D. W. Rahoi, and A. H. Tuthill entitled, "Stainless Steels for Bioprocessing", previously published in *BioPharm*, April-July, 1992.

Characteristics and Chemical Composition of Stainless Steels

Stainless steel is a family of iron-based alloys that exhibit phenomenal resistance to corrosion in most environments. The family comprises more than 100 alloy compositions or "grades", all of which have one essential feature in com-

mon: a chromium content of between 11% and 30%. A few stainless steels contain only iron and various levels of chromium. Most grades of stainless steel also contain between 5% and 30% nickel, which greatly enhances the ductility and fabrication qualities of the stainless steel and which also contributes to additional corrosion resistance. Some grades contain additions of up to 7% molybdenum for even greater corrosion resistance. Other elements including manganese, nitrogen, niobium, titanium, copper, tungsten, and aluminum may be added to some grades to obtain specific corrosion or mechanical properties. The carbon content of stainless steel is always extremely important and is controlled very precisely within the specified levels for various grades.

Stainless steels owe their corrosion resistance to a phenomenon called passivity. When exposed to air and water, stainless steels start to corrode, but the reaction is stifled immediately by the formation of a very thin, impervious, and adherent film of complex chromium oxides on the surface. Only a few molecular layers thick, the film is invisible, even under high magnification. It's formation and stability are enhanced in oxidizing environments; the film tends to degrade in reducing environments, especially those containing halide ions. When damaged, the passive film tends to repair itself spontaneously in an oxidizing environment. Higher levels of chromium, nickel, and molybdenum contribute to the stability of the passive film and therefore provide improved corrosion resistance to the alloy in more severe environments.

Despite the large number of alloys contained in the stain

less steel family, more than 95% of all the stainless steel produced and sold in the world comprises only a few grades. Some of the more important grades are shown in *Table 1*. By far, the most widely used grade is Type 304 or UNS Alloy Designation S30400. Type 304L (S30403), Type 316 (S31600), Type 316L (S31603), Type 409 (S40900), Type 410 (S41000), and Type 430 (S43000) are also very important commercial grades. Not all the grades in Table 1 have significant application in the bioprocessing industries.

It should be noted that the casting alloys, although conveniently shown in Table 1 as equivalent to the wrought alloys, are not identical to them. Minor variations in chemical composition are often necessary in casting alloys to facilitate the flow of the liquid metal in the mould and control the solidification characteristics.

Stainless steels are most conveniently classified metallurgically by their microstructures. The five principal classifications in the stainless steel family are martensitic, ferritic, austenitic, duplex, and precipitation hardening stainless steels. The martensitic and ferritic grades are strongly magnetic while austenitic are not (see further below).

Martensitic Stainless Steels

The martensitic grades are alloys of iron and chromium, plus carbon and minor other elements. The body-centred ferritic crystal structure ("ferrite") is transformed during cooling from elevated temperature to form the acicular, needle-like structure called "martensite". It is the distorted martensite structure which causes hardening after heat treatment. The hardened alloys are characterized by very high strength and limited ductility. They are also magnetic. Variations in times and temperatures in the heat treatment can greatly affect the final mechanical properties of martensitic stainless steels.

Type 410, or UNS Alloy Designation S41000, is the most widely used martensitic stainless steel. Its most important applications are cutlery and components of pumps, valves, furnaces, and other high-temperature equipment. Some martensitic stainless steels may contain up to 18% chromium and up to 1.2% carbon for extreme hardenability.

Ferritic Stainless Steels

Ferritic stainless steels are also iron-chromium alloys, usually of a higher chromium content (e.g. 17%). The balance of elements, including carbon, is such that on cooling, the alloy forms a body-centred cubic crystal structure called ferrite. Ferritic stainless steels are not hardenable by heat treatment or work hardening, and they are magnetic. Sometimes used for processing equipment in highly oxidizing environments such as nitric acid, they are somewhat difficult to fabricate and weld.

Type 409 and Type 430 stainless steels, or UNS Alloy Designations S40900 and S43000, are the two most widely used ferritic stainless steels. Type 409 is a utility grade of stainless

Table I Designations and nominal compositions for some important wrought and cast stainless steels.

Traditional designation	UNS designation	Microstructure	Nominal chemical composition, % by weight					ACI cast equivalent	UNS cast equivalent
			C	Cr	Ni	Mo	Other		
Type 409	S40900	ferritic	<0.08	10.5-11.8			Ti: (6x%C)-0.75 max		
Type 430	S43000	ferritic	<0.12	16.0-18.0					
Type 410	S41000	martensitic	<0.15	11.5-13.5				CA-15	J91150
Type 304	S30400	austenitic	<0.08	18.0-20.0	8.0-10.5			CF-8	J92600
Type 304L	S30403	austenitic	<0.03	18.0-20.0	8.0-10.5			CF-3	J92500
Type 316	S31600	austenitic	<0.08	16.0-18.0	10.0-14.0	2.0-3.0		CF-8M	J92900
Type 316L	S31603	austenitic	<0.03	16.0-18.0	10.0-14.0	2.0-3.0		CF-3M	J92800
Type 317	S31700	austenitic	<0.08	18.0-20.0	11.0-15.0	3.0-4.0		CG-8M	J93000
Type 317L	S31703	austenitic	<0.03	18.0-20.0	11.0-15.0	3.0-4.0		CG-3M	
Type 347	S34700	austenitic	<0.08	17.0-19.0	9.0-12.0		Nb: >10x%C	CF-8C	J92710
Proprietary	S31254	austenitic	<0.02	19.5-20.5	17.5-18.5	6.0-6.5	N: 0.18-0.22	CK-3MCuN	J93254
	N08925*	austenitic	<0.02	19.0-21.0	24.0-26.0	6.0-7.0	N: 0.10-0.20	CN3MN	J94651
Type 329	S32900	duplex	<0.08	23.0-28.0	2.5-5.0	1.0-2.0			
2507	S39275	duplex	<0.03	24.0-26.0	6.0-8.0	3.0-4.0	N: 0.24-0.32		
17-4PH	S17400	precipitation hardening	<0.07	15.5-17.5	3.5-5.0		Cu: 3.0-5.0 Nb: 0.15-0.45	CB-7-Cu1	J92150
PH15-7Mo	S15780	precipitation hardening	<0.09	14.0-15.3	6.5-7.75	2.0-2.75	Al: 0.75-1.25		

*N08925, although considered a super-austenitic stainless steel, contains less than 50% iron and is, therefore, technically classified as an alloy of nickel with an UNS designation beginning with the letter "N".

steel used primarily for automotive exhaust systems. Type 430 is used widely for automotive trim and domestic appliance parts. Occasionally, highly specialized ferritic stainless steel containing as high as 30% chromium and 2-3% molybdenum may be specified for some corrosive services.

