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STAINLESS STEELS FOR CORROSIVE ENVIRONMENTS

AUSTRALASIAN CORROSION ASSOCIATION INC.

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Stainless Steels For Corrosive Environments

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This Technical Note:

The 1998 Edition of this Technical Note is a revision of the 1983 edition which it supersedes. This Technical Note is designed provide guidance on the selection of stainless steels for different environments, summarise information from a wide range of sources and lists references for further reading and assistance for designers, detailers, fabricators, students interested in stainless steels use and fabrication

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Future Revisions

This Technical Note will be revised from time to time and comments aimed at improving its value to industry will be welcome.

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Contents

INTRODUCTION

The use of stainless steels in fabricated construction has grown over the years to the extent that they now represent a very important class of structural material. Stainless steel may be specified in a particular application for a variety of reasons, such as:

- inherent corrosion or heat resistance in a particular environment;
- low maintenance requirement compared, for example, with coated or plated mild steel;
- aesthetic appeal;
- hygienic nature, ease of cleaning and sterilising;
- high strength to weight ratio;
- exceptional cryogenic properties;
- low magnetic permeability.

The severity of the corrosive environment encountered can vary from the mild atmospheric conditions to which urban architectural structures are subjected, to the severely corrosive conditions of chemical plant.

A comprehensive series of standard stainless steel grades is available in Australia, with their compositions varied to produce levels of corrosion resistance to suit a wide range of environments, together with a number of proprietary speciality alloys to handle specific chemical environments.

There is a general lack of knowledge and understanding throughout industry of the way in which the correct grade selection, fabrication techniques, methods of design and maintenance can ensure that stainless steels are utilised to provide maximum economic benefit. For example, the most corrosion resistant grades can give inferior performance unless close attention is given to selection of a suitable welding technique, appropriate consumables and a satisfactory weld geometry.

SCOPE

This Technical Note aims to provide information which will enable the most effective use to be made of stainless steels in corrosive environments. This information is presented in the following format:

- standard grades of wrought stainless steels, their compositions, properties and applications;
- types of corrosive attack to which stainless steels are susceptible, and grade selection to minimise corrosion;
- welding methods and design to minimise corrosion problems;
- cleaning and maintenance to minimise corrosion;
- selection of stainless steels for specific environments.

GRADES OF WROUGHT STAINLESS STEELS, THEIR COMPOSITIONS, GENERAL PROPERTIES AND APPLICATIONS

The term 'stainless steel' is used to cover a wide variety of grades and compositions. Traditionally, a stainless steel is considered to be an iron-based alloy containing more than 12% chromium. However, the Australian Customs Service classifies alloys with greater than 10.5% chromium as stainless steel. These steels can be classified into five basic groups:

a) Austenitic stainless steels, AISI 200 or 300 series steels (UNS S30000 or S20000 series);
b) Ferritic stainless steels, (AISI 400, UNS S40000 series);
c) Duplex stainless steels;
d) Martensitic stainless steels (AISI 400, UNS S40000 series);
e) Precipitation hardening stainless steels.

Grades commonly used in Australia are listed in Tables 1 to 4, and the way in which families of grades have evolved from a single base grade in each class is illustrated in Figures 1 to 3.

3.1 Austenitic Stainless Steels

These steels are all alloys of iron, chromium and nickel. They have a crystal structure similar to copper or aluminium and are non magnetic in the annealed condition. Their mechanical and physical properties are more similar to those of brass than of plain carbon steel. They are not hardenable by heat treatment, but are readily strengthened by cold work, the rate of work hardening being affected mainly by the nickel content of the alloy. Higher nickel contents reduce the propensity to work harden.

These alloys are very easy to weld, using electric welding techniques (arc, resistance, seam), and generally require no pre- or post- weld heat treatment. The family of steels is illustrated in Figure 1, and listed in Table 1.

The austenitic steels are the most commonly encountered of all stainless steels types, accounting for over 70% of consumption in Australia. Grade 304 is the closest current equivalent to the so-called "18/8" stainless steel with which many people are familiar.

Although Grade 304 is resistant to many common environments, it is susceptible to pitting corrosion in a chloride environment, particularly if the temperature is elevated. The addition of molybdenum improves pitting resistance, hence the development of Grade 316, with 2% Mo.

Other grades of austenitic stainless steel which do not appear in the AISI standard range are also in commercial use. These are usually more highly alloyed steels, developed for specific chemical plant applications. Examples of these alloys would be the 'Alloy 20' type and its derivatives, such as 904L (N08904). Typically these alloys contain 0.02% C, 25% Ni, 20% Cr, 4% Mo and 2% Cu and are designed for resistance to corrosion by strong reducing acids such as sulphuric acid, and warm or hot salt water and chemical plant applications. These lightly alloyed grades are often referred to as 'super austenitics'.

For very aggressive chemical environments, such as hydrochloric acid and halogen salts, which cannot be handled by stainless steels, higher nickel alloys and nickel base alloys are available. Incoloys, which overlap with the higher alloyed stainless steels, are iron based alloys used for hot salt water applications. They generally behave in a similar manner to stainless steels in their welding and forming characteristics.

A feature of the austenitic grades is their very high ductility. This results in excellent formability. Applications such as deep drawn troughs and kitchen sinks are only possible because of this ductility.

"Improved Machinability" (IM) versions of the common austenitic steel grades are available in bar products. By modification of the steel inclusion morphology, these achieve significant improvements in cutting speed together with lower tool wear rates compared to their standard grade equivalents. Their machinibility is not as high as the true free machining grade 303 where high cutting performance is achieved by substantial sulphur additions. However, the IM grades do not suffer from the poor corrosion resistance, weldability and formability that is suffered by 303. The IM grades are not standardised but use trade names such as "Mecamax", "Prodec", "Sanmac" and "Ugima".

3.2 Ferritic Stainless Steels

These steels are alloys of iron and chromium with small additions of other elements in some grades. They have body centred cubic structures similar to mild steel and are not hardenable by heat treatment. They may be readily resistance, spot or seam welded, and inert gas welded in thin sheet form. They are, generally speaking, not suitable for heavy welds requiring large heat inputs, or multiple pass welding, due to their susceptibility to grain growth in the weld zone.

Table 1: Common Austenitic Stainless Steel Grades & Their Applications

Grade	UNS. No.	Forms Available	Typical Analysis (%)						Typical Applications
			C	Cr	Ni	Mo	Ti	Other	
301	S30100	Steel & Coil	0.08	17.0	7.00	-	-	-	General purpose steel with good corrosion resistance for most applications. Employed where its high work-hardening exponent is desirable. Can be supplied cold worked to give high strength and ductility. Used for structural applications such as rail carriages and wagons.
302	S30200	Sheet & Coil, Bars	0.08	18.0	9.0	-	-		General purpose steel with good corrosion resistance for most applications. Previously used for architecture, food processing, domestic sinks and tubs. Mostly replaced by 304.
303	S30300	Bars	0.12	18.0	9.0	-	-	0.25S	Free machining steel used where extensive machining is required. Corrosion resistance and weldability inferior to 302.
304	S30400	Sheet & Coil Plate & Bars	0.06	18.5	9.0	-	-	-	Similar corrosion resistance to 302 and now generally replaces 302. Used where higher resistance to weld decay is needed e.g. in brewing.
304L	S30403	Sheet & Coil Plate	0.02	18.5	9.5	-	-	-	Chemical plant and food processing equipment, where freedom from sensitisation is required in plate.
305	S30500	Sheet & Coil, Wire	0.03	18.0	12.0	-	-	-	Spun sheet parts, cold headed screws.
253MA	S30815	Sheet, coil, plate, pipe, bar	0.08	21.0	11.0	-	-	1.8 Si 0.16 N 0.05 Ce	High temperature applications to 1150°C. Excellent resistance to scaling; high temperature strength
309	S30900	Sheet & Coil, Plate, Bar	0.15	23.0	13.5	-	-	-	High temperature, oxidation resistant. Furnace parts
310	S31000	Sheet & Coil, Plate & Bars	0.12	25.0	20.0	-	-	-	Furnace parts and equipment. Resistant to temperature 900^0C to 1100^0C.
316	S31600	Sheet & Coil, Plate & Bars	0.06	17.0	12.0	2.25	-	-	Used where higher corrosion resistance is required, ie. marine equipment, chemical industry equipment. Can be welded up to 3 mm without subsequent heat treatment
316L	S31603	Sheet & Coil, Plate	0.02	17.0	12.0	2.25	-	-	A low carbon modification of 316 where heavy section weldments are required without the risk of intergranular corrosion.
317	S31700	Sheet & Coil, Plate	0.06	19.0	13.0	3.25	-	-	For chemical plant-has a greater corrosion resistance than 316 in certain applications, notably in contact with brines and halogen salts. More usually available in the low carbon "L" grade
321	S32100	Sheet & Coil, Plate & Bar	0.06	18.0	10.0	-	0.5	-	Heavy weldments in chemical and other industries. Suitable for heat resisting applications to 800^0C. Not suitable for bright polishing.
201	S20100	Sheet & Coil, Plate	0.12	17.0	4.5	-	-	6.5 Mn 0.15 N	Lower cost, reduced nickel version of Grade 301
202	S20200	Sheet & Coil, Plate	0.08	18.0	5.0	-	-	9.0 Mn 0.15 N	Lower cost, reduced nickel version of Grade 302.

Table 2: Common Ferritic Stainless Grades and their Applications

Grade	UNS No.	Forms Available	Typical Composition (%)					Typical Applications
			C	Cr	Mo	Ti	other	
405	S40500	Sheet & Coil	0.06	12.0	-	-	0.2Al	Welded fabrications for mildly corrosive environments and in heat resistant applications.
409	S40900	Sheet & Coil	0.06	11.5	-	0.5	-	Heat resistant steel, easily formed and welded. Mainly used for automotive exhausts or welded applications where superior performance to galvanised steel is required.
410S	S41006	Sheet & Coil, Plate & Bar	0.06	12.5	-	-	-	Used for heat resistant applications up to 650^0 C in power plant and oil refineries, where high strength at elevated temperatures is not required.
430	S43000	Sheet & Coil, Plate & Bar	0.08	17.0	-	-	-	Interior architectural component, stove and automotive trim. Welds tend to be brittle.
444	S44400	Sheet & Coil	0.02	18.5	2.0	0.4	-	Heat exchanger and hot water tanks, and in chloride containing waters. Not prone to chloride stress corrosion - superior resistance to pitting, crevice and intergranular corrosion. Possesses excellent deep drawing properties.
182	S18200	Bar	0.07	18.25	2.0	-	0.20S	Free machining bar variant of 444. Superior machinability to 303.
3Cr12 5Cr12	S41003	Plate, Sheet & Coil	0.02	11.5	-	-	-	Utility steel used primarily in wet abrasion applications. good weldability even in heavy sections.

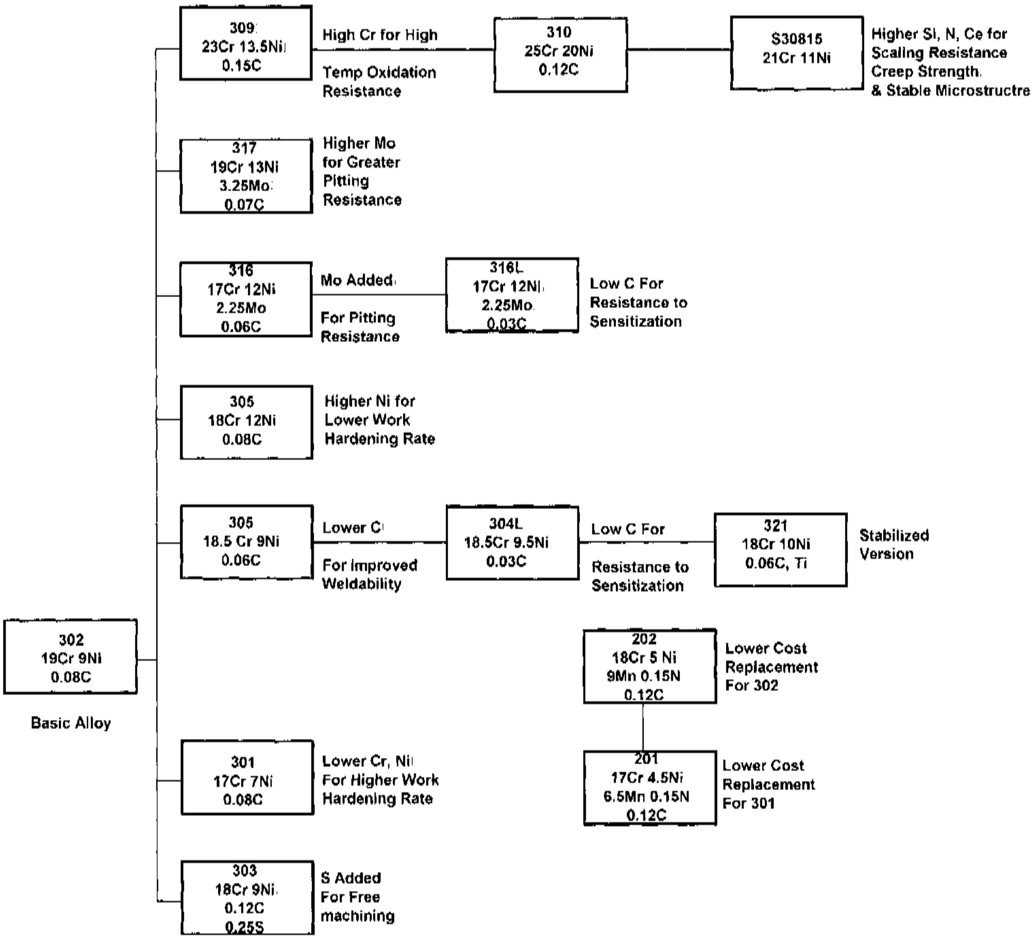


Fig. 1 Austenitic Stainless Grades

The family of ferritic steels is illustrated in Figure 2 and listed in Table 2. Their corrosion resistance is generally less than that of the austenitic alloys, and so most of their applications are in non-aggressive environments (such as Grade 430 for some refrigeration cabinets) or for non-decorative components. A particularly useful ferritic grade is 1.4003/ UNS S41003 (also known by proprietary designations 3CR12 or 5CR12). This grade finds wide usage in wet abrasion resisting applications particularly in coal, sugar and mineral handling, but its low alloy content does not totally prevent corrosion. A very similar alloy is grade 409. This titanium stabilised ferritic grade is widely used in auto exhaust and catalytic converter applications.

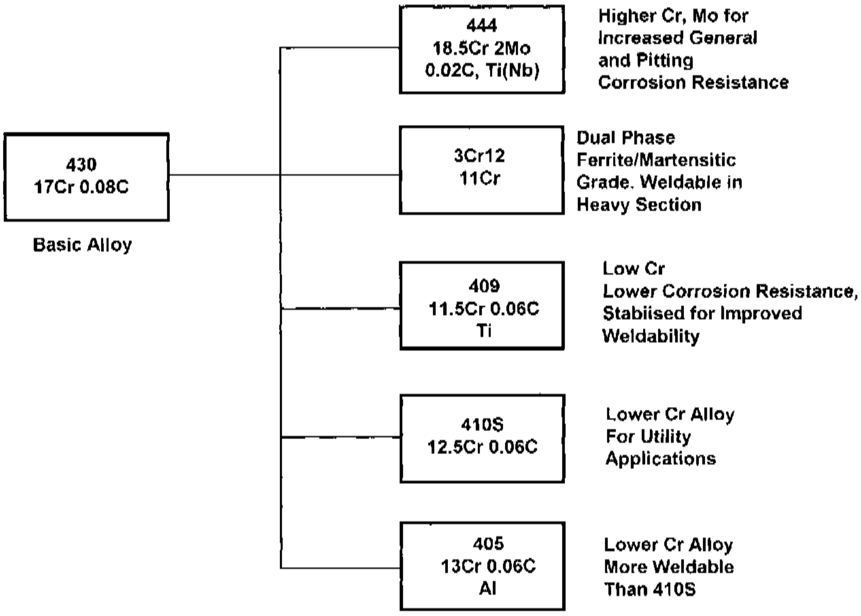


Fig. 2 Ferritic Stainless Grades

3.3 Duplex Austenitic/Ferritic and Super Duplex Stainless Steels

3.3.1 Duplex Austenitic/Ferritic

Duplex stainless steels are alloys of iron with higher chromium and lower nickel than the austenitic alloys. They also have small (0.1 to 0.2%) levels of nitrogen and usually contain molybdenum. These duplex alloys have a two phase microstructure typically with 45 to 65 % ferrite and 55 to 35% austenite. They are magnetic and have weldability similar to austenitic alloys although the heat input must be controlled to preserve the microstructure. They are stronger and more resistant, to stress corrosion cracking and pitting corrosion, than austenitic stainless steels. They have thermal expansion coefficients near that of carbon steels. A disadvantage is their embrittlement after extended periods above 300YC.