Austenitic Stainless Steels

The addition of 8 percent nickel to a stainless steel containing about 18% chromium produces a remarkable change in microstructure and properties. The alloy solidifies and cools to form a face-centred cubic structure called austenite, which is non-magnetic. Austenitic stainless steels are highly ductile, even at cryogenic temperatures, and have excellent weldability and other fabrication properties. They are not hardenable by heat treatment, but they can be work hardened. About 75% of all stainless steel produced and sold in the world is austenitic. Type 304, or UNS Alloy Designation S30400, is the most widely used austenitic stainless steel and is often referred to as "18-8". There are many variations to the basic 18-8 composition of S30400.

The most common variation is a low-carbon stainless steel called Type 304L or S30403, which will exhibit better resistance to intergranular corrosion after welding than S30400 with a normal carbon level. Low-carbon S30403 also exhibits slightly lower strength than S30400. Type 347 or S34700 is stabilized with a small addition of niobium, which improves the resistance of welded material to intergranular corrosion without reducing the carbon level and preventing any loss of strength. Type 321, or S32100, (not shown in Table 1) contains a small addition of titanium instead of niobium to achieve the same result. Low-carbon or stabilized grades of stainless steel are specified when the material is to be welded and exposed to specific environments that cause intergranular corrosion of welded S30400.

Another important variation in austenitic stainless steels is the addition of molybdenum for improved corrosion resistance, particularly resistance to pitting corrosion in chloride-containing waters and acids. Type 316 or S31600 and Type 317 or S31700 are two examples of molybdenum-bearing stainless steels. Both of these have low-carbon variations—S31603 and S31703—for improved corrosion resistance of welded material. Type 316L or S31603 is the most widely used grade of stainless steel for bioprocessing applications.

Recent advances in steelmaking technology have reduced the cost of producing highly alloyed stainless steels and made possible the commercial development of a new group of materials sometimes called super-austenitic stainless steels. The super-austenitics are low-carbon alloys enriched in nickel (between 18% and 26%), molybdenum (about 6%), and chromium (up to about 22%), and containing small amounts of nitrogen (up to 0.25%). Most of the super-austenitics are proprietary to various stainless steel producers, and each has a slightly different composition range from the others. S31254 and N08925 are two examples shown in Table 1. Super-austenitics exhibit extraordinary corrosion resistance to chemical and natural environments and are used where this corrosion resistance is required. Bleach plants in the pulp and paper industry and flue-gas desulphurization scrubbers for coal-fired electricity generating stations are two examples of end-use applications for super-austenitic stainless steels.

Duplex Stainless Steels

Under some conditions, austenitic stainless steels can be subject to a particularly insidious form of localized corrosion in hot chloride environments called stress-corrosion cracking (SCC). By increasing the chromium and reducing the nickel contents of the basic 18-8 composition, a mixture of ferrite and austenite can be produced that is much more resistant to SCC. A stainless steel exhibiting this mixture of nominally 50% ferrite and 50% austenite in its microstructure is called a duplex stainless steel.

Most duplex stainless steels are low-carbon grades and usually contain molybdenum. Some contain nitrogen, and like the super-austenitics, can exhibit extraordinary corrosion resistance in many environments, particularly pitting-corrosion resistance in sea water. However, they can be less corrosion resistant than austenitic stainless steels in some acids. Special welding techniques are generally required for duplex stainless steels.

Duplex stainless steels exhibit about twice the yield strength as austenitic stainless steels and generally have higher tensile strengths as well. They are used for off-shore oil-production pipelines and other specialized applications where both their excellent resistance to pitting and SCC and their high strength make them more economical than other materials.

Precipitation-hardening Stainless Steels

Some special grades of stainless steel are hardened by the controlled precipitation of intermetallic compounds within the austenitic or duplex microstructure rather than by the transformation of martensite. Most precipitation-hardening stainless steels are somewhat leaner in chromium and nickel than the basic 18-8 composition and contain small additions of aluminum or of copper and niobium to form the precipitate within the crystal structure. Some grades also contain molybdenum for added corrosion resistance.

Most precipitation hardening stainless steels were developed as proprietary alloys for the aircraft industry. However, they are sometimes used in the process industries for pump shafts, bearings, wearing surfaces, springs and retainer rings. Their corrosion resistance is superior to most martensitic stainless steels but inferior to most of the austenitic stainless steels.

Criteria for Materials Selection in the Bioprocessing Industries

Materials selection involves choosing the optimum material to perform a given function reliably and safely under certain environmental conditions at the lowest cost. Whether the alternative materials for consideration in bioprocessing are corrosion-resistant alloys such as stainless steel, coated materials such as vitreous coatings on steel, or non-metallic materials such as ceramics or plastics, materials selection must take into account the technical needs of the operation, reliability and safety, the limits imposed by economics, the requirements of various governmental and non-governmental regulatory agencies, and, of course, prior experience and history of performance.

Technical Needs for Construction Materials

Four technical needs stand out for consideration in materials selection for the bioprocessing industries: corrosion resistance, mechanical properties, physical properties, and fabricability.

Corrosion Resistance - Corrosion resistance is perhaps the most obvious of the technical needs. Corrosion is the chemical or electrochemical reaction between a material and its environment; it affects both the material and the environment, which, in the case of bioprocessing, are the processing and storage equipment and the products being manufactured respectively. Corrosion affects the surface of a material and, therefore, its cleanability. Corrosion resistance is essential not only to the life and performance of the processing equipment but to the quality of the product. Even superficial corrosion is objectionable if it leads to contamination or discoloration of the product.

Corrosion of materials is affected by a number of environmental factors: chemical composition, temperature, dissolved gases, suspended solids, flow rates, differential aeration, pH, presence of certain microbial species, and others. It can be affected by excursions from normal operating conditions including shut-downs. It is affected by the design of processing equipment: the presence of crevices, the radius of curvature in piping systems, and the presence of traps that cannot be drained or that leave vapour spaces that cannot be filled. In metallic structures, it can take many forms: general or uniform corrosion, pitting, crevice corrosion, intergranular corrosion, stress-corrosion cracking, galvanic corrosion, and others.

Ideally, materials of construction for processing equipment should be resistant to all types of corrosion in the processing environment under normal operation conditions and during any possible excursions of operating conditions from the norm. In reality, most materials of construction will provide satisfactory corrosion service for some finite period of time, after which the equipment must be maintained or replaced. A sub-

stantial body of corrosion data for stainless steels and other materials exists in publications by the National Association of Corrosion Engineers (NACE), the Materials Technology Institute of the Chemical Process Industries (MTI), and in technical journals of various scientific and engineering societies to help specifiers in their selection.

Mechanical Properties - Mechanical properties include the strength, hardness, and ductility of a material. They are dependent primarily on the composition of the material, the thermal and mechanical treatment of the material during manufacture and fabrication, and the temperature of the material in service. Mechanical properties can sometimes be adversely affected by corrosion, and the selection of materials must include the consideration of the effect of corrosion on these properties. Minimum standards for mechanical properties of stainless steels are included in various standards published by the American Society for Testing and Materials (ASTM), other national standards-writing organizations such as BSI, DIN, and AFNOR, and in product literature published by the stainless steel producers.

Physical Properties - Physical properties are dependent almost entirely on the chemical composition and crystal structure of a material. They include density, melting point, magnetic properties, and thermal and electrical conductivity. Thermal conductivity is particularly important for heat exchangers. Materials with excellent thermal conductivity that develop a voluminous layer of corrosion product during service may lose their initial advantage based on this important property and become inferior to materials, such as stainless steels, which have somewhat lower thermal conductivity but which do not develop insulating films of corrosion product.

Fabricability - Fabricability is the intrinsic ability of a material to be formed, cut, shaped, bent, stretched, joined, and heat treated for conversion into useful products—into processing and storage equipment. Fabricability is dependent to a large extent on the mechanical properties of a material and, therefore, on the composition. It may be affected by the thermal and mechanical treatment of the material before or during manufacturing and on the temperature at which the fabrication takes place. Some specific parameters in fabricability are weldability, machinability, heat-treatability, and formability. Surface finishing is an important aspect of fabrication and, in bioprocessing, can have a significant impact on the cleanability of processing equipment during service and maintenance.

Stainless steels provide a wide range of corrosion resistance, mechanical and physical properties, and fabricability to meet the technical needs for use in the manufacture of process equipment. The optimum stainless steel alloy for a piece of bioprocessing equipment should be determined in

consultation between experts in the specific processing technology and experts in stainless steel properties and performance.

Reliability and Safety

Process equipment must provide the desired service life with a minimum risk of fire, explosion, or inadvertent release of substances that could endanger the plant, its personnel, the community, or the environment.

The corrosion resistance, mechanical properties, and excellent fabricability of stainless steels provide a wide margin for reliability and safety of equipment made from it. Good engineering design and adequate process controls are essential in all cases irrespective of the material of construction.

Government and Non-Government Regulatory Requirements

Materials of construction must meet certain requirements imposed by various national and regional authorities for health, safety, and the environment. In the United States, they must meet requirements imposed by the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, the ASME/American National Standards Institute (ANSI) Code for Pressure Piping, and applicable standards and specifications by organizations such as ASTM. In other countries, similar standards must be met.

Stainless steels have a long history of excellent performance in the process industries and are widely recognized and included in all the national and international regulatory requirements for materials in the process industries.

Economic Considerations

After identifying a number of candidate materials meeting the appropriate technical criteria, requirements for reliability and safety, and applicable regulatory requirements, one must impose economic considerations during the selection process.

The cost of a piece of equipment can best be defined as the sum of the initial cost, operating cost, maintenance cost, and replacement cost less the residual value of the equipment at the end of its life cycle. Operating and maintenance costs include not only energy, materials, and labour, but the loss of production during shutdowns for maintenance and repairs. Clearly, the initial cost of equipment, although an important criterion in the selection of construction materials, is not the only criterion to consider. Materials should be selected on the basis of the life-cycle cost of the equipment from which it is made.

Stainless steels, although not always the lowest initial-cost alternative, are often the lowest life-cycle cost materials for the construction of process equipment. Detailed methods for calculating the life-cycle cost of materials and process equipment are widely available in textbooks and in the literature of various engineering societies.

Prior Experience and History of Performance

Service experience is one of the most important criteria for the selection of materials. This is not to say that there is no new ground to be broken or that new materials should not be tried and used. But if a material has been shown to provide reliable and economic service in a piece of process equipment, the risk of the same material failing in a similar piece of equipment under similar operating conditions is considerably reduced. If reliable corrosion data are available for a material in a process environment, there is usually no need to re-evaluate that material in the same environment.

Throughout the latter half of the 20th century, stainless steels have been widely used in the bioprocessing industries for mixers, reactor vessels, piping, valves, distillation units, driers, storage tanks, incubators, autoclaves, packaging machinery, and a host of other equipment. Corrosion data are readily available, and the mechanical and physical properties of stainless steels are widely published. No other material of construction has a comparable history of successful application in this important industry.
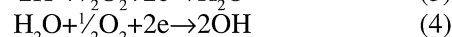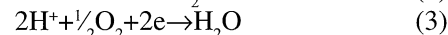
Corrosion and Corrosion Control

Corrosion of metals is the electrochemical reaction that occurs between the metal and its environment. As in any electrochemical reaction, there is an anodic half-cell reaction at which oxidation occurs and a cathodic reaction at which reduction occurs. Ions migrate through the electrolyte, and electrons flow through an external circuit.