3.3.2 Super Duplex Stainless Steels

Super duplex stainless steels are often referred to in the literature as "25% Cr" duplex grades, but are usually defined as those with a Pitting Resistance Equivalent number (PREN) of at least 40, calculated as PREN = %Cr + 3.3x(%Mo + 0.5%W) + 16x%N. The PREN is an index that provides a simple ranking and is applicable to most grades. Tungsten has also been found to have a beneficial effect on PREN and a value of 1.6%W has been used. Both calculations are shown in Table 3. Most manufacturers would guarantee all their product as complying with this definition. The commercially available wrought duplex and super duplex grades at present are shown in Table 3. Note that some of these are much more readily available than others.

More precautions need to be taken in the welding of the super duplex alloys because their high alloy additions hasten the onset of embrittlement at elevated temperatures. Alloy segregation effects are also more common with the super duplex grades.

3.4 Martensitic Stainless Steels

These steels are alloys of iron and chromium, which can be hardened by heat treatment. They are magnetic. Generally speaking, they are difficult to weld, due to their susceptibility to hardening in the weld zone. Pre- and post-heating is required.

They are mainly used in bar form, because of their high mechanical strength, and the difficultly in avoiding

Table 3: Duplex and Super Duplex Stainless Steels (nominal values)

Grade	UNS No	Cr	Ni	Mo	N	Cu	W	PREN	PREW
2304	S32304	23	4	0	0.1	-	-	25	25
2205	S31803	22	5	3	0.15	-	-	34	34
Ferralium 255	S32550	25	5	3	0.2	2	-	38	38
2507	S32750	25	7	4	0.25	-	-	42	42
Zeron 100	S32760	25	7	3.5	0.25	0.7	0.7	41	42
UR52N+	S32520	25	6.5	3.7	0.25	1.6	-	41	41
DP3W	S39274	25	7	2.7	0.27	0.4	2.0	38	42

Table 4: Common Martensitic Stainless Grades and their Applications

Grade No.	UNS. No.	Forms Available	Typical Analysis (%)					Typical Applications
			C	Cr	Ni	Mo	Other	
410	S41000	Bars	0.10	12.5	-	-	-	General purpose grade for use in mildly corrosive environments.
403	S40300	Bars	0.15	13.0	-	-	-	Capable of attaining higher hardness than 410.
416	S41600	Bars	0.10	12.5	-	-	0.20 S	Free machining variation of 410.
420	S42000	Bars	0.25	12.5	-	-	-	General engineering uses, such as pump and valve shafts.
420C	-	Sheet & Coil, Plate & Bars	0.30	12.5	-	-	-	Developed for high hardness after heat treatment. Used for cutting tools, surgical knives, etc.
431	S43100	Bars	0.18	16.0	2.0	-	-	Hardenable steel with corrosion resistance approaching 302. Used for pump shafts etc. Should be double tempered after hardening.
440C	S44004	Bars	1.10	17.0	-	0.40	-	Capable of being hardened to 60 HRC. Highest hardness and abrasion resistance of all the stainless steels. Corrosion resistance similar to 410.

distortion when heat treating light sheet metal components. A family of steels have evolved (Table 4) with varying carbon contents to provide a range of strength and hardness levels, as illustrated in Figure 3

These grades are usually supplied either in the annealed condition or hardened and highly tempered so that subsequent machining can be carried out. As for the other steels the hardness achievable after hardening heat treatment is largely a function of carbon content. Typical applications are pump shafts, thread fasteners and valve spindles. The free machining grades are readily machined but suffer from localised corrosion and exfoliation.

3.5 Precipitation Hardening

Stainless Steels

Precipitation hardening stainless steels are iron, chromium and nickel alloys with other additions, such as copper or aluminium. They are high strength alloys which must be heat treated to give the balance of corrosion resistance and strength. They are classified into three subgroups of martensitic, semi-austenitic and austenitic. The formation of intermetallic phases or precipitates gives their high strength. The martensitic and semi-austenitic grades are readily weldable but the austenitic grade, because of the austenitic weld structure and liquation cracking, requires care for welding. The other grades do not require preheat but will require ageing to provide optimum properties.

The principal advantage of these grades is that they can be purchased in the solution treated condition, in which the steel can be machined. A final relatively low temperature aging treatment then lifts the strength significantly. Because this treatment is low temperature, distortion is minimised so it is possible to readily heat treat long shafts. The most common grade is 17/4 PH (also referred to as UNS S17400 or Grade 630), which finds application in boat shafts, threaded fasteners, pump shafts and valve spindles. Grade 17/7PH (Grade S17700 or 631) is used for manufacturing wire. Typical analyses are given in Table 5.

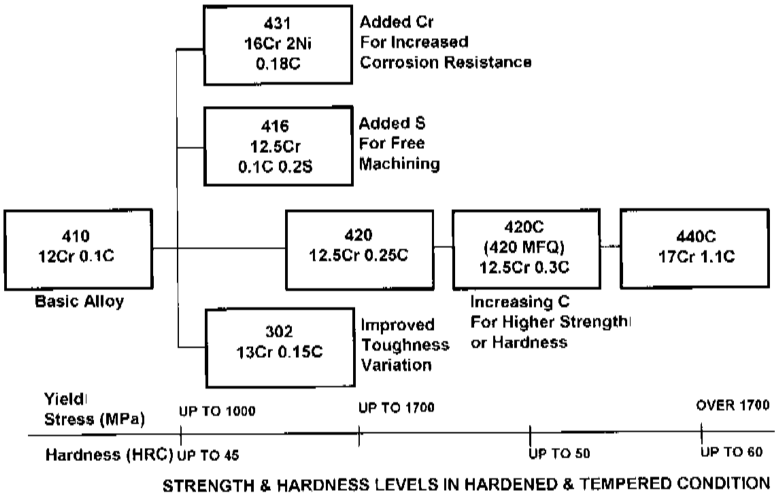


Fig. 3 Martensitic Stainless Grades

Table 5: Typical Compositions of Some Precipitation Hardening Stainless Steels

UNS No	Name	Composition (%)									
		Cr	Ni	C	Mn	Si	Cu	Mo	Ti	Al	Other
S17600	StainlessW	16.75	6.75	0.07	0.50	0.50	-	-	0.80	0.20	-
S174000	17-4PH	15.60	4.25	0.04	0.40	0.50	3.60	-	-	-	Nb+Ta 0.25
S45000	Custom 450 (xM-25)	14.90	6.50	0.03	0.30	0.25	1.50	0.80	-	-	Nb+Ta 0.25
S13800	PH 13-8 Mo(xM-13)	13.0	8.00	0.04	0.05	0.05	-	2.25	-	1.00	0
Semi Austenitic											
S17700	17-7PH	17.00	7.00	0.07	0.70	0.40	-	-	-	1.15	-
S15700	PH 15-7 Mo	15.00	7.00	0.07	0.70	0.40	-	2.25	-	1.15	0
S3500	AM-350	16.50	4.25	0.10	0.75	0.35	-	2.75	-	-	N 0.10
Austenitic											
-	17-10P	17.00	16.50	0.12	0.75	0.50	-	-	-	-	P 0.28
S66286	A286	15.00	25.00	0.06	1.20	0.50	-	1.20	2.00	0.25	V 0.30

TYPES OF CORROSIVE ATTACK

Stainless steels are more resistant to more corrosive agents than any other commonly used metals. They are most satisfactory in oxidising environments. However, since stainless steels rely for their corrosion resistance on the maintenance of a thin, self healing passive oxide film, they are susceptible to various forms of localised attack when the passive film breaks down. The various types of corrosion which can be encountered are listed below. Stress corrosion cracking, crevice corrosion, intergranular corrosion and galvanic corrosion are more likely to be associated with welded structures.

4.1 General or Uniform Corrosion

This type of corrosion results from even dissolution or oxidation of the steel surface. It is usually only encountered with stainless steels in highly corrosive environments, such as strong reducing acids, which may cause the surface to go "active". If stainless steels are used in such environments, then selection will be based on iso-corrosion curves or tabulated data and probably trial exposures. Fig. 4 shows the 0.1 mm/year corrosion rate contours for 304(18-10), 316 (17-12-2.5) and other alloys with higher alloy content. These curves must be used with care as chlorides severely increase corrosion rates while oxidising cations can reduce corrosion rates substantially.

When stainless steels are used in high temperature environments, alloys with higher chromium and/or silicon or aluminium offer more resistance, especially when alloyed with rare earths, e.g. cerium or yttrium. Sulphidation attack also results in general loss although the attack is by finger-like penetrations. High temperature corrosion is discussed in section 7.5.

4.2 Pitting Corrosion

This type of corrosion is more commonly encountered with stainless steel. It can be caused by a number of factors, acting singly, or together. These are:

(i) Exposure to solutions containing halide salts. Pitting may occur depending on the concentration of the salt solution (which can increase with time due to evaporation effects), the temperature of the solution, the velocity of the solution, and the grade of stainless steel. The more highly alloyed grades, particularly the molybdenum bearing grades, are more resistant to pitting corrosion in these environments.

(ii) Surface contamination and deposits. Contamination by iron particles on the surface can lead to "rust" spots and pitting due to the conversion of the iron to

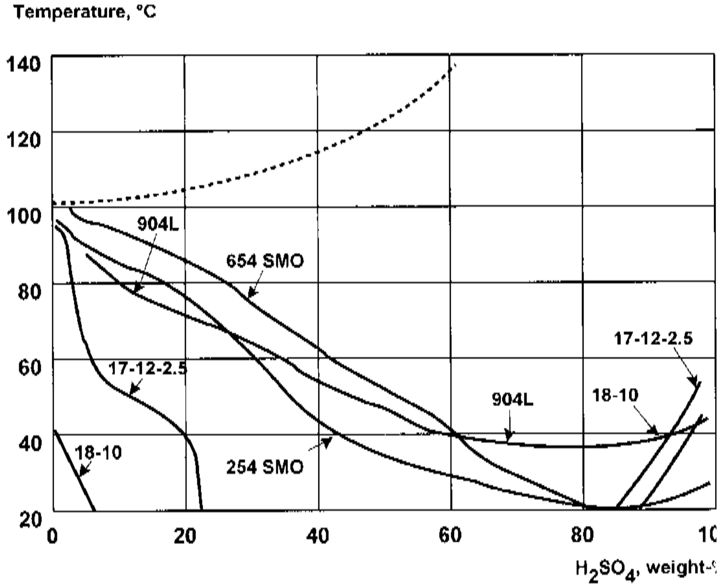


Fig. 4 Isocorrosion Diagram, 0.1 mm/yr, for Austenitic Stainless Steels in Naturally Aerated Sulphuric Acid of Chemical Purity. Broken-line curve represents the boiling point.

ferric chloride, an aggressive corrodant of stainless steel. Care must be taken to remove such contamination (from grinding wheels, for example) by acid cleaning prior to service.

Surface deposits caused by scaling or the growth of bacteria or algae can also promote pitting.

(iii) Inclusions in the steel. In the free machining stainless steels, manganese sulphide inclusions are incorporated in the steel to act as chipbreakers to facilitate machining. These inclusions can act as pit nuclei, so that the free machining stainless steels are generally more susceptible to pitting corrosion than the lower sulphur types, and should be used with care in environments which can promote pitting attack. The titanium or niobium carbides in stabilised austenitic steels can also act as nucleation sites.

(iv) Surface finish. Rough surfaces are more likely to cause localised variations in concentrations of the solution in contact with the surface. If conditions are severe enough to cause pitting on a polished surface, the pits will tend to be fewer, but larger than those encountered on a rougher surface.

The resistance of stainless steels to pitting corrosion increases as the chromium, molybdenum and nitrogen contents are raised, generally as given by the Pitting Resistance Equivalent Number (PREN).

4.3 Crevice Corrosion

This is due to the change of chemical composition of a corrodent within a crevice. It can commonly occur in a poorly designed joint incorporating a tight crevice, or under blankets of chemical deposits or scale on the steel surface. It is the result of the formation of a local concentration cell due either to the deoxygenation of the liquid in the crevice, compared with the liquid outside the crevice, and/or the preferential build up of detrimental ion species, such as chloride ions, within the crevice. The crevice created by oxide produced during welding or cutting is particularly harmful. The metal in a thin layer beneath the oxide is depleted in chromium and hence has less corrosion resistant than the base metal. The galvanic and concentration cells produced can rapidly cause crevice attack which usually leads to pitting.

Design to eliminate the crevice, or select a more crevice corrosion resistant alloy if the crevice cannot be eliminated. Generally speaking, the higher the chromium, molybdenum and nitrogen content of the steel, the better is the crevice corrosion resistance. Steels with high PREN values also have high resistances to crevice corrosion. This can be measured by exposure tests (ASTM G48) or electrochemical measurements.

4.4 Intergranular Corrosion

This form of corrosion occurs when the corrodent preferentially attacks a second phase precipitated in the metal grain boundary, or a zone adjacent to it, which has been depleted in an alloying element necessary for adequate corrosion resistance. This results in sensitisation and 'weld decay' in stainless steels, where chromium depletion occurs near the grain boundaries in the weld zone, due to chromium carbide precipitation at the grain boundaries. It is caused by incorrect heat treatment, or excessive time at sensitising temperature in the weld area. The higher the carbon content of the steel, the more rapid and severe is the sensitisation. An example of this type of failure is shown in Fig. 5.

Fig. 5: Intergranular Corrosion in an Austenitic Stainless Steel

Intergranular corrosion can be overcome by specifying L grades, e.g. C<0.03% for austenitic stainless steels, using very thin sections or low heat input. Material in a solution annealed condition is not susceptible as the grain boundary precipitates have been redissolved. It can also be prevented by the use of stabilised stainless steels e.g. Grades 321 or 347. Duplex austenitic-ferritic alloys are very resistant to sensitisation.

Testing to determine the degree of sensitisation in welded or heat treated stainless steels should be carried out as specified in AS/NZS 2038 and ASTM A262. Tests for intergranular corrosion of ferritic steels are contained in ASTM A763. Further details of this problem and its prevention are given is section 5.4.

4.5 Environmentally Assisted Cracking

This is the premature failure of a metal under the joint action of corrosion and tensile stress as shown in Fig. 6. It includes stress corrosion cracking (SCC), hydrogen embrittlement, sulphide stress cracking and corrosion fatigue.

As a guideline, austenitic stainless steels are prone to stress corrosion cracking in the presence of chloride (or other halide) containing neutral pH aqueous solutions at elevated temperatures, around 60Υ C or above. SCC has been reported at lower temperatures but only with high stresses and very long initiation periods. The problem can be avoided by modifying the environment e.g. lower temperature, solution annealing, use of inhibitors etc. where feasible. If this is not possible, other stainless steels, such as Grade 444, high nickel alloys containing greater than 30% nickel, or duplex austenitic-ferritic alloys may be specified.