The anodic reaction is the oxidation of the metal to produce metal ions and free electrons. An example is the formation of ferrous ions from steel—an oxidizing process:

$$Fe \rightarrow Fe^{++} + 2e \qquad (1)$$

This anodic reaction cannot proceed without a simultaneous cathodic reaction, which is the reducing process that consumes the released electrons. These electrons travel through the external circuit to react with some species at the cathode. In water, depending on the pH, the cathodic reaction may be any one of the following:

$$2H^+ + 2e \rightarrow H_2 \qquad (2)$$
$$2H^+ + \frac{1}{2}O_2 + 2e \rightarrow H_2O \qquad (3)$$
$$H_2O + \frac{1}{2}O_2 + 2e \rightarrow 2OH \qquad (4)$$

Positive ions, or cations, migrate through the electrolyte toward the cathode; negative ions, or anions, are attracted to the anode. In chemical streams, other electrode reactions may occur and determine whether a solution is oxidizing or reducing. The net effect produces the redox potential of the solution.

The electrochemical potential difference between the anode and cathode, usually measured in millivolts, drives the electrochemical reaction. These potential differences may occur locally on a single piece of apparently uniform metal due to variations in cold working, different crystal structures, or

minute impurities. They can result from different concentrations of oxygen or other oxidizing reactant at different places on the metal surface due to crevices, surface deposits, or differential aeration. They can also result from the galvanic differences between two different metals in contact.

Polarization is the change in the potential of an electrode resulting from the flow of electrical current. It is illustrated in *Figure 1*, a polarization diagram for hypothetical anodic and cathodic reactions in which the potential, E, is plotted against the logarithm of the current, *log i*.

In Figure 1, the potential, E_A, is the open circuit potential of the anode with no current flowing. E_{C1} and E_{C2}, are the open circuit potentials of two hypothetical cathode reactions. As the anodic and cathodic currents increase, the potentials of the two half-cells approach each other until they intersect at E_{corr1} or E_{corr2}, the corrosion potentials. The electrical currents, i_{corr1} and i_{corr2}, that flow at those potentials are the corrosion currents, which are a measure of the corrosion rates in accord with Faraday's law. Clearly the corrosion rate associated with cathode reaction 1 is much higher than that with cathode reaction 2. The illustration in Figure 1 is simplified and limited to a system that is controlled by the concentration of the cathodic reactant. Other systems may have differently shaped curves.

Materials that exhibit passivity, such as stainless steel, usually have a much more complex polarization diagram, as shown in *Figure 2*.

In this diagram, E_A, is again the open-circuit potential of the anode. However, in this situation, the anodic polarization curve is more or less "S" shaped, and at some potential level, the current suddenly decreases to a very low value over a fairly wide potential range. This is called the "passive region". As in the previous example, the corrosion rate of the anode will depend on the point of intersection of the cathodic polarization curve. The first cathodic polarization curve, E_{C1}, clearly intersects the anodic polarization curve below the passive region, allowing active corrosion to occur. The second curve, E_{C2}, intersects the anodic polarization S-curve in several places and active corrosion may or may not take place. The third curve, E_{C3} intersects in the passive region of the anodic polarization curve and the metal will exhibit excellent corrosion resistance.

As indicated in the introduction to this article, passivity in stainless steel occurs spontaneously in most oxidizing environments, and its stability is enhanced with increasing amounts of chromium, nickel, and molybdenum in the alloy. Passivity in stainless steel is destabilized in reducing acids and in chloride environments.

The application of an external current source will also affect the electrochemical potential of the anodic and cathodic reactions, and the corrosion potential can be made to move up and down along the anodic polarization curve. Anodic protection and cathodic protection are electrochemical corrosion control techniques in which external currents are applied to
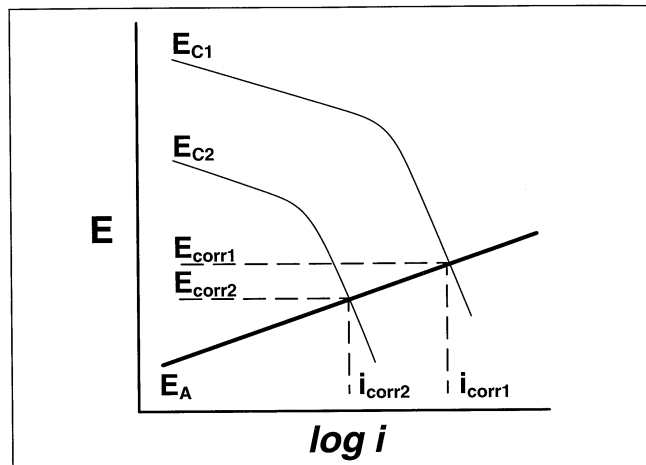
Figure 1 Simple polarization diagram for a metal not exhibiting passivity.
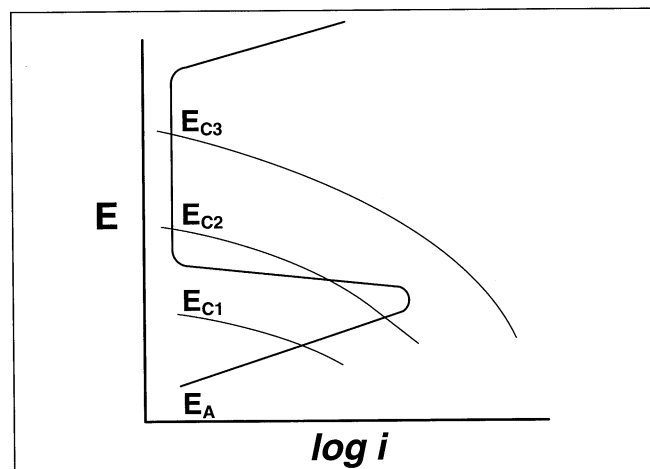
Figure 2 Complex polarization diagram from a metal that may exhibit passivity.

control the corrosion potential to a level at which the corrosion current, and therefore, the corrosion rate, is very low.

Types of Corrosion

Corrosion can take many forms, and corrosion control requires the recognition of these forms and the causes that are specific to each. The forms of corrosion most likely to be encountered with stainless steel are general or uniform corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, stress-corrosion cracking, and galvanic corrosion. General or uniform corrosion represents approximately 10% of the corrosion problems with stainless steel. By far, the most serious corrosion problems are those involving localized corrosion.

General or Uniform Corrosion — General corrosion of stainless steel is most frequently seen in non-oxidizing acids, such as sulphuric acid, when passivity breaks down. It is characterized by a uniform reduction in thickness, which can be measured over time as millimetres per year
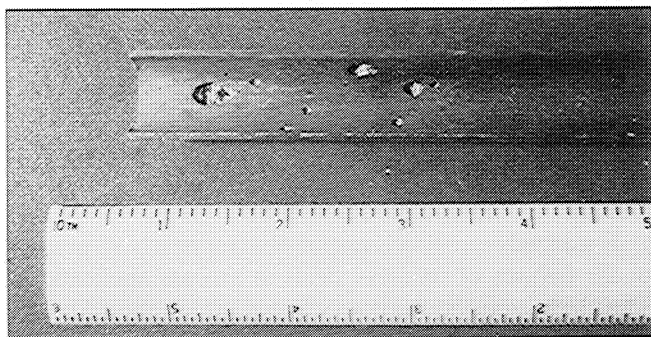
Figure 3 Pitting of a 316 tube.
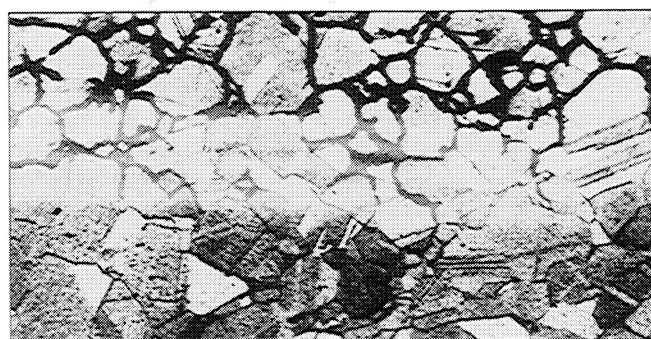
Figure 4 Photomicrographic, intergranular attack (IGA).

(mm/yr) or mils per year (mpy), the most common units for expressing corrosion rates.

General corrosion of stainless steel and other materials in process equipment can be tolerated if the rate of corrosion is low enough, (e.g. <4 mpy (0.13 mm/y), to provide an economically viable service life and if the corrosion products that are generated can be tolerated in or removed from the finished product.

Excessive general corrosion of stainless steel is usually the result of inappropriate materials selection or of a process going out of control. General corrosion can often be controlled by electrochemical means through the use of anodic or cathodic protection.

Pitting Corrosion — Pitting is one of the most frequently seen forms of localized corrosion on stainless steel. It is characterized by the presence of one or more highly localized points of attack on an otherwise unaffected surface. Pitting is common on stainless steel cutlery that is washed regularly in a domestic or commercial dishwasher. The rate of corrosion within a pit may be very high, and local perforation can sometimes occur with the surrounding surface showing no sign of corrosion. Pitting of austenitic stainless steels is almost always associated with high levels of chloride in the corrosive environment.

Pitting is more likely to occur in stagnant chloride solutions or in association with very low flow rates. It can be avoided through the use of stainless alloys containing higher amounts of nickel, molybdenum, and nitrogen. An example of severe pitting corrosion is shown in *Figure 3*.

Crevice Corrosion — Crevice corrosion is another form of localized corrosion sometimes seen on stainless steel. Crevices may be found under deposits of biomass, organic films, and inorganic residues. They may also be found in welded joints, under washers or bolt heads, and in poorly gasketed joints. Crevice corrosion is characterized by corrosion in the occluded area with no sign of corrosion on the surrounding boldly exposed metal. It is usually the result of a concentration cell caused by the depletion of dissolved oxygen in the occluded area, which becomes boldly anodic to the exposed adjacent surfaces where oxygen is freely available to maintain a stable passive film. Crevice corrosion can also result from concentration cells caused by dissolved sulphur gradients.

Mechanical crevices can be prevented by proper design and fabrication of process equipment. Deposits usually occur in low-velocity streams or are associated with biological activity. High-velocity streams tend to remove deposits or prevent their formation and to repair the passive film on stainless steel in an oxidizing environment. Frequent cleaning of process equipment to remove deposits may be beneficial.

Stainless steel alloys with higher nickel, molybdenum, tungsten, and nitrogen contents are more resistant to crevice corrosion.

Intergranular Corrosion — Intergranular corrosion is localized corrosion at the microscopic grain boundaries of the alloy. In stainless steel, it usually results from the depletion of chromium at the grain boundaries in heat-affected zones. When austenitic stainless steels are welded, there is a zone near the weld in which the metal is heated to approximately 550° to 700°C. In that temperature range, carbon reacts with chromium at the grain boundaries to precipitate complex chromium carbides. The metal matrix around the carbide precipitate is depleted in chromium content and becomes anodic to the unaffected adjacent stainless steel surface. The condition is called "sensitization."

Intergranular corrosion is characterized by the disintegration of the metal into loose, unattached microscopic grains. In some environments, for example, boiling 65% nitric acid, sensitized stainless steel may exhibit a corrosion rate, as measured by weight loss, several hundred times higher than the identical material that has not been sensitized. *Figure 4* shows a microscopic view of severe intergranular corrosion of sensitized stainless steel.

Intergranular corrosion is prevented by the use of low-carbon grades of stainless steel, such as S30403 or S31603, or stabilized grades, such as S32100 or S34700, for welded assemblies.

Stress-Corrosion Cracking — Many metals can be subject to a highly localized form of corrosion known as stress-corrosion cracking. It takes the form of branching cracks in apparently ductile material, and it can occur with

little advance warning. In heat exchangers, piping systems, storage tanks, and other low-pressure vessels, the first sign of stress-corrosion cracking is usually a leak. Some catastrophic failures of high-pressure vessels have occurred due to stress-corrosion cracking.