Fig. 6: Stress Corrosion Cracking in a Grade 304 Stainless Steel Hot Water Vessel

Sensitised austenitic stainless steels are subject to room temperature polythionic stress cracking and intergranular SCC in high temperature, high purity water containing oxygen. Austenitic stainless steels also suffer caustic embrittlement at temperatures above 100Υ C with caustic concentrations above 25%. A further cracking problem with austenitic grades is liquid metal embrittlement caused by lower melting point metals such as zinc or copper. This may arise if welding galvanised and stainless steel components.

Martensitic and ferritic steels are susceptible to hydrogen embrittlement.

Test procedures for assessing the susceptibility of stainless steels and stainless steel weldments to stress corrosion are covered in ASTM G36 and C692 while NACE TM-0177 gives test procedures for assessing SCC.

4.6 Galvanic Corrosion

This can occur when two different metals in contact are exposed to a conductive solution. The tendency for galvanic corrosion to occur between any pair of metals can be estimated from the electrochemical series; the further apart they are on the series, the more likely corrosion is to occur. When considering stainless steels, the possibility of either active or passive states mean it may dissolve or be protective depending on condition. In the case of a few metals, it is possible to use the series to predict the direction of the galvanic reaction. In general, the series should only be used as a rough guide, as it can be misleading. The degree of corrosion is greatly affected by the relative areas of the two metals, the concentration of the solution, the temperature and the velocity of the solution, to name only a few of the relevant factors.

Galvanic corrosion may occur in a weld if the previously molten zone is electrochemically different from the parent metal. The anodic metal will be dissolved, and the cathodic metal will be unaffected. Ideally, the anodic metal should be the one with the larger area, i.e. the parent metal, and care must be taken with selection of filler metal to ensure that the weld zone is at least as corrosion resistant as the base metal.

4.7 Microbially Influenced Corrosion (MIC)

For decades, MIC has been widely recognised as a factor in corrosion in the oil industry, the pulp and paper industry and sewage systems. In the last 20 years, MIC has been more widely recognised in, for example, water and aqueous waste systems including hydrotest fluids. MIC is generally encouraged by high nutrient levels, near neutral pH, stagnant conditions, warm temperatures and crevices or surface roughness or deposits. Microbial activity may cause slimes or deposits and hence MIC is inherently a promoter of localised corrosion.

Control of MIC requires clean conditions both generally and locally. Biocides can be effective provided they are matched to the infestation. Diagnosis is a specialised process and various test kits are available. Change of materials is often ineffective, ie stainless steels may suffer severe attack (1).

WELDING PROCEDURES TO MINIMISE CORROSION

Any form of unsoundness or variability in stainless steel is a potential source of pitting, crevice, stress, intergranular or galvanic corrosion.

The corrosion resistance of stainless steels can be impaired in the following ways:

(a) Surface preparation contaminating the parent material (e.g. embedment of mild steel or other foreign material);
(b) The weldment having reduced or incompatible corrosion resistance;
(c) The heat affected zone becoming susceptible to corrosion (e.g. intergranular corrosion due to chromium carbide precipitation);
(d) The welding process may result in high stresses in the weld region or distortion of the structure. These stresses are often higher in stainless steels due to their higher coefficient of expansion and lower thermal conductivity compared to mild steel. High stresses can lead to cracking or stress corrosion cracking in service;
(e) Failure to clean and passivate the weld area after completion of welding will lead to reduced corrosion resistance. Welding defects such as lack of fusion, insufficient penetration, hot cracks, porosity and slag inclusions, undercut, slag or spatter may reduce the corrosion resistance. The acceptance of crevices needs careful consideration with regard to the possibility of crevice and pitting corrosion. High temperature (dark) oxide scale residues also result in reduced corrosion resistance.

Details of welding procedures including filler electrodes are given in WTIA Technical Note 16 and AS/NZS 1554 Part 6 "Welding of Stainless Steels". Procedures for cleaning and passivation of stainless steel are given in Section 6 of this Technical Note.

5.1 Selection of Welding Techniques

Since the corrosion resistance of stainless steels is controlled by the chromium content of the steel surface, all fusion welding should be carried out with appropriate shielding to prevent chromium loss by oxidation. Gas tungsten arc welding (GTAW) or gas metal arc welding (GMAW) processes are particularly suitable. For GTAW, argon, helium, or mixtures of the two can be used. Argon-hydrogen mixtures are used to increase welding speed but are only suitable for use with austenitic grades as the hydrogen causes embrittlement of ferritic and martensitic grades. For GMAW, argon-oxygen mixtures or argon containing small quantities of CO_2 can be utilised. Helium or helium-argon mixtures may also be used with additions of oxygen or CO_2. However, to ensure maximum intergranular corrosion resistance in ferritic alloys such as Grade 444, the non CO_2 containing gases only should be used.

Submerged arc welding is an accepted method for the welding of thick stainless steel sections. Resistance spot and seam welding are suitable for thick sheet. Where manual metal arc is used, electrodes must be low in hydrogen to prevent formation of cracks and fissures. Austenitic stainless steels are readily welded by electron beam and laser processes but they may suffer hot cracking at compositions that would be safe if arc welded. This is because of the deep, narrow weld bead and rapid cooling especially in thicker materials. In all shielded welding, imperfections which permit nitrogen access, will reduce the ferrite level and may cause cracking or, in the case of duplex, poor phase balances.

Control of penetration can be assisted by welding into a backing bar or using backing tapes. However extreme care should be exercised in selection of such tapes as some fibreglass tapes can deposit carbon on the back of the weld, leading to sensitisation and weld embrittlement. Generally ceramic block type backing tapes are satisfactory.

5.2 Selection of Welding Consumables

The preferred types of consumables for each of the grades given in Tables 1 to 4 are given in Technical Note 16. Welds in austenitic stainless steels are susceptible to various forms of hot cracking, centre line cracking and micro-fissuring. Fully austenitic welds are the most susceptible, and selecting filler metals to provide welds of composition which solidify as austenitic with the minimum % of the ferrite in the structure (0-10%) will greatly reduce this cracking tendency. A composition diagram introduced by Schaefler and modified by De Long and later by the WRC (Fig. 7), can be used to predict the amount of ferrite obtained with welds of a given dilution, when welding a stainless steel grade to the same grade, another grade, or even to mild steel. The amount of ferrite required to prevent hot cracking is dependant on the level of impurity elements in the steel. The higher are the sulphur, phosphorous, boron and oxygen contents, the more ferrite is required.

It is important that the weld metal should have a higher corrosion resistance than the base metal to ensure against galvanic corrosion of the weld. As the weldment usually constitutes a smaller surface area than the base metal, it must not be anodic. It is possible to use austenitic filler wires with ferritic stress corrosion resistant grades, such as Grade 444, without problem since the weld area is galvanically protected by the base metal, and is therefore not subject to stress corrosion attack.

Duplex austenitic/ferritic weld metal can suffer preferential attack on the ferrite phase in certain environments, particularly strong acids. Hence highly alloyed filler wires may have to be specified to produce single-phase austenitic welds for certain critical applications. It is also common to use super duplex filler wires when welding standard duplex grades (e.g. 2205) destined for highly corrosive environments.

For ferritic and martensitic steels, ferritic filler wires can be used when the weldment is to be subsequently heat treated. When used in the as-welded condition, austenitic wires are preferred to produce duplex weld structures which are ductile and corrosion resistant.

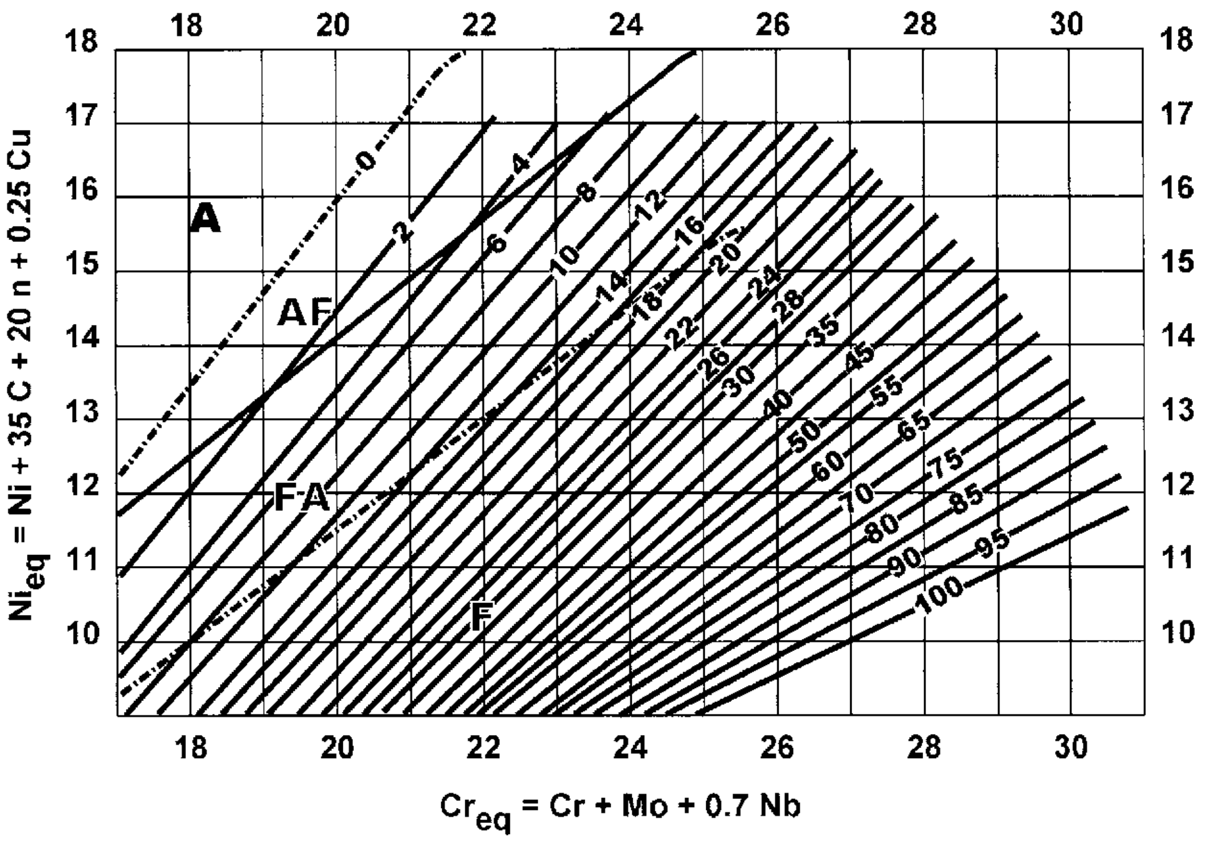

The WRC-1992 Diagram

Fig. 7: Constitution Diagram for Stainless Steel Weld Metal [(4)]

5.3 Weld Stressing and Distortion

Heavy distortion and stressing of a fabrication can lead to cracking and stress corrosion problems.

The ferritic and martensitic stainless steels have coefficients of expansion about 10 per cent less, and thermal conductivity about 50 per cent less, than mild steel, so that their tendency to distort during welding operations is similar to that of mild steel.

Austenitic stainless steels, however, have a coefficient of expansion up to about 50 per cent higher and thermal conductivity about 65-70 per cent lower compared to mild steel; consequently the distortion and stressing aspects are much greater.

The distortion can be controlled with chill plates, usually copper, placed close to the weld zone. These are often further incorporated into jigs and fixtures which give even more control. Controlling distortion by minimising heat inputs and avoiding excessive weld deposits is most efficiently achieved by increasing travel speed. Lower heat input also has beneficial effects on the weld zone microstructure by avoiding or reducing the possibility of carbide precipitation, which can lead to intergranular corrosion.

5.4 Techniques to Reduce Intergranular Corrosion

The stainless steel microstructure becomes susceptible to intergranular corrosion in certain media when the weld or heat-affected-zone (HAZ) remains within a critical temperature range (425°C to 815°C) for sufficient time. Chromium in the grain boundary regions combines with carbon to produce carbide networks, depleting the near-grain-boundary area of chromium. This depleted zone or, in certain media, the carbides themselves, tend to dissolve preferentially giving the phenomenon of weld decay.

The Time-Temperature-Sensitisation relationships for the common Grade 304 austenitic grade, with different carbon contents, are illustrated in Fig. 8. This shows that a steel with 0.058% carbon can be held at 700°C for about 6 minutes without suffering intergranular attack in subsequent corrosion testing. Note that the time at temperature is cumulative, i.e. a weld followed by a weld repair means all the time in the susceptible range must be added together.

Such a typical Grade 304 composition can readily be welded in moderate thicknesses without problem since the heat input would not be high. With heavy plate thicknesses, however, the time in the critical region can be much longer, so that a lower carbon content is required. A Grade

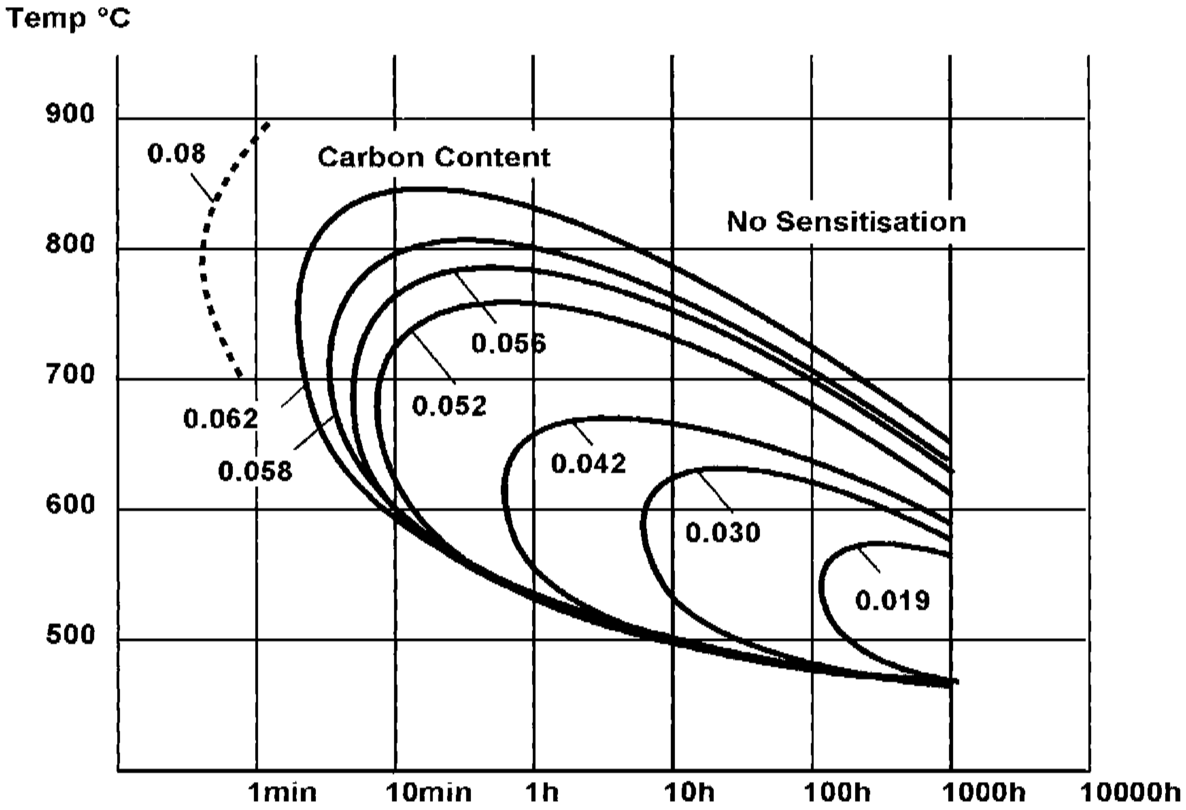


Fig. 8 Time-Temperature-Corrosion Diagram for Grade 304 Steel of Varying Carbon Content

304L steel, containing less than 0.03% carbon, can be seen from Fig. 8 to be capable of being heated for up to 10 hours without suffering sensitisation.