For stress-corrosion cracking to occur, two criteria are essential: a) the surface of the material exposed to the corroding medium must be under tensile stress; b) the corroding medium must specifically cause stress-corrosion cracking of that metal. Tensile stresses may be the result of applied loads, internal pressure in piping systems and pressure vessels, or residual stresses from prior welding or bending.

Austenitic stainless steels can be subject to stress-corrosion cracking in hot chloride solutions, in hot caustic soda, and in chloride solutions containing sulphides or polythionates. Stress-corrosion cracking of austenitic stainless steels in chlorides without sulphides or polythionates is rare if the temperature is below 50°C. Insulated stainless steel vessels and piping systems can also be subject to external stress-corrosion cracking from exposure to chlorides in the insulation if there is a moisture source from condensate or leaks in surrounding equipment.

The risk of stress-corrosion cracking can be reduced by stress-relieving stainless steel equipment that may be exposed to hot chloride environments. Success has also been achieved by introducing compression stress into the metal surface by shot peening. Alloys high in nickel, such as N06625, are resistant to stress-corrosion cracking in hot chlorides and sulphides. Duplex and ferritic stainless steels are more resistant to stress-corrosion cracking in hot chlorides than austenitic stainless steels. Protective coatings can be applied to protect the outside of stainless steel vessels from exposure to chlorides in insulating jackets. An example of stress corrosion cracking is shown in *Figure 5*.

Galvanic Corrosion — Galvanic corrosion results when a less noble metal, such as zinc, is connected to a more noble metal, such as iron, in a corroding electrolyte. It may result when iron is connected to the more noble copper. The less noble material becomes the anode and will undergo accelerated corrosion; the more noble becomes the cathode and does not corrode. Stainless steel is more noble than most engineering materials, and galvanic corrosion is uncommon. An occasional exception is the localized galvanic attack of weld metal.

The high temperature of welding stainless steel sometimes causes a depletion of alloying elements, particularly chromium, in the weld metal. This depletion can leave the weld metal less noble than it was originally. If the welding electrode or filler metal is originally the same composition as the stainless steel being joined, galvanic corrosion of the alloy-depleted weld metal may result. The relatively small surface area of the anodic weld metal coupled to the large surface area of

stainless steel being joined produces a high current density at the anode with a correspondingly high corrosion rate.

Good practice is to use an over-alloyed welding electrode or filler metal: for example, S30800 filler for welding S30400, and S31703 or N08904 filler for welding S31603.

Design to Minimize Corrosion

Localized corrosion is responsible for nearly 90 percent of the failures of stainless steels in process applications. Therefore, stainless steel vessels and piping should be designed, purchased, and maintained to minimize the risk of localized attack. Crevices, pockets, and traps should be avoided to reduce the risk of crevice corrosion. All fabrication steps—bending, forming, welding, etc.—should conform to standard procedures. The importance of the design of welded joints cannot be overemphasized. Welded joints can create crevices and subsequent severe corrosion problems. *Figures 6, 7*, and *8* illustrate some principles of welded joints in stainless steel process equipment and piping. Fillet welds should be smooth and continuous, and undercutting should be avoided. Butt welds should be smooth. Corner welds should be avoided in tanks if possible; side-wall welds are preferable.

Lines and vessels in bioprocessing equipment should be sloped and self-draining. Top nozzles, side ports, and bottom nozzles must be properly designed to permit cleaning. *Figure 9* illustrates good design for drainage.
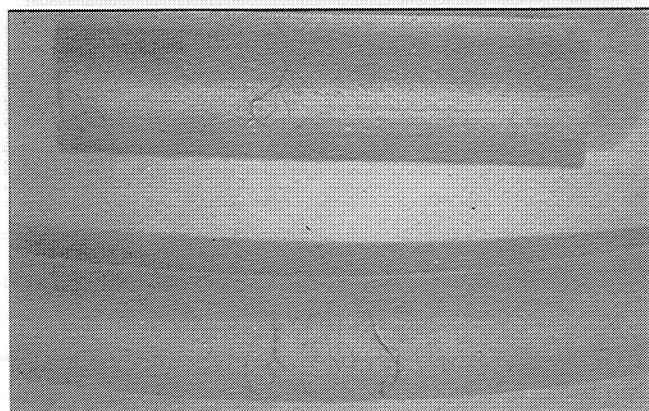


Figure 5 Stress corrosion cracking (SCC) of tubing.
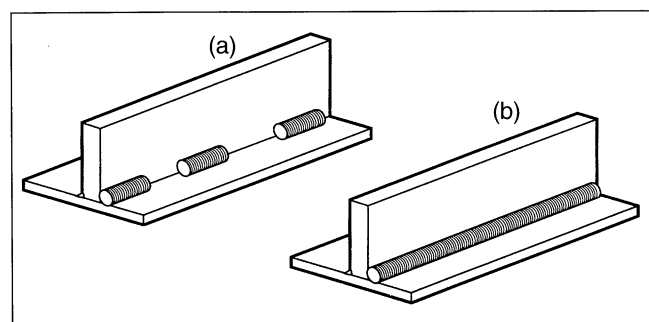
Figure 6 Vertical beams: (a) staggered fillets, severe crevice; (b) continuous fillets, both sides, crevices sealed.


Low-carbon or stabilized grades should be used for welded assemblies, and weld metal should be more highly alloyed than the metal being welded. High residual stresses should be avoided in contact with hot chloride solutions, and if necessary, fabricated assemblies should be stress-relieved. The selection of alloys should be made on the basis of their resistance to corrosion in the specific service environment.
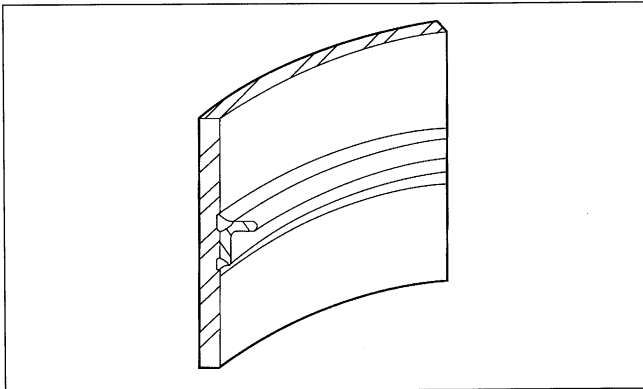
Figure 7   Tray support, full seal weld top and bottom – best crevice resistance.
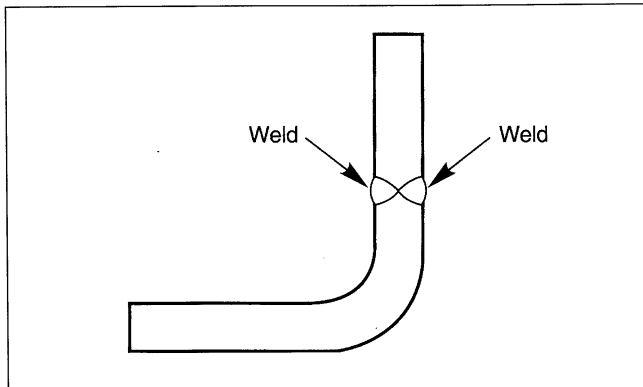
Figure 8   Side wall in lieu of corner weld – best inside, good outside, fatigue resistant.
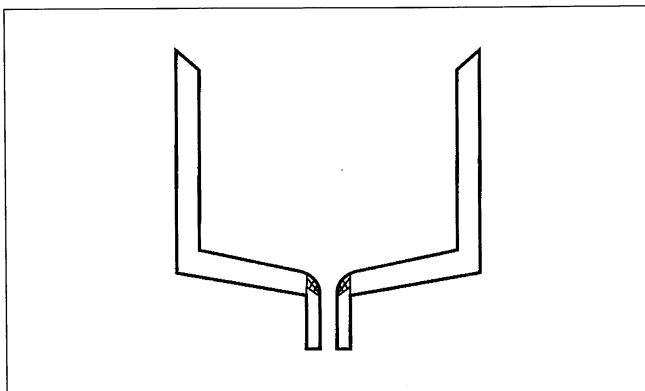
Figure 9   Drain nozzle design, center outlet recessed and sloped – best.

Principles of Quality Assurance for the Procurement of Stainless Steel Equipment

It is considerably easier and less expensive to identify and solve potential problems before process equipment is installed than to solve a problem after it has occurred. This applies to all process equipment, whether it is made from stainless steel, coated steel, or non-metallic materials. Proper measures to prevent future problems or failures combine attention to procurement details, quality assurance tests, post-fabrication cleanup, supplementary requirements, passivation, and sanitizing. Adequate inspection at appropriate phases of the process is mandatory.

Procurement

Materials must be properly selected for the anticipated service conditions, and it is usually insufficient to stipulate only the grade of stainless steel desired. The alloy designation and/or corresponding UNS number must be wedded to an appropriate ASTM or ASME specification together with the necessary supplements[1].

For example, welded stainless steel tubing should be "full-finished" to obtain premium quality. This requires cold-worked and annealed tubes per ASTM A249 plus the stipulation that tubing be cold-drawn to a minimum of 15% in wall thickness or 35% or cross-sectional area before the final anneal. The process not only tests every millimetre of the weld but causes recrystallization of the cold-drawn weld to a wrought structure during annealing, thereby ensuring optimum corrosion resistance. Full-finished welded tubing is less expensive and often of better quality than seamless tubing.

For castings purchased to ASTM A743, a higher annealing temperature of about 1120°C should be specified for CF8M and CF3M (the cast counterparts of S31600 and S31603 respectively) to reduce molybdenum gradients. If regular carbon grades are used, specify ASTM A744 to ensure a post-weld heat treatment after any welding repairs.

Quality Assurance

To ensure proper control of the carbon content in low-carbon stainless steels, adequate stabilization with niobium or titanium, or appropriate post-fabrication solution heat treatment, stainless steel products can be tested for their resistance to intergranular corrosion. One such test, the so-called Huey test, is described in ASTM A262. This procedure is not applicable to S31603, which should be checked by the EOAE (Practice A), followed, if necessary, by an appropriate chemical test from this specification.

When molybdenum-bearing grades such as S31603 are specified, it is good policy to verify the actual presence of molybdenum by chemical spot-test (the molybdenum thiocyanate test) or by other means such as nuclear mag

netic resonance for alloy identification. Stainless tubing and pipe and other products are sometimes mislabeled in distributor warehouses. The materials identification program is the responsibility of the buyer, whether the analytical procedures are performed in-house or by a commercial testing laboratory. Except for a few specific services (nitric acid, for example), molybdenum-bearing grades can be substituted for the non-molybdenum grades; the converse is not true.

Post-weld Cleanup

During fabrication, stainless steels are potentially subject to contamination by steel particles or iron oxides and to heat tints from internal or external welding. Stainless steel surfaces may be cleaned with acid solutions or pastes, mechanically cleaned with a stainless steel wire brush or a clean abrasive disk, or hydroblasted with high-pressure water of potable quality (<250 ppm Cl⁻). Detailed procedures are given in ASTM A380, "Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems." Demineralized water is usually specified for biotech services, but a 25 ppm chloride limit should be adequate.

Iron may be embedded on a stainless steel surface during fabrication and handling. This embedded iron, which is subject to air oxidation, turns to rust, which coats the stainless steel surface to give it a rusty appearance. Mill scale. heat tint, and other high temperature scale may also compromise the surface quality. A solution of 10%-15% HNO_3 mixed with 1%-3% HF is used as a bright pickle to remove visible oxides. Commercial pastes of similar composition are available for localized application. These can constitute a health hazard and a disposal problem, but they are very effective. The HNO_3-HF mixture, unlike HNO_3 itself, is a reducing acid intended to remove metallic oxides by chemical reduction. It is not a passivating medium. However, a uniform passive oxide film will reform on the clean surface after removal from the pickling bath and washing with clean water.

Recent investigations indicate that a warm, dilute citric acid treatment is effective in removing weld heat-tints, without the waste-disposal problems inherent in the nitric-HF procedure.