In weldments, sensitisation can occur in the weld or heat-affected-zone (HAZ) where time-temperature relationships for the particular composition and steel type are appropriate. The use of stringer beads and multipass, low heat input procedures (rather than weaving), will reduce the probability of sensitisation.

Intergranular corrosion of welded austenitic steels is dependent on the degree of sensitisation produced in the HAZ and the corrosivity. It is frequently over-emphasised. The degree of sensitisation is dependent on the time spent in the critical temperature range, and hence to a large extent is determined by the thickness of steel to be welded. Experience has shown that austenitic stainless steels with the following maximum carbon levels will not usually be sensitised to a degree which will seriously impair corrosion resistance:

Up to 1 mm	0.10%C	(e.g. 301)
3 mm	0.08%C	
12 mm	0.06%C	(e.g. 304)
19 mm	0.05%C	
25 mm	0.04%C	
>25 mm	0.03%C	(e.g. 304L, 316L)

These are generalisations. Welding of complicated sections, or of heavy sections to light sections, with higher heat inputs would lower these recommended maximum carbon contents, as would the use of higher heat input welding processes, such as submerged arc. With careful selection of welding parameters heavier sections can be handled successfully, however, qualification procedures are advisable.

The second technique for avoiding sensitisation is to use "stabilised" grades of stainless steel. Grade 321 (stabilised with titanium) is available in heavy thickness plate. Because titanium has a higher affinity for carbon than does chromium, exposure to sensitising temperatures does not result in chromium depletion from the near-grain boundary zones. Note that because titanium is not readily transferred through a high temperature arc the filler wire used to weld Grade 321 is 347, stabilised with niobium.

The problem of sensitisation can also be overcome by re-heat treatment. By heating the austenitic steels to between 1000°C - 1100°C, the carbide networks are redissolved and rapid cooling by water quenching or air cooling, depending on size, prevents their re-precipitation. Stress-relief at 900-950°C followed by slow cooling can be particularly harmful. Carbides, nucleated at the high temperatures, grow during cooling and can readily cause the development of an extremely narrow sensitised region - even in low carbon grades. Stress-relief at or above 1000°C followed by slow cooling is less harmful.

Due to scaling, distortion and often the size of the fabrication, heat treatment is not always a practical solution. Selection of a stabilised or extra low carbon (L) grade is often more appropriate.

5.5 Special Precautions

With the stabilised grades there is a form of corrosion, known as "knife-line" corrosion. This occurs only with high concentrations of hot nitric acid. Although somewhat similar to intergranular corrosion, this cannot be overcome by solution heat treatment. The cause of this corrosion is the presence of niobium or titanium-rich eutectic carbides formed from the liquid phase in the weld pool. These carbides are readily attacked by hot concentrated nitric acid. The corrosion is typified by a fine line of attack adjacent to the weld metal.

The use of low carbon "L" grades of stainless steel (less than 0.03% carbon) with which carbide precipitation does not occur within the practical times involved, is the commonly accepted solution to intergranular corrosion and "knife-line" corrosion.

The ferritic and martensitic stainless steels are more susceptible to sensitisation than austenitic steels, and in the sensitised condition are attacked by a wider variety of corrodents. Sensitisation cannot readily be removed by heat treatment, and can only be controlled by use of a stabilised grade. Particular care must be taken to completely shield the molten weld pool from air when welding ferritic grades. These alloys readily absorb nitrogen which can cause sensitisation, even in stabilised grades. The austenitic alloys are tolerant of nitrogen contamination and can readily absorb over 0.1% without nitride precipitation. Nitrogen is , however, a potent austenite stabiliser and cracking problems commonly associated with fully austenitic deposits may arise unexpectedly from this source.

With some of the ferritic grades, martensite formation in the weld area can occur, so that equal care in pre- and post-weld heat treatment is needed. Stabilised grades have their composition balanced so that martensite cannot occur, and special heat treatment is not required. With high heat inputs these latter steels may suffer from severe grain growth in the weld region, leading to some loss in toughness and ductility. Optimum weld properties are produced with these steels if the heat input is controlled to as low a level as possible, consistent with the requirement to ensure full penetration.

The higher alloyed super austenitic and super duplex grades are susceptible to embrittlement due to precipitation of iron-chromium sigma phase especially in the presence of molybdenum or other heavy elements. Sigma phase also reduces the corrosion resistance especially if dispersed along grain boundaries. This phase forms at temperatures between 560 and 980°C with a maximum rate of formation about 825 °C although this depends on the alloy composition. Highly alloyed "super" grades are also subject to embrittlement from other precipitated phases if held at temperatures above 300 °C for extended periods. Fig. 9 illustrates several of the possible phases which can form.

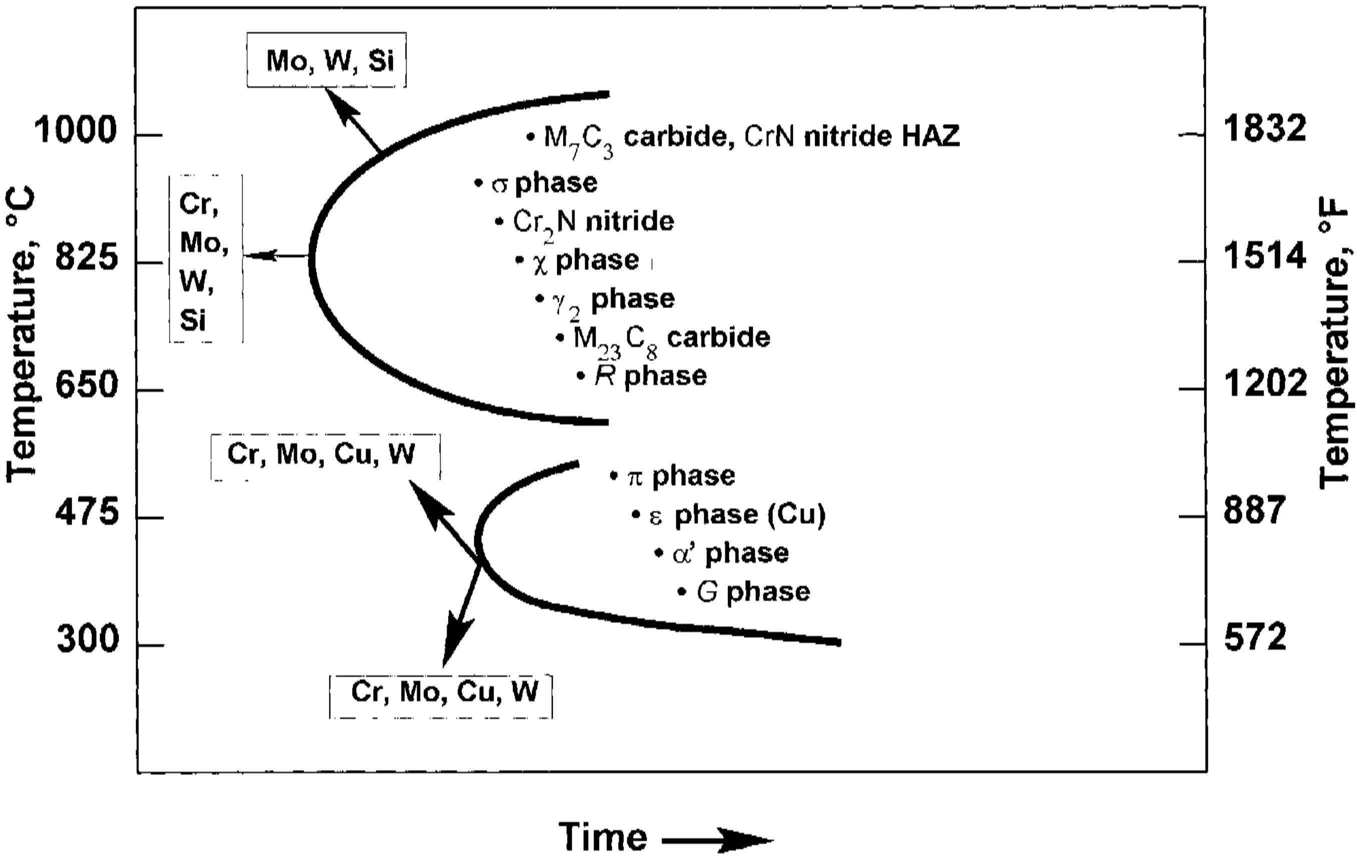


Fig. 9: Time-temperature Transformation Diagram Showing Effect of Alloying Elements on Precipitation Reactions in Duplex Stainless Steels [5]

DESIGN AND FABRICATION FOR MAXIMUM LIFE

Design, material selection, fabrication and cleaning must be considered at the outset when welded stainless steel fabrications are being planned.

Each of these aspects has a critical bearing on the service life of the welded fabrication.

As plant fabricated from stainless steel components ages, owners and operators alike need to be aware of the available options; repair, replace or leave untouched. It may be necessary to carry out a remanent life assessment to determine the best one. However the available life of such plant can be extended by using various methods to get the most life from the plant.

6.1 Design

The design of stainless steel fabrications must take account of those factors which can reduce the life of the structure by localised corrosion. Some of these factors are illustrated in Fig. 10.

Surfaces should always be smooth and streamlined. Obvious problems such as surface defects, inherent or introduced during fabrication, such as slivers, scratches, scoring, foreign metal pick up, weld slag inclusions and porosity can all be initiators for pitting and general types of corrosion. The finish is mostly dictated by end use, however it should always be the best attainable.

Crevice conditions such as in open laps must be avoided, corners should be rounded. Butt joints are preferred to fillet joints as they maintain surface continuity.

In vessels, free drainage should be incorporated to reduce sediment deposition problems and ensure ease of cleaning. Surface to volume ratios should preferably be low, and the vessel either completely filled or adequately vented to prevent condensation, evaporation and concentration effects in the air space, leading to accelerated corrosion. Distribution of mechanical stresses in fabrications used for stress corrosion prone applications can be modified by design. In addition, a stress relieving or annealing treatment can be included. The high thermal expansion coefficient and low thermal conductivity of austenitic stainless steel (in comparison to carbon steel or ferritic stainless steel) may cause expansion or contraction stresses during temperature excursions especially if restraints are poorly designed.

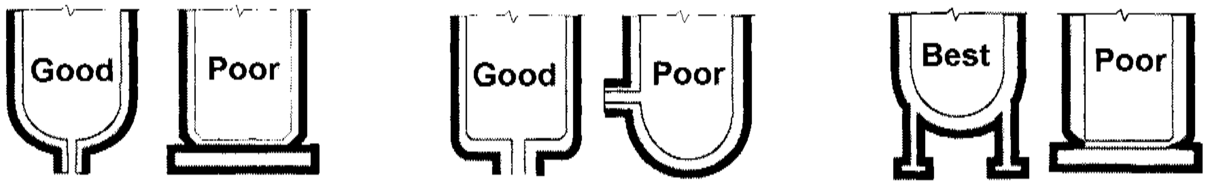
Other components used in conjunction with stainless steel vessels and equipment such as thermostats, pressure and volume gauges, pipes, flanges, gaskets etc. must be of compatible materials on the galvanic series. Crevice conditions and stagnant pocket conditions in the placement and provision for these items must be avoided. Where dissimilar metals must be in contact, the exposed area of the less noble metal should be kept large relative to the more noble. Gasket materials should be non-absorbent, and in particular, be free of asbestos and chlorides. Carbon (graphite) loaded gaskets can cause galvanic corrosion problems for stainless steels.

Lagging materials for thermal insulation of vessels or pipework must be free of chlorides if there is any possibility of these becoming wet - the outside of the vessel may be more corrosive than its contents!

Tight crevice conditions can sometimes be opened to advantage allowing liquid circulation around the component by interspacing with non-metallic, non-absorbing washers or gaskets, as in Fig. 11. These can also provide electrical insulation between dissimilar metals. Fig. 12 shows welding design features intended to avoid crevice formation.

6.2 Fabrication Practices

Stainless steel is a premium material and to obtain optimum corrosion resistance, its fabrication must follow established procedures. This requires training and written



Keep surfaces smooth and streamlined

Ensure free drainage and ease of cleaning

Allow for circulation of air around equipment

Keep surface to volume ratio low

Provide for complete filling of vessels and heat exchangers

Select joining methods carefully

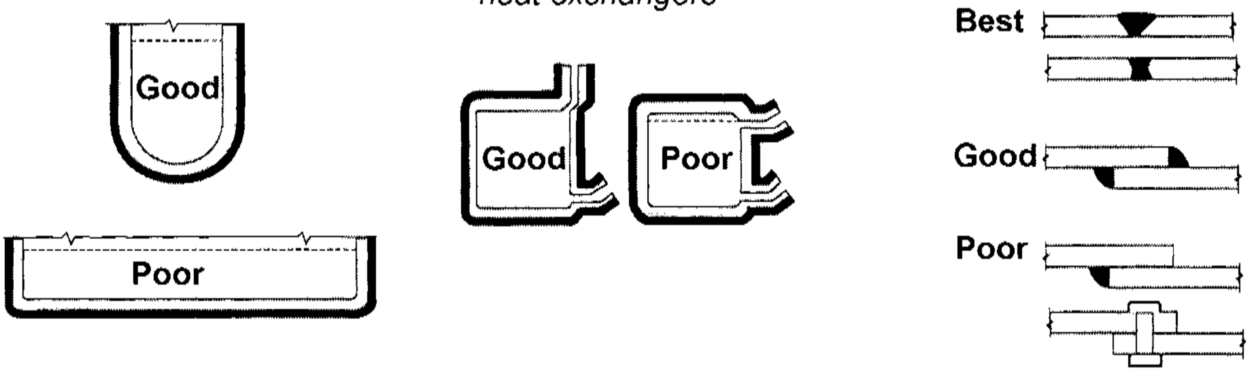


Fig. 10: Design of Stainless Steel Vessels

instructions. Fuller details are provided in AS/NZS 1554.6 and WTIA Technical Note16 but some important features are emphasised below. Particular points to note include:

- Positive identification and control of materials;
- Isolation of stainless steel working areas and tools to prevent iron contamination from mild steel with consequent reduction of corrosion resistance. This includes iron free grinding, blasting and polishing media;
- Avoidance of burrs on edges or scratches on exposed surfaces or notches or undercut at welds as they provide possible crevice corrosion initiation sites;
- Preservation of the passive film on the surface by minimising local heating during cutting or grinding of the low thermal conductivity material;
- Avoidance of low melting point metal contamination (eg, lead, zinc or copper) as it may result in cracking during heating;
- Matching surface polishing to the as-supplied finish to reduce the tendency for preferential local attack;
- Tack welding with the same consumables as the final weld;
- Use of PVA tape rather than PVC and use of chloride free marker pens;
- Carbon contamination can occur by using marker pens or greasy handling equipment or walking on sheets of stainless steel. If the contaminated area is welded, then carbon pickup can give sensitisation and consequent corrosion problems.

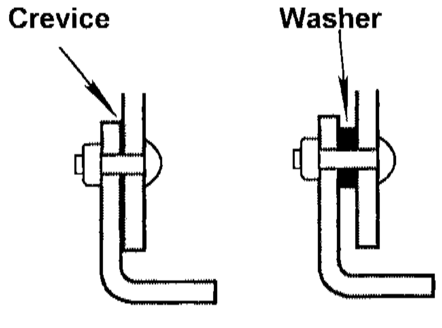


Fig. 11: Elimination of a Tight Crevice

6.3 Cleaning and Passivation

The cleaning of weld joint areas before and after welding is most important to ensure maximum corrosion resistance of any fabrication. The area must be free of oil, grease and other contaminants which could otherwise affect the weld composition. The area on both sides of the weld should be cleaned before welding by brushing with a clean stainless steel brush and wiping with a solvent moistened cloth.

After welding, weld spatter, flux, scale, arc strikes and the overall heat discolouration should be removed. Cleaning of fabricated stainless steel and passivation is a two stage process comprising removal of soil by solvents or alkaline detergents followed by either grinding and polishing, brushing with a stainless steel wire brush, or use of a descaling or pickling solution or paste. The preferred procedure is usually dictated by end use. An adherent oxide layer will then form (the passive film) in air but if there are aggressive chemicals present, the film may be defective. For this reason, a passivation process is recommended for welded and worked areas as it provides a thicker and more stable passive layer with greater corrosion resistance than an air formed film.

Even in benign environments, for optimum corrosion resistance, cleaning of welded areas should always be followed by a "passivation treatment". The exception is welds cleaned by pickling agents which contain nitric acid. These function as both descaling (or pickling) and passivating agents. Fig. 13 illustrates the effect of welding on the protective chromium oxide layer. If the only process is removal of the welding tint or scale, then the exposed surface has a depleted chromium content and is more susceptible to corrosion.

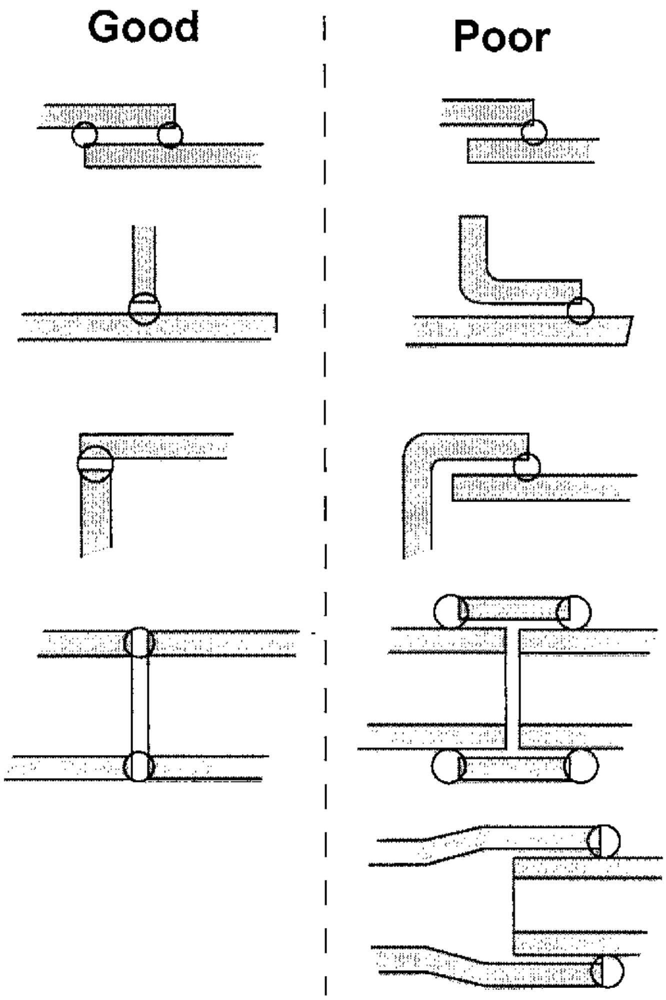


Fig. 12 Design Features where Crevices are Created (from Miller & Boulton, Guide to Stainless Steel Fabrication Design ...)

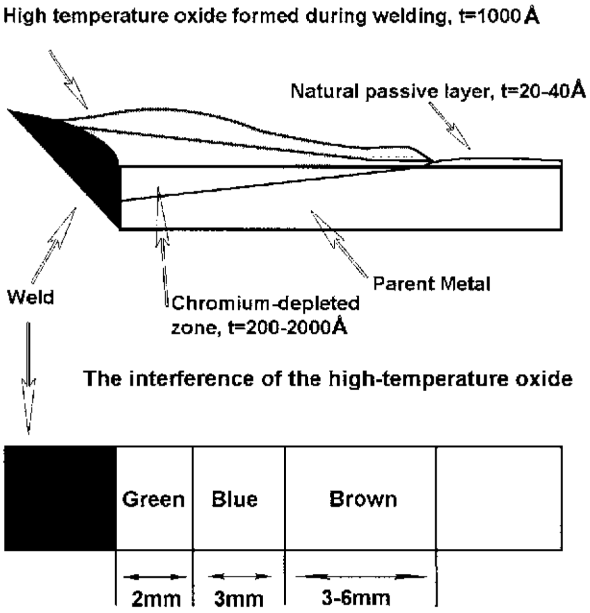


Fig. 13 Oxides Formed on the Root Side During Welding of Stainless Steels - A General Characterisation.

The importance of the pickling and passivation of stainless steel fabricated structures cannot be overemphasised. Its beneficial effects are threefold, namely:

a) Pickling removes the weld scale and discolouration. In aggressive media, the lower surface chromium content under the discolouration, and the masking effect on the surface, can lead to a form of crevice corrosion in the weld or HAZ. Crevice attack frequently initiates severe pitting attack if chlorides are present;

b) Removal of iron contamination which can be picked up during fabrication and which can lead to the formation of "rust" spots and pitting attack; and

Table 6: Acid Descaling and Cleaning Techniques for Stainless Steel [(6)]

Alloy	Condition	Solution (vol %)	Temperature (°C)	Time (min)
Acid Descaling (Pickling) Solutions				
200, 300 and 400 series; Precipitation hardening, and maraging, except free machining	Fully annealed	H_2SO_4, 8 to 11%	65	5 to 45
200 and 300 series; 400 series (>16% Cr), precipitation hardening except free machining	Fully annealed	HNO_3, 15 to 25% and HF, 1 to 4%	20 to 60	5 to 30
Free machining and 400 series (<16% Cr)	Fully annealed	HNO_3, 10 to 15%, and HF, ½ to 1½ %	20 (up to 60 with caution)	5 to 30
Nitric-Hydrofluoric Acid Cleaning Solutions Removes residual scale particles and smut; produces a uniform white pickled finish.				
200 and 300 series, 400 series (>1 6% Cr), and precipitation hardening	Fully annealed	HNO_3, 6 to 15%, and HF ½ to 1½%	20 to 60	10
Free machining, maraging, and 400 series, (<1 6% Cr)	Fully annealed	HNO_3, 10%, and HF ½ to 1½%	20 (up to 60 with caution)	1 to 2
Nitric Acid Cleaning Solutions Removes soluble salts, corrosion products, free iron, and other metallic contaminants.				
200, 300 and 400 series, precipitation hardening, and maraging (>16% Cr) except free machining	Annealed, cold rolled, or work hardened (dull finish)	HNO_3, 20 to 40%	50 to 70 20 to 40	20 to 30 60
200, 300 and 400 series, precipitation hardening, and maraging (>16% Cr) except free machining	Annealed, cold rolled, or work hardened (bright finish)	HNO_3, 20 to 40%, and $Na_2Cr_2O_7.2H_2O$, 2 to 6 %mass	45 to 55 20 to 40	20 to 30 60
400 series, maraging, precipitation hardening (>16% Cr) and high carbon, straight chromium, except free machining	Annealed or hardened (dull finish)	HNO_3, 20 to 50%	45 to 55 20 to 40	20 to 30 60
400 series, maraging, precipitation hardening (>16% Cr) and high carbon, straight chromium, except free machining	Annealed or hardened (bright finish)	HNO_3, 20 to 40%, and $Na_2Cr_2O_7.2H_2O$, 2 to 6 %mass	45 to 55 20 to 40	20 to 30 60
200, 300 and 400 series, free machining alloys	Annealed or hardened (bright finish)	HNO_3, 20 to 50%, and $Na_2Cr_2O_7.2H_2O$, 2 to 6 %mass	45 to 55 20 to 40	20 to 30 60
200, 300 and 400 series, free machining alloys	Annealed or hardened (bright finish)	HNO_3, 20 to 50%, and $Na_2Cr_2O_7.2H_2O$, 1 to 5% mass	50 to 60	10
200, 300 and 400 series, free machining alloys	Annealed or hardened (bright finish)	HNO_3, 12%, and $CuSO_4.5H_2O$ 4 % mass	50 to 60	10
Special free machining 400 grades (>1.25% Mn or >0.40%S)		HNO_3, 40 to 60%, and $Na_2Cr_2O_7.2H_2O$, 2 to 4% mass	50 to 70	20 to 30
Other Acid Cleaning Solutions Used for general applications				
200, 300 and 400 series, (except free machining), precipitation hardening, and maraging	Fully annealed	Citric acid, 1% mass and $NaNO_3$, 1% mass	20	60
200, 300 and 400 series, (except free machining), precipitation hardening and maraging	Fully annealed	Ammonium citrate 5 to 10 %mass	50 to 70	10 to 60
Assemblies of stainless and carbon steel	Sensitised	Inhibited solution hydroxyacetic acid, 2% mass, and formic acid, 1% mass	95	6 Hr
Assemblies of stainless and carbon steel	Sensitised	Inhibited ammonia neutralised solution EDTA. Hot water rinse. Dip in solution of 10 ppm NH_4OH and 100 ppm hydrazine	Up to 120	6 Hr

c) Passivation assists the establishment of an adherent oxide film on the stainless steel surface which provides maximum corrosion protection or passivity.

Descaling and passivation solutions and their application are shown in Table 6. Some appropriate solutions can be mixed with constituents such as barium sulphate or diatomaceous "Fullers earth" to form a paste which can be applied to weld discolouration and scale areas in vertical or difficult positions where the solution could not be contained. "Pickling paste" is particularly effective for descaling, cleaning and passivating narrow weld runs. Some physical abrasion may be required with pastes in the field as the temperatures may not be sufficient for rapid reaction. The acids are very corrosive and adequate protective measures must be taken especially with hydrofluoric acid containing mixtures. Following use, neutralisation is also required before disposal.

Proprietary solutions and pastes are also available. More detailed advice is available from the NiDI handbook No. 9001 "Cleaning and Descaling of Stainless Steels"[56]. It is important that strongly acid pickling and cleaning solutions and pastes are completely removed by washing prior to service. Final cleaning may be minimal if proper care has been exercised through the preceding fabrication and cleaning stages. This may be a hot water detergent wash followed by thorough rinsing.

With fabrications which cannot readily be cleaned after welding, such as pipelines, it is necessary to arrange an adequate internal purge with an inert gas to minimise discolouration (oxidation) during welding. This will be particularly required if the material carried by the pipe is very corrosive, e.g. hot high chloride waters.

6.4 Maintenance

A major attribute of stainless steels is their low maintenance requirement. There are however situations where continual maintenance checks are critical.

It is important with many fabrications, especially vessels, that at some short time interval after commissioning they are inspected for corrosion leaks and other possible problems. The most common problems are associated with iron contamination, porosity or minor cracks in weld areas, which quickly show corrosion discolouration products around the active site.

Rectification may consist of no more than polishing to below the pit depth and then passivating the affected area. In more serious cases where the extent of damage is more severe a weld repair patch or cover can be welded over the damaged region preferably using a documented weld repair procedure. Grinding out a pit followed by a spot weld repair is not recommended as the added heat input from the weld repair may cause a deleterious microstructure to form which can be prone to further corrosion.

At the same time sedimentary deposits and foreign matter should be removed and the unit maintained clean.

If there are no indications of any corrosion the interval between further inspections can be appropriately extended. In practice it has been found that some catastrophic vessel failures could have been prevented by relatively little maintenance.

6.5 Hydrotesting

Once fabricated, many vessels constructed from stainless steel are required to undergo pressure testing using a high pressure water supply in order to check the vessel's performance. Often this hydrotesting procedure occurs prior to commissioning of plant, although regulations may enforce more inspections at later stages of a vessel's service life. The use of water contaminated with high levels of chloride or other corrodents in this procedure can however lead to corrosion problems often relatively soon after testing. It is thus strongly recommended where possible that brackish water, river water and similar waters be avoided when this type of testing is conducted. Good quality chloride free potable water is most suited.

In addition, such tests should only be carried out on clean vessels. Residues from the fabrication process such as surface iron contamination, welding slag and heat tints must be removed before hydrotesting commences. It is also extremely important once testing has been completed to dry the vessel. Again, cleanliness is essential, dirty rags and heavy, contaminated footwear should not be used.

6.6 Safety

Safety in welding is covered in detail in WTIA Technical Note 7 (64). This section considers particular issues that arise for stainless steels, i.e. fume and the use plus disposal of cleaning and passivation chemicals. It is intended to alert users to particular hazards and is not a substitute for study and planning before working with potentially hazardous processes.

6.6.1 Fume and heat

Stainless steels contain chromium and there is a particular concern about the health risks associated with heavy metal fume. Ventilation and suitable extraction systems may be required to avoid exposure to dangerous concentrations of heavy metal, ozone or other fume depending on the location and type of weld procedure. Regulations controlling operator exposure to welding fume must be understood and followed. In addition, the low thermal conductivity of austenitic stainless steels means that heat may dissipate more slowly than in carbon steels with the possibility of contact with hot items for a longer period.

6.6.2 Cleaning and Passivation Chemicals

Stainless steel weldments are pickled and passivated using combinations of strong acids including oxidising nitric acid and extremely corrosive hydrofluoric acid. Contact with either should be avoided by use of protective clothing including safety glasses and gloves and work must be planned so that handling and the potential for accidents is minimised. There is some evidence that long term exposure to low levels of fume can cause problems, and hence work should be planned to avoid breathing even low levels of acid fumes. If pickling pastes are used, then during the pickling period, casual contact with the coated item should be prevented and suitable warning signs erected. After use, the acid wastes must be rinsed from the treated item and the acid waste neutralised before disposal. Apart from the damage to waste disposal lines, failure to neutralise wastes prior to disposal will attract heavy penalties from waste disposal authorities.

If acids are spilled onto personnel, then immediate flushing with copious quantities of water is essential. This is particularly important with hydrofluoric acid as the acid is readily absorbed through the skin and can cause long term lesions and bone damage. Specific safety instructions for proprietary chemicals such as pickling paste are given on their containers and on material safety data sheets (MSDS). Users should be familiar with these.

STAINLESS STEEL SELECTION FOR SPECIFIC ENVIRONMENTS

The corrosion resistance of stainless steels in a wide variety of corrosive environments has been reviewed and compiled in a number of publications (5, 7, 8, 9, 10, 26) including trade literature of stainless steel manufacturers. Selection of stainless steel grades for specific chemical environments is not considered in detail here. Where such information is required it can be obtained from section 8, from the references listed in the bibliography, or by referral to the appropriate supplier. It is the purpose of this section to consider the performance of stainless steels only in environments of interest to the general fabricator or design engineer.

7.1 Atmospheric Corrosion

Stainless steels have exhibited excellent functional and aesthetic performance in out-door atmospheres for many years.

The resistance of stainless steels to atmospheric corrosion is dependent on the steel characteristics and the nature of the atmosphere. Composition, surface finish, degree of cold working, heat treatment, welding and interaction with other materials may all affect performance, while the corrosion by the atmosphere is markedly affected by temperature, moisture content, the presence of pollutants and salt spray.

In addition, regular washing of accumulated dirt from the surface will reduce corrosion and discolouration. Hence the angle of exposure and access to rain and wind of a stainless surface will affect performance. Stainless steels generally resist atmospheric corrosion better if fully exposed to the weather that if under a sheltering canopy.

The 300 series of austenitic steels are generally most resistant to atmospheric corrosion, and are commonly used in architectural applications. The 200 series steels are also very resistant although very rarely used. The use of straight chromium, 400 series steels is limited to less aggressive atmospheres. The ferritic-martensitic alloys (e.g. 3CR12/5CR12) offer good functional resistance to mild atmospheric corrosion, although they are generally not acceptable for decorative or aesthetic applications. For simplicity, conditions may be classified into 5 groups; Interior, Rural (very light pollution), Urban (light pollution, relatively dry), Industrial (heavy pollution) and Marine (moist, high salt contents, coastal regions).

7.1.1 Indoor Atmospheres

Internal atmospheres are generally dry and hence non-corrosive. Both 400 and 300 series stainless steels are used successfully with both smooth and brushed finishes. Problems can arise in condensing environments such as laundries and swimming pools. In the latter case the combination of chlorine and condensates means that the molybdenum containing grades are required for adequate corrosion resistance although even these may not have adequate corrosion resistance in very severe swimming pool environments.

7.1.2 Rural Atmospheres

In clean rural air, moisture condensing on the stainless steel surface is relatively pure and non-corrosive. Under these conditions, the 17% Cr steel, Grade 430, has proved to be completely satisfactory, regardless of surface finish. Even a ferritic stainless steel with a chromium content as low as 13% suffered only light surface discolouration after 19 years exposure.

7.1.3 Urban Atmospheres

In lightly polluted city areas, all of the 300 series steel are immune from corrosive attack and maintain a bright original finish for many years. Little difference has been observed between Grade 304 and the molybdenum-bearing Grade 316 because of the low levels of chloride.

The molybdenum-free ferritic 400 series steels are not generally considered satisfactory in building applications, being subject to pitting corrosion and discolouration. However, Grade 430 with bright annealed finish is used for automotive trim, and maintains its lustre for many years. Provided therefore, that the surface can be regularly cleaned, Grade 430 material can be and is used for special architectural applications. The higher alloyed ferritics, such as Grade 444, offer superior performance to 430 and 304.

7.1.4 Industrial Atmospheres

The corrosivity of industrial atmospheres is associated mainly with the presence of sulphur compounds, particularly SO_2 and SO_3, which combine with moisture to form sulphurous and sulphuric acid. In addition, carbonaceous particulate matter from the burning of fuels acts as nuclei for corrosion cells, leading to pitting attack.

Exposure tests in industrial atmospheres have shown performance to be dependent primarily on composition, and relatively independent of surface preparation (11).

7.1.5 Marine Atmospheres

Because stainless steel structures close to the sea can be subject to deposition of chlorides from salt spray, molybdenum containing grades (usually 316) are normally specified although even these require periodic cleaning. It should be noted that pitting and crevice corrosion are heavily dependant upon temperature - "marine" in Cairns is more severe than "marine" in Hobart. A marine environment includes structures on the water, such as yachts and piers, but also extends inland from the shore. The distance from the shore which is subject to high corrosion rates may be only one or two hundred metres, or up to ten or twenty kilometres, depending on wind direction and strength and severity of wave action and other factors.

7.2 Corrosion When Buried

Stainless steels are frequently used in vessels or pipelines which are buried in the ground, with or without some form of surface protection. As with other metals, resistance to soil attack is dependent on such soil variables as pH, resistivity, total acidity, moisture content, air pore space, volume shrinkage and chloride content, and to other variables such as ground water table level, bacterial activity, stray currents, temperature, etc.

Because of their tendency towards crevice corrosion in the absence of oxygen, stainless steels exhibit susceptibility to corrosion in clay soils with poor drainage. Tapes and adhesive labels should not be used as they have frequently caused crevice attack. Wherever possible stainless steel structures should be laid in a sand bed to allow free access of air to maintain aerobic conditions.

The lower corrosion resistant grades such as the martensitic, ferritic and ferritic-martensitic grades should not be used in underground situations unless the soil conditions are very favourable i.e. low conductivity well aerated open soils containing low chloride levels. In a comprehensive underground testing program in the USA (12) in which a range of stainless steels were exposed to 15 different types of soils the ferritic and martensitic grades corroded and pitted badly at most locations. A similar test program carried out in Japan (13) showed that ferritic steels with more than 16% Cr and 1% Mo performed much better than the 11-12% Cr grades although both suffered some corrosion.

Austenitic and the austenitic-ferritic duplex grades of stainless steel perform much better in underground situations. In the USA testing program mentioned above Grade 302 and 304 grades suffered some corrosion after 14 years at half the sites whereas Grade 316 was unattacked. In the Japanese test program Grade 304 and 316 had not suffered any corrosion after five years.

In very aggressive soil conditions such as encountered in tidal zones where anaerobic high chloride water logged soils exist even Grade 316 can suffer pitting and crevice corrosion. For such conditions the higher alloyed austenitic grades ie 904L or Alloy 28 (14) and the more corrosion resistant duplex grades such as 2205 should be used. Even these alloys might be attacked if the temperature rises above ambient.

Stress corrosion cracking can be a problem with the austenitic grades of stainless steels if chlorides are present and temperature rises above 60°C. Stresses required to produce cracking should be assumed always to be present (15). Residual stresses from forming, bending, or joining operations are sufficient for cracks to form. The duplex grades of stainless steel are more resistant than the austenitic grades as far as SCC is concerned.

Hydrogen stress cracking can be caused by cathodic protection of buried martensitic or cold worked austenitic stainless steels. Even direct contact between these types of stainless steel and galvanised steel (16) results in a galvanic cell which can generate hydrogen at the stainless steel surface particularly in acidic soils. The use of cathodic protection to allow the less corrosion resistant martensitic grades of stainless steel may be used underground but care must be taken to avoid over-protection which could cause hydrogen embrittlement (26).

7.3 Corrosion in Water

While stainless steels generally have a high resistance to corrosion in waters they are susceptible to certain types of localised corrosion in aggressive waters, particularly those with a high chloride ion content. Grades commonly used for water containment are 304, 304L, 321, 316, 316L.

7.3.1 Domestic Water

Most stainless steels exhibit a high resistance to general corrosion in ambient domestic water, with the oxygen content of the water maintaining a protective passive film on the steel surface. Very low oxygen contents (few ppb oxygen) are usually sufficient to retain passivity in the absence of film damaging impurities like chlorides.

The tendency for localised pitting attack, however, increases with increasing water temperature and chloride content, and lower pH. Resistance to pitting increases with the stainless steel's chromium, nitrogen and molybdenum content. Grades 304, 304L and 321 grades have adequate pitting resistance when fully immersed in ambient domestic water or in up to 95°C water containing < 200 ppm Cl^- . From 200 to 1000 ppm Cl- their performance is marginal, depending on water temperature and the level of other anions (OH^-, NO_3^-, SO_3^{2-}) which can normally act as inhibitors (17). In the absence of crevices and deposits, molybdenum bearing austenitic stainless steels are resistant to ambient brackish water and sea water and alkaline, neutral or moderately acidic hot waters containing up to 500 ppm chloride. Stainless steels in order of increasing pitting resistance include, for example, Grades 304, 316 and 2304, 904L and 2205, super austenitic and super duplex grades.

The precipitation of sludge or scale from stagnant waters can produce conditions for crevice corrosion under an adherent sludge layer. This is only a problem in relatively hard waters (>100 ppm total hardness) with a fairly high chloride content (> 1000 ppm chloride).

Intergranular corrosion of austenitic stainless steels is rarely a problem in neutral or alkaline water that does not exceed ambient temperature. With single pass welding of relatively thin steel (up to 3.0 mm) 304 is satisfactory. When steel of greater thickness, requiring multipass welding, is used, or when aggressive waters are involved, a low carbon or stabilised grade is preferred. Grades 316 and 904L have a similar resistance to intergranular corrosion, and 2307 and 2205 have better resistance. Alloy 28 and super duplex grades have an even greater resistance to intergranular corrosion.

Sensitisation of ferritic stainless steels can occur over a wider range of welding conditions than for the austenitic steels, and sensitised ferritic steels are more susceptible to corrosive attack in water than sensitised austenitic steels. Therefore, if welding of ferritic steels is carried out, only stabilised grades should be considered in water environments.

After welding all welds should be passivated and decaled before being put into use. All pipes, particularly small bore pipes, should be purged with inert gas during welding and no grinding is allowed on any surface exposed to the corrosive environment (see section 6 and WTIA Technical Note 16 for more details).

Stress corrosion cracking of austenitic stainless steels can occur rapidly when the water temperature is above 60°C. This cracking generally only occurs with high chloride waters, or where the conditions of service are such to allow concentration of Cl- to high levels. It is particularly a problem in heat exchangers where the steel surface temperature may be high enough to permit incipient boiling.

Stress corrosion cracking (see Section 4.5 in Types of Corrosive Attack) can usually be eliminated by proper design, by solution annealing the structure to lower residual tensile stresses (although thermal expansion stresses may still cause the problem), or by treating the water with inhibitors, such as nitrates or acetates. It should be noted, however, that solution annealing is not always a practical treatment, particularly for large objects and other methods must be used.

Alternatively, a more stress corrosion-resistant grade should be employed. The duplex alloys and the higher nickel austenitic grades are essentially immune to SCC in domestic waters; the molybdenum-bearing grades performing particularly well. Ferritic stainless steels and nickel based alloys are generally immune to stress corrosion cracking. In waters at high temperatures and high chloride contents, high alloy special grade stainless steels should be used. Duplex alloy 2304 is not suitable in oxygen bearing chloride solutions above 150°C, 904L has slightly better resistance, followed by 2205, Alloy 28 and the super duplex grades.

Accelerated corrosion due to dissimilar metal contact is an infrequent problem with stainless steel in domestic water. When it occurs, it usually involves corrosion of the coupled metal, since passive stainless steel is highly cathodic to most other metals. While copper and copper alloys are anodic to passive stainless steel, the voltage difference is not large and the relative areas of copper fittings in a stainless steel tank are such that little corrosion is encountered in practice.

Coupling with mild steel usually leads to rapid dissolution of the mild steel, particularly where the exposed area of mild steel is small, thus mild steel may be used for sacrificial protection. Mild steel bolts in contact with stainless steel disappear very quickly. The resultant corrosion products may, however, initiate pitting or crevice attack in the stainless steel.

Martensitic stainless steels are not normally recommended for use in domestic water above ambient temperature unless kept clean and free from deposits, nor are unstabilised ferritic steels. Among the austenitic grades, Grade 304 has given excellent service in several countries for domestic water reticulation, hot and cold. With correct attention to design and passivation, Grade 316 has performed well in domestic hot water tanks, even in waters of quite poor quality (>200 ppm Cl^-, >350 ppm total hardness).

The free machining grades 303 and 416 are not recommended for any application involving water, of any quality or temperature.

7.3.2 Salt Water

Stainless steel in marine environments has been the subject of several excellent reviews (18 19 20). In stagnant sea water, crevice corrosion can be a major problem, particularly when biofouling occurs. Stainless steel is not, therefore, a suitable material for boat hulls, except for work boats which are continually on the move, or for small craft which can be cleaned regularly. For boat decks and fittings on the other hand, Grade 316, the pitting resistant grade, has become a very popular material.

In quiescent, ambient temperature sea water (flowing at < 0.6 m/sec), Grade 316 will fail by crevice corrosion unless regularly cleaned, or cathodically protected. Protection from adjacent steel structures may be sufficient, but Grade 304 requires higher degrees of protection The higher strength martensitic, duplex or precipitation hardening grades, which are not recommended for cathodic protection due to the danger of hydrogen cracking, are unsuitable for quiescent sea water. These may be used for pump shafts etc. and will require a coating system or other protection. Alternatively, super duplex stainless steels may be used and combine high strength with excellent corrosion resistance so that an extra coating system will not be required.

In ambient temperature sea water which is flowing at a high velocity (> 1.0 m/sec), biofouling does not occur and Grade 316 can give long life. In fact the resistance of stainless steel to erosion-corrosion and cavitation damage at high water velocities is a positive advantage. However, any design crevices such as flanges will cause corrosion failure.

As water rises to temperatures above 24°C the pitting corrosion rate of Grade 316 can become significant and the use of more highly alloyed stainless steels containing copper and higher molybdenum concentrations, or cathodic protection, may be justified.

The life of Grade 316 when used in tidal areas, where it is alternately immersed in salt water and exposed to the air, is substantially greater than when continually immersed. The rate of pitting attack for example, is an order of magnitude slower. Grade 316 is therefore an appropriate material for cladding steel structures provided that deposits do not cause severe crevices.

Resistance to localised corrosion in sea water above ambient temperatures is a requirement for materials used in a variety of marine heat exchanger applications such as sea water cooled ships engines and exhaust systems, feedwater heater and condenser tubing in seaboard power stations, and salt water cooling for chemical plant. Since tubing used in these applications is thin walled, pitting and crevice corrosion cannot be tolerated. Cooling water systems also include pipes, valves, screens and pumps. The corrosion rate of Grade 316/316L at higher temperatures increases considerably, therefore 316/316L is unsuitable for use in the above applications.

Grade 316/316L tubing has given variable performance depending on the regularity with which it has been cleaned. The increased use of continuous cleaning systems has improved performance of Grade 316, although deposit build-up on surfaces during stagnant shut-down situations must be avoided.

Superior pitting resistance alloys are required for corrosion free performance in hot sea water. Such alloys include 904L, 2205 and the super austenitic and super duplex grades. The high inclusion content of the sulphur bearing free machining grades 303 and 416 means they have poor resistance to pitting attack and are not recommended for marine exposure at any temperature.

7.4 Corrosion in Aggressive Chloride Environments

The alloys referred to in this section are shown in Table 7.

7.4.1 Pitting Corrosion

The resistance of a stainless steel to pitting depends primarily on its contents of chromium and molybdenum, but is also affected by its nitrogen content, the chemical composition and shape of its slag inclusions and the presence of segregation and intermetallic phases, if any. As explained in Section 3.3 the Pitting Resistance Equivalent Number (PREN) has been found to give a good indication of the relative pitting resistance of various grades of stainless steels. The PREN values of a number of stainless steels for chloride environments are given in Table 7; Grade 304 is included for comparison.

A calculation based on the sum of the percentage by weight of chromium and three times the percentage by weight of molybdenum and 16 times the percentage weight of nitrogen will thus make it possible to rank stainless steels by their resistance to pitting (See Table 7).

Results obtained in potentiodynamic measurements in 3% NaCl at various temperatures confirm this ranking. (See Fig. 14). Similar techniques confirm this ranking for both austenitic and ferritic steels.

*Table 7: Alloy Designation, Typical Main Element Composition and Actuals with Pitting Resistance Equivalent Numbers (PREN) PREN = % Cr + 3.3 * % Mo +(16) *%N*

UNS No	Grade	Typical Main Elements (%)					PREN
		Cr	Ni	Mo	Cu	Other	
S30400	304	18.5	9.0				18
S31600	316	17.0	12.5	2.5			25
S31703	317L	18.5	14.5	3.2			29
S31803	2205	22.0	5.5	3.0		0.14N	34
S31500	-	18.5	4.7	2.75		0.075N	29
N08825	825	21.5	42.0	3.0	1.8	0.7 Ti	31
N08020	20	20.0	34.0	2.2	3.3	0.4 Nb	27
N08028	28	27.0	31.0	3.5	1.0		39
N08904	904L	20.0	25.0	4.5	1.5		35

When choosing material for a chloride-containing environment, the pitting resistance of the steel can be measured electrochemically and is expressed in terms of the critical pitting temperature (CPT), the temperature above which pitting will occur in a given chloride solution. The potential is kept constant and the temperature is raised gradually until pitting attacks occur. This is indicated by a sudden increase of the polarisation current (22). Results from such measurements are shown in Fig. 14.

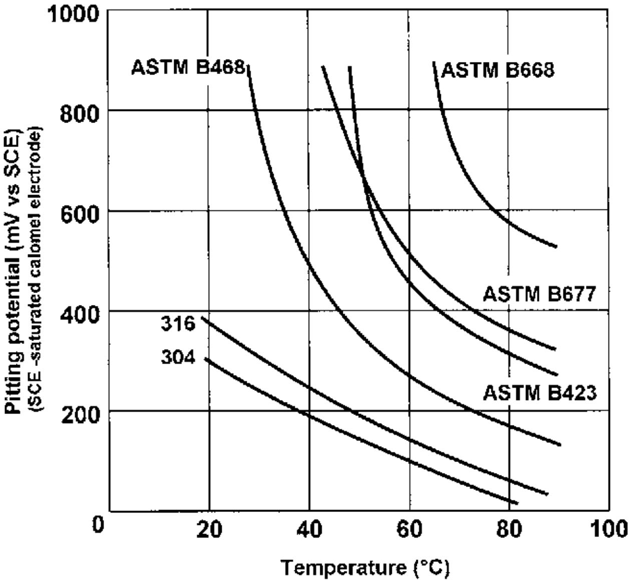


Fig. 14 Pitting Potentials in 3% NaCl. (Scan Rate 20 mV/min, (80 mV/min for Alloy 20))

ASTM B468 ≅ Alloy 20
ASTM B668 ≅ Alloy 28
ASTMB677 ≅ 904L
ASTM B423 ≅ 825

The results indicate a superior resistance of the high alloy austenitic stainless steels and also of the duplex grades. The results in Fig. 15 have been confirmed by practical experience.

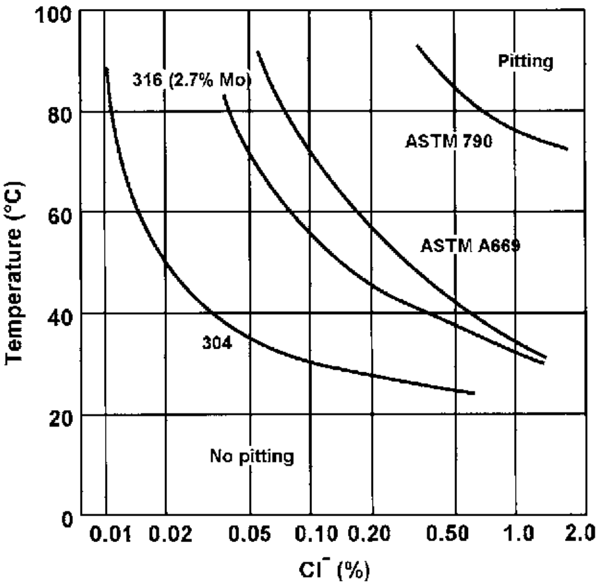


Fig. 15 CPT (Critical Pitting Temperatures) for Different Grades in Neutral Chloride Solutions (Potential = + 300 mV SCE). This data is from accelerated tests and should not be used for design purposes.

ASTM 790 ≅ 2205, ASTM A669 @≅ S31500 (duplex)

7.4.2 Crevice Corrosion

Since this form of corrosion occurs more easily than pitting, crevices should be avoided as far as possible. As with pitting, the alloying elements which most improve the resistance to crevice corrosion are chromium, molybdenum and nitrogen.

To investigate the corrosion resistance in acidic chloride solutions, weight loss measurements have been made in hydrochloric acid and electrochemical corrosion tests in acidified sodium chloride solutions. Weight loss data showed Alloy 28 was more corrosion resistant in hydrochloric acid than 904L, 825, and 316 stainless steel, although it is not usual to specify stainless steels for concentrated acidic chloride solutions.

Electrochemical polarisation investigations are used to define critical crevice corrosion solutions as the pH at which the passive corrosion current (i_{max}) surpasses 10 $\mu A/cm^2$. A low value implies good resistance to crevice corrosion. From studies made at the Swedish Corrosion Institute, Stockholm it appears that Alloy 28 has far better resistance to crevice corrosion than 904L and 316. A detailed review is available, which discusses the use and determination of electrochemical data in aggressive chloride containing environment (23).

7.4.3 Stress Corrosion Cracking

The relative resistance to SCC of various alloys can be measured by laboratory testing in concentrated chloride solutions. Low oxygen content reduces susceptibility to SCC. Considerably higher stresses are needed to induce SCC in the duplex stainless steels S31500 as well as in the high nickel austenitic steels 904L and Alloy 28, than in 304 and 316. Super duplex stainless steels are even more resistant. This indicates much higher SCC resistance of the former alloys which has also been confirmed by extensive practical experience. The ferritic steels are essentially immune to this mode of attack below 200°C.

7.5 High Temperature Corrosion

Stainless steels resist high temperature corrosion by forming Cr_2O_3 scales. These act as diffusion barriers between the steels and their environments, substantially reducing corrosion rates. For service temperatures above 650°C, stainless steels are frequently the materials of choice for their combination of strength, corrosion resistance and economy. A successful choice of stainless grade is one which will form, maintain and if necessary reform a compact, protective Cr_2O_3 scale in the service environment in question.

Austenitic grades are preferred when structural strength is required, as austenite is intrinsically superior to ferrite in its high temperature tensile properties and creep resistance, Fig. 16. However, if strength is not a requirement, as for example in the case of a cladding or weld overlay, a ferritic grade may be preferable. This is because the coefficient of thermal expansion is much lower for ferrite than austenite, and the protective Cr_2O_3 scale is less likely to spall during heating or cooling.

Apart from mechanical property requirements, the key variables affecting stainless steel choice are temperature and the chemical nature of the environment. Gases are commonly described as oxidising if they contain significant levels of molecular (or "free") oxygen, and reducing if oxygen is present in other forms such as CO_2 or H_2O or not at all. In the oxidising situation, a Cr_2O_3 scale will form, whereas in reducing gases some other form of corrosion may predominate. The two are discussed separately.

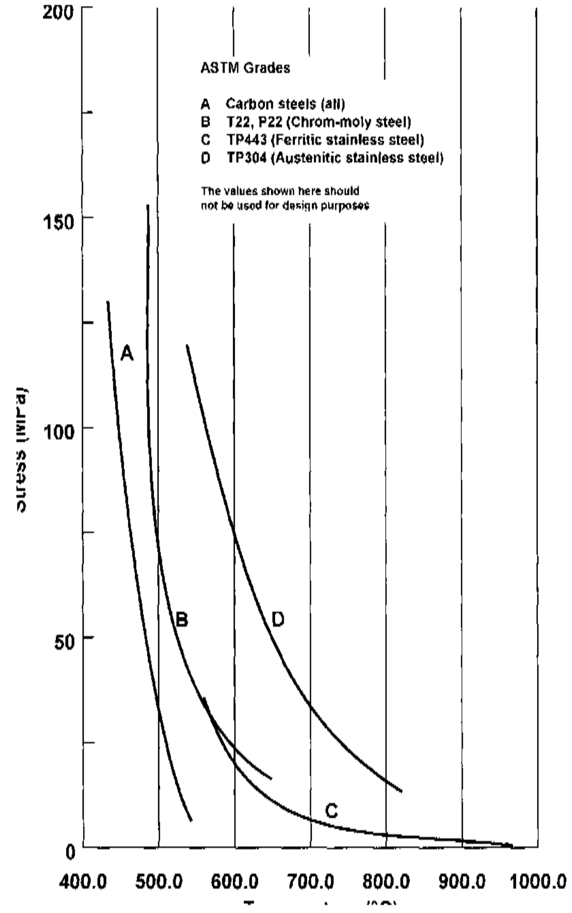


Fig. 16 Creep Strengths of Stainless Steels (24)

7.5.1 High Temperature Oxidation

Considerable information is available on the oxidation behaviour of stainless steels (5, 24, 25). Maximum service temperatures in air for standard grades of stainless steel are shown in Table 8 (24). It is seen from this table that performance improves with increasing chromium concentrations. This can be understood from the fact that chromium is being selectively oxidised and thereby removed from the surface region of the alloy. This causes the concentration of chromium at the steel-scale interface to be decreased, and the concentration of iron to increase. Because iron to some extent can dissolve in, and diffuse through, the Cr_2O_3, it is important that the level of chromium at the alloy surface not fall below the minimum necessary to maintain the Cr_2O_3 scale and prevent the formation of fast-growing iron-rich oxides. The ability of a steel to do this increases with its initial chromium concentration and hence so too does its temperature capability.

Oxidation data for stainless steels shows that increased nickel levels improve oxidation resistance for a given chromium concentration. This has been suggested to be due to improved Cr_2O_3 diffusion properties (26) and to a decreased susceptibility of the scale to iron dissolution and iron-rich oxide formation (27).

The silicon content of an austenitic stainless steel is important in determining its oxidation resistance. For example, Grade 302B (3% Si maximum, 18% Cr) has much higher temperature capabilities than Grade 302 (1% Si maximum, 18% Cr). The effect is due to formation of SiO_2 at the Cr_2O_3-steel interface, and a resulting decrease in the diffusion which permits scale growth (28 29). It may also be due in part to the promotion by silicon of Cr_2O_3 nucleation at the surface (30) and to the ability of SiO_2 to key the Cr_2O_3 scale to the surface. Commercial steels which benefit from the silicon effect include 302B (S30215), 308 (S30800), RA 85H (S30615), 153MA, 253MA (S30815) and 353MA.

The resistance of austenitic stainless steel to oxidation is reduced in conditions of intermittent service, as shown in Table 8. This effect is due to the difference in coefficient of thermal expansion between stainless steel and the Cr_2O_3 scale. Thermal cycling places the oxide under stress, the magnitude of which increases with scale thickness, until mechanical failure occurs. The cracking or spallation of the scale permits gas access to the steel surface which will be somewhat depleted in chromium. Repetition of this phenomenon leads eventually to a reduction in the steel surface chromium level below the critical minimum for re-formation of Cr_2O_3, and rapid corrosion follows. This appears not to apply to ferritic grades, as seen in Table 8. This may reflect the fact that the coefficient of thermal expansion of ferrite is about half that of austenite, and the accumulation of stress in the oxide scale during thermal cycling is consequently less.

The performance of austenitic grades under temperature cycling conditions can be improved by increasing their chromium levels so as to maintain the depleted surface concentrations at an adequate level for a greater number of cycles. Alternatively, the depletion phenomenon can be avoided by preventing scale separation from occurring. This can be achieved by adding low levels of the so-called "reactive elements" to the steel. These elements are metals which form very stable oxides and sulphides, examples being yttrium, cerium, lanthanum, zirconium, hafnium, etc. These elements affect the chromia scale-forming process in a number of ways, including refinement of oxide grain size, alteration of diffusion processes in the scale, removal of sulphur from the scale-metal interface and improved nucleation of protective Cr_2O_3 (32 33). The effect is quite dramatic, as shown in Fig. 17 (34).

Table 8. Generally Accepted Maximum Services Temperatures in Air for Wrought Stainless Steels (1)

Material	Intermittent Service (°C)	Continuous Service (°C)
Austenitic		
201	815	845
202	815	845
301	840	900
302	870	925
304	870	925
308	925	980
309	980	1095
310	1035	1150
316	870	925
317	870	925
321	870	925
330	1035	1150
347	870	925
Ferritic		
405	815	705
406	815	1035
430	870	815
442	1035	980
446	1175	1095

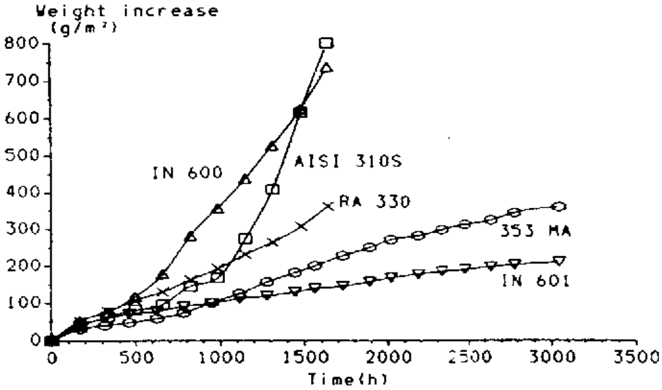


Fig. 17: Results of 5-7 day Cycles of Oxidation at 1150° C. The reactive element-containing steel 353MA performs almost as well as the nickel-base alloy IN601 (33).

The high temperature oxidation behaviour of cast heat-resistant steels can be understood in the same terms as the wrought stainless steels discussed above: the effects of chromium, nickel and silicon levels and the presence of reactive elements are the same.

7.5.2 High Temperature Carburisation and Metal Dusting

When stainless steels are exposed to reducing, carbonaceous atmospheres at high temperature carbon dissolves in the steels, diffuses inwards and precipitates chromium carbides. This can cause cracking of the underlying steel as a result of the large volume expansion accompanying precipitation. It also embrittles the sub-surface zone.

The depth of the precipitation zone, X, increases with time, t, according to the parabolic equation

$$X^2 = kt \qquad (1)$$

where k is the parabolic rate constant. It has been shown that for a range of stainless and heat-resistant steels (34 35 36) the rate constant can be predicted by Wagner's (37) expression

$$k = \text{constant}\ \frac{D_c N_c}{N_{Cr}} \qquad (2)$$

where D_c, N_c are the diffusion coefficient and solubility of carbon in the alloy surface region and N_{Cr} is the original concentration of chromium in the steel. Thus carburisation rates are decreased by increasing chromium levels and by modifying the steel composition so as to reduce carbon solubility. The most effective way of doing this is to increase the silicon concentration. Increasing the nickel content of the steel is also beneficial through its effects on both D_c and N_c (38). Some comparative carburisation data is shown in Table 9. Rates increase rapidly with temperature as both D_c and N_c are strongly temperature dependent.

Carburisation is encountered in the petrochemical industry, notably in pyrolysis furnaces, and in the heat treatment industry. It is much less of a problem if sufficient steam is present to make the atmosphere oxidising to chromium, as for example in steam reforming units. However, metal dusting can then occur.

Table 9. Parabolic Rate Constants ($10^3\ \mu m^2/hr$) for Carburisation in Propylene-Hydrogen

	Steel				
T/°C	309	310	304	308	353MA
850	4.0	3.0	5.9	1.4	-
950	8.4	3.8	12	2.8	0.1
1050	39	28	43	48	10
1150	-	197	-	196	54

Metal dusting is a particularly rapid form of high temperature attack which, in the case of stainless steels, occurs in a rather localized pattern and gives rise to pitting. This form of attack is most likely when the gas is supersaturated with respect to carbon as can happen when the slow reactions (3) and (4) fail to reach equilibrium.

$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$

$$2CO \rightarrow C + CO_2 \qquad (4)$$

These reactions are catalysed by iron and nickel surfaces, causing deposition of solid carbon and the accumulation of a fragmentary mixture of carbon, carbides and metal particles. Under high gas flows and erosive conditions this "dust" is rapidly removed and metal wastage can occur at rates of up to 15 mm per year.

Dusting of stainless steels is associated with carburisation. The precipitation of chromium carbides removes chromium from the steel leaving behind an iron-nickel matrix. When this contacts the gas, reaction (3) or (4) is catalysed, leading to the onset of dusting. Metal-gas contact can only occur when the surface Cr_2O_3 scale is damaged, and it is for this reason that dusting of stainless steels tends to be localised.

The retention of a stable, dense oxide scale associated with appropriate alloy levels of chromium and silicon will prevent metal dusting. Alternatively, if the gas is reducing with respect to Cr_2O_3 and no scale can form, then inhibition of dusting and carburisation can be achieved by adsorbing sulphur onto the metal surface. The addition of appropriate levels of H_2S or mercaptans to gas streams is used in industry for this purpose.

7.5.3 High Temperature Sulphidation

In contrast, under reducing conditions (e.g. desulphurisation plant) the presence of H_2S or sulphur vapour is quite destructive of stainless steels (39). The basic reason is that sulfide scales are much less effective diffusion barriers than oxides. High nickel austenitic grades can undergo catastrophic attack as a result of liquid formation, as shown in Table 10. Resistance to sulphidation increases with increasing chromium levels and additions of both silicon and aluminium are beneficial.

At modest temperatures, stainless steels provide much better resistance to reducing sulfurous gases than other steels, as shown in Fig. 18 (40). Isocorrosion plots are available (41) for Grade 304 and are shown in Fig. 19. Other austenitic grades are similar in their performance and it is clear that these stainless steels are of limited use under such severe conditions. Under these conditions the nickel-free ferritic stainless steels can be effective (Grade 446 with 24% Cr). The ferritic grades have much lower strengths at high temperatures compared to austenitic grades, however.

7.5.4 Molten Salt Corrosion

Deposition of ashes and salts on equipment surfaces is common in fossil fuel fired plant and incinerators. Depending on their composition, the deposits can interact with the steel oxide scale to form a liquid, thus fluxing the scale and destroying its protective value. The combination of vanadium pentoxide and sodium sulphate produced in the combustion of some fuel oils is particularly aggressive. Higher chromium levels provide somewhat improved resistance, but avoidance of the fuel contamination is to be preferred.

Molten salt baths are used for heat treatment of metals and alloys, and considerable information on the performance of stainless steels in these environments is available [42]. Generally speaking, increased nickel levels improve performance.

Table 10. Melting Points of Metal-Metal Sulfide Eutectics

Eutectic	MP/°C
$Ni\text{-}Ni_3S_2$	645
Fe-FeS	985
Cr-CrS	~1350

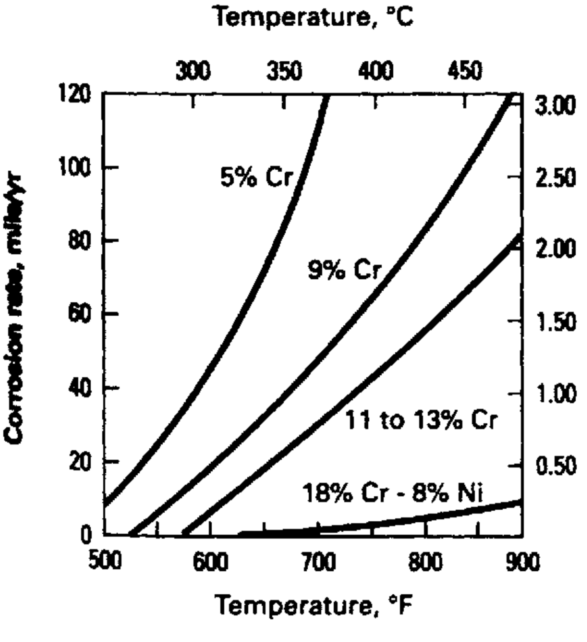


Fig. 18: Corrosion Rates of Stainless Steels in H_2-H_2S Environments [40].

7.5.5 Molten Metal Corrosion

Low melting point metals can attack stainless steels in a variety of ways: uniform thinning, intergranular penetration or preferential dissolution (dealloying) [43]. At temperatures above its melting point of 419°C, zinc diffuses into austenitic stainless steels forming a zinc alloy layer at temperatures below 710°C. At higher temperatures, and in the presence of tensile loadings, cracking along grain boundaries can occur. If zinc is present during the welding of stainless steel, cracking can result. Copper, which is frequently used in heat sinks, jigs and fixtures may also cause hot cracking by the same mechanism.

Extensive data on corrosion by other liquid metals can be found in the Liquid Metals Handbook [44].

7.5.6 Corrosion by Halogen Gases

At high temperatures the corrosion of stainless steels in chlorine is controlled by the formation of volatile metal chlorides. For this reason, high nickel levels are advantageous, as the nickel chloride is the least volatile. At lower temperatures chloride scales form at rates governed by solid-state diffusion.

For stainless steels, the upper temperature limits for service in chlorine or fluorine are about 320 and 240°C, respectively [45]. At higher temperatures, nickel-base alloys or even pure nickel are to be preferred.

The introduction of water vapour into chlorine accelerates the corrosion of stainless steels at lower temperatures. Dry hydrogen chloride is slightly less corrosive than dry chlorine.

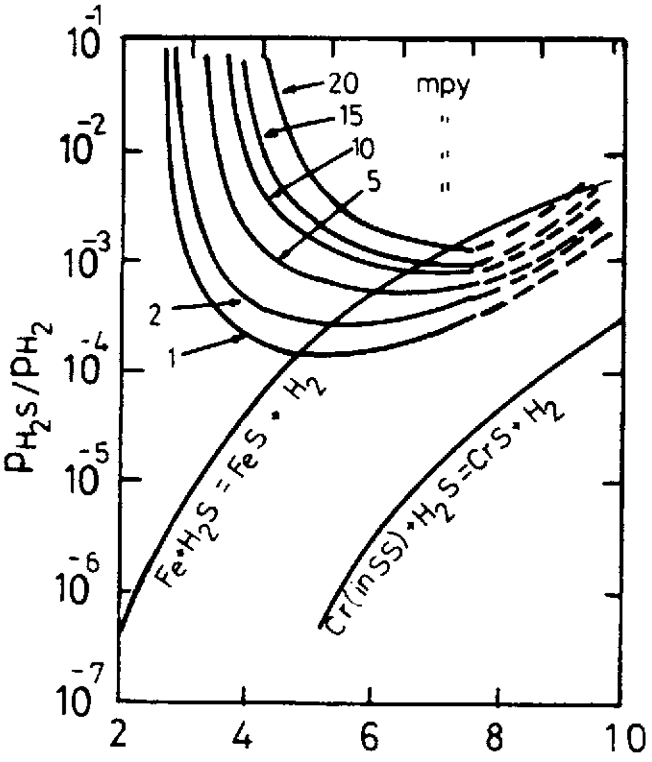


Fig. 19: Isocorrosion Plots for Grade 304 in H_2-H_2S Environments [41].

7.5.7 High Temperature Corrosion in Mixed Gases

Industrial process gases are usually quite complex, and contain a number of corrodents. For example, combustion gases contain CO, CO_2, H_2O and SO_2 as well as nitrogen, and the potential corrodents are oxygen, carbon and sulphur (and perhaps nitrogen under some circumstances). It is therefore necessary to establish how the other gas species affect oxide scale growth and whether they can, in addition, penetrate the scale and attack the underlying steel.

The presence of water vapour in air increases the rate of stainless steel oxidation substantially (46, 47, 48,49). An example of the deleterious effect on the oxidation of 310 during thermal cycling is shown in Fig. 20 (26). Suggested reasons for this behaviour are decreased scale plasticity and doping of the oxide. The temperature limits for service in moist air should be reduced by 38-65° C from those given in Table 8 (24). Service temperature limits in steam are provided in reference 47.

The presence of sulphur and/or carbon in the gas can be very destructive of stainless steels, depending on the relative activities of the different corrodents. Pure dry SO_2 corrodes stainless steels somewhat faster than does air as a result of simultaneous formation of chromium sulphides and Cr_2O_3. Maximum service temperature limits are shown in Table 11 (50). The presence of SO_2 in air increases corrosion rates, as would be expected from a comparison of Tables 7 and 10. Downstream low temperature dewpoint corrosion should also be considered when gas streams contain sulphur compounds, chlorides or water vapour.

Table 11: Generally Accepted Maximum Service Temperature in Pure, Dry Sulphur Dioxide for Selected Stainless Steels

Material	Temperature (°C)
304	800
321	800
347	800
310	1050
410	700
430	800
446	1025

The effect of SO_2 is much more marked in reducing atmospheres. Because the oxygen activity is low, the sulphur activity is increased and more rapid attack occurs. This can lead to internal precipitation of chromium sulfide within the alloy beneath a chromia scale (36, 51). The precipitation lowers the concentration of free chromium in the sub-surface zone of the steel, decreasing its ability to regrow protective chromia in the event of scale failure. Under these circumstances, equipment lifetimes are substantially reduced.

Carbon has a similarly destructive effect on stainless steels exposed to low oxygen potentials. Evidently CO can penetrate chromia scales (52, 53) and cause internal carburisation. The process is much more rapid than internal sulphidation, and the effect on material lifetime is therefore more marked. When both sulphur and carbon are present, their effects on the steel are additive, and even more rapid failure results.

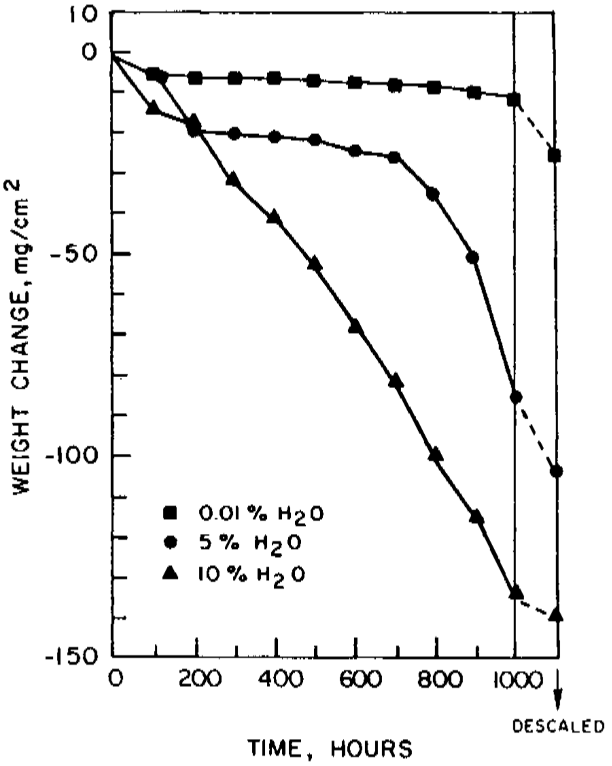


Fig. 20: Effect of Water Vapour Additions to Air on the Cyclic Oxidation Resistance of Grade 310 at 1100° C (26).

7.5.8 Metallurgical Changes at High Temperature

In addition to undergoing corrosion, stainless steels can be susceptible to metallurgical transformations during extended periods of high temperature service. Ferritic grades are subject to "475° C embrittlement" caused by precipitation of an iron-rich phase when the steels are held at temperatures of about 275 to 550° C. Higher temperatures (560-980° C) can also cause embrittlement by precipitation of a sigma phase. At still higher temperatures, no embrittling phases form but extensive ferrite grain growth leads also to embrittlement. Whilst these changes have little or no effect on corrosion resistance, they seriously reduce the steel's room temperature ductility and impact resistance.

Austenitic stainless steels do not undergo 475° C embrittlement, and are much less susceptible to grain growth. However, they too are subject to sigma phase formation and also to the phenomenon of "sensitisation". Austenites can become susceptible to room temperature intergranular corrosion after service at temperatures in the range 480 to 815° C. The effect is caused by precipitation of chromium carbides at grain boundaries and depletion of chromium from a narrow region adjoining the boundaries. The effect can be minimised by using very low carbon grades or by using "stabilised" grades. The latter contain elements such as titanium (321) or niobium (347) which form carbides even more stable than those of chromium, thereby preventing any depletion of that metal. While not strictly a corrosion problem, increasing the temperature of a cold worked austenitic stainless steel above about 400 °C will result in stress relief and loss of strength. Duplex stainless steels are also subject to embrittlement due to intermetallic precipitates and problems may arise from 300-350 °C especially in the more highly alloyed materials.

7.6 Chemical Corrosion

Stainless steels are extensively used in chemical environments where the appropriate grade can be selected from the range available to suit the particular environment. Where the conditions are too aggressive for the standard range of stainless steels, many special highly alloyed proprietary steels have been developed. While the topic is too broad to be covered in this review in any detail, some general guidelines can be given. For more specific information, several excellent references are available (7, 8, 54).

7.6.1 Inorganic Acids

The performance of stainless steels in inorganic acids depends on the acid type, concentration and temperature. Stainless steels are not recommended for use with hydrochloric acid, which destroys passivity and induces rapid pitting attack. With sulphuric acid, Grade 316 stainless steel can be used at room temperature to contain acid concentrations less than 20%, or greater than 85%. It corrodes rapidly at concentrations between these, and at elevated temperatures. Several special stainless steel grades containing combinations of copper and molybdenum have been developed for sulphuric acid service including 904L, 2205 and in particular the copper containing super duplex grades. Electrochemical, i.e. anodic, protection has also been used. Nickel contributes to the resistance of stainless steels to sulphuric acid, so that ferritic grades are less suitable than austenitic grades.

Pure phosphoric acid can be handled by Grades 430 or 304 at most concentrations and temperatures. For nitric acid, stainless steels show excellent resistance to corrosion at all concentrations, and all but the highest temperatures. The stabilised or extra low carbon austenitic grades are usually preferred, as nitric acid can rapidly attack any sensitised regions.

7.6.2 Organic Acids

Stainless steels are generally very resistant to organic acids (55) and are widely used in the food, petroleum, soap, pharmaceutical and chemical industries where organic acids are common. Grade 304 grade performs well for most organic acids over the complete concentration/temperature range. Hot formic and lactic acids can cause pitting and the molybdenum-containing grades, 316 or 317, are preferred for handling these materials (8).

7.6.3 Bases

Since their passive surface film under alkaline conditions becomes very stable, stainless steels are most suitable for use with strong bases. While stress corrosion cracking may occur with the austenitic steels in hot NaOH or KOH solutions, Grade 304 stainless steel shows little attack in 50% NaOH solutions at temperatures up to 100°C. Grade 304 is used for ammonia stills and for ammunition reactions.

7.6.4 Halogen Salts

Since halogen ions induce pitting, the use of stainless steel with halogen salts must be approached cautiously. This is especially true with acid salts, which cause pitting under oxidising conditions, and general attack under reducing conditions.

With neutral or alkaline salts, it has been observed that there is a critical temperature above which rapid pitting (CPT) occurs, and this temperature is higher for Grade 316 than for Grade 304. With sodium chloride solutions, corrosion rate increases rapidly up to a concentration of 4%, above which there is little further effect of concentration.

CORROSION IN SPECIFIC INDUSTRIES

8.1 Selection of Stainless Steel for the Pulp & Paper Industry

Pulp and Paper plants use large volumes of process waters and liquors and consequently have large fabricated vessels and piping runs. Stainless steels are well suited for use in this industry due to their range of corrosion resistance, ease of cleaning, and ease of fabrication. To achieve plant reliability there must be correct selection of stainless steel grades for the applications, and correct fabrication methods and post-weld cleaning. Paper machine process waters are in the pH range 4.5 to 7, with sulphate about 200 to 500 ppm and chloride about 100 to 400 ppm. Stainless steel Grade 304 can give satisfactory service with chloride of up to 200 ppm, 316 up to 400 ppm.

Microbiologically influenced corrosion (MIC) of stainless steel can occur when the mill has a partly or fully closed water system and is more likely with increasing degree of closure. 304 stainless steel is readily attacked by MIC in paper machines, 316 has improved resistance, but is not immune. MIC can be prevented by elimination of the microbes, addition of biocides and maintaining paper machine piping and vessels in a clean condition using regular wash ups with alkaline solutions. Pitting corrosion of 304 stainless steel can also be caused by thiosulphate at a concentration of 5 ppm in process water, particularly in newsprint paper machines where hydrosulphite is added as a brightener, and some conversion to thiosulphate occurs.

To achieve maximum corrosion resistance of stainless steel formation of welding oxide should be prevented by thorough argon back-purging of pipe welds, alternatively welding oxide should be removed by buffing or chemical cleaning. This is particularly important to prevent occurrence of MIC.

Welded austenitic stainless steels (AISI 300 series) are prone to stress corrosion cracking (SCC) in near neutral chloride solutions (> 40ppm Cl^- above 50°C) but SCC can occur in sensitised Grade 304 close to ambient temperatures (65). Stress is mostly residual stress from welding, e.g. T weld joints have high residual stress. Duplex stainless steels such as 2205 and 2304 are highly resistant to SCC and are suitable for high chloride applications such as hypochlorite modified starch, high chloride dyes, or high temperature moderate chloride concentration applications such as mill water at 95°C, e.g. for felt sprays.

Austenitic stainless steels used in corrosive vibration conditions such as vibrating screen, or under cyclic stress, such as rotating shafts, are prone to corrosion fatigue. Duplex stainless steel has much improved resistance to cracking in these conditions.

Pulp mills use processes ranging from alkaline-sulphide (Kraft) to acid bisulphite pulping, and bleaching by chlorine and its compounds, oxygen and its compounds, and combustion recovery of spent liquor. Kraft process liquors are satisfactorily handled by 304L up to 200°C. At temperatures above 200°C caustic SCC of 304L can occur in Kraft liquors. Bisulphite pulping requires 316L with 2.5% Mo, 317L or 2205 for cooking liquor and spent liquor depending on the process variables.

Pressure vessels, e.g. digesters, use 304 stainless steel as a cladding on carbon steel to avoid possible SCC problems with solid