Weld spatter can be minimized with the application of a commercial anti-spatter paste before welding. Any adhering weld spatter should be removed by flapper wheel, stainless steel wire brush, or hydroblasting. Welds should, of course, be free of pits, craters, ridges, and foreign embedded materials.

Post-machining Requirements

Machined components frequently require nitric acid passivation after they have been degreased. Passivation cleans the surface and enhances the naturally occurring film to ensure a high-quality corrosion-resistant surface.

Supplementary Requirements

Stainless steel sheet is produced in several commercial finishes. Arranged in decreasing order of surface roughness, they are numbered 1 (hot-rolled, annealed, pickled) through 8 (mechanically polished and buffed specular finish with no visible abrasive scratches). For bioprocessing application, a number 2B (cold-rolled, annealed, pickled, temper-rolled) or a number 4 (2B plus 150-grit abrasive belt grinding) finish are commonly specified.

Where extra smoothness is required for non-stick applications or to facilitate removal of bacterial contamination, stainless steel may be electropolished by an anodic treatment in appropriate chemical solutions to produce a mirror finish if a commercial number 8 finish is not available or is inappropriate for the component. Electropolishing also enhances passivation. Stainless steels containing stabilized carbides, i.e. titanium or columbium, are not easily polished.

Organic surface contamination from residual oils or fingerprints is not only a sign of poor housekeeping in a bioprocessing operation; it is a potential source of carbon contamination during welding that can have long-term effects on corrosion resistance. Organic films should be removed by organic solvents, preferably non-chlorinated solvents to prevent possible subsequent chloride-related corrosion associated with pyrolysis during welding or hydrolysis in service (for example, of low molecular weight polyvinyl chloride).

Passivation

Previously mentioned in a perfunctory way, chemical passivation in an oxidizing solution is a means to assure the maximum stability of the passive film and to remove many of the surface contaminants that can have deleterious effects and destabilize the passive film. Electropolishing involves active dissolution but is followed by an anodic oxidation which enhances the final passive film.

Oxidizing solutions that are effective in passivating stainless steel are warm dilute nitric acid (not HNO_3-HF, which is used for pickling), ammonium persulphate (very safe to handle), dilute hydrogen peroxide, or citric acid-sodium nitrite mixtures. Of course, adequate provision must be made for proper disposal of the solution in accordance with environmental regulations.

Table A2.1 of ASTM A380, Part II, suggests passivation with 20%-50% nitric acid at 50° to 70°C for 10-30 minutes or at 20° to 38°C for 30-60 minutes for dull or non-reflective surfaces. In the latter treatment, a 10% caustic soda, 4% potassium permanganate solution is recommended for smut removal after the final rinse. For bright machined or polished surfaces, a 20% to 40% nitric acid with 2% to 6% sodium dichromate is suggested in lieu of straight nitric acid.

The citric acid-sodium nitrate solution for passivation is covered in Part III of ASTM A380.

Some non-oxidizing solutions, also covered in Part III of ASTM A380, can be effective for enhancing subsequent air passivation because they effective remove surface contaminants that may interfere with this spontaneous reaction. These include ammonium citrate, hydroxyacetic-formic, EDTA. The dairy industry has used both a 0.5% to 1.0% nitric acid for 10 minutes at 65°C to 80° C and a similar strength of phosphoric acid, which is a non-oxidizing acid.

Sanitizing

A word of caution about the use of chlorine or hypochlorite solutions to remove bacteria or other microorganisms from process equipment is in order. Thorough flushing with clean water and draining of stainless steel equipment after sanitizing are essential to remove residual chlorine compounds from the system. These residues can not only destabilize the passive film but can initiate chloride-related localized corrosion such as pitting and stress-corrosion cracking. Any crevices or traps in the system will greatly magnify the corrosive effect of residual chlorine sanitizing compounds. Re-passivation is beneficial, provided residual chlorides are effectively flushed from the system.

Alternatives to chlorine sanitizing compounds include non-chlorine-containing oxidizers such as ammonium persulphate, hydrogen peroxide, dilute peracetic acid, citric-nitrite solutions, or chromic acid (with proper handling and disposal procedures). Environmentally acceptable non-oxidizing biocides such as hexamethylene biguanide offer another possible approach free of the hazards associated with chlorine compounds.

Cleaning and Inspection

Bioprocessing equipment is exposed to many different compounds, including proteins, lipids, carbohydrates, and salts, that may leave difficult-to-remove residues. Proteins are the most complex structures, the most likely to foul surfaces, and the hardest to remove. Although physico-chemical forces cause the proteins to adsorb on stainless steel, they can be removed by chemical cleaning.

Two bioprocessing industry standards, 21CFR211.76 and 21CFR820.60, govern cleaning operations. Clean-in-place operations may be effected by steaming, followed by an alkaline rinse (often containing sodium hypochlorite as a biocide), water, phosphoric acid, and a final water rinse. Adding detergents or wetting agents can be helpful. Lines should be pressure washed at ≥ 1.6 m/s; process and storage vessels may be sprayed. The effectiveness of the cleaning should be validated.

Avoid cleaning with hydrochloric acid solutions if at all possible. If there is no practical alternative, the HCl must be completely removed—especially from crevices—with alkaline neutralizing agents and fresh water rinses.

After post-service cleaning, vessels and piping should be repassivated with dilute nitric acid or other oxidizing solutions to assure the maximum restoration of their original corrosion-resistant conditions.

Finally, visual inspection should be employed at appropriate intervals in the fabrication, erection, and cleanup operations. Regular inspections during shutdown are also required to ensure that the desired cleanliness and finishes have survived normal operation and post-service cleaning.

Summary

The austenitic stainless steels, together with duplex or high-performance alloys as required in special circumstances, offer a unique combination of corrosion resistance, ductility, and fabricability when properly specified, designed, and used. Stainless steels can be used with a high degree of confidence in bioprocessing operations in which high-quality surface finishes, cleanliness, and maintenance of sanitary conditions are essential.

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[1] While this article refers to American specifications published by ASTM, ASME, and other US organizations, standards writing organizations in other countries publish similar or equivalent specifications which should be referred to in procurement documents originating in these countries.

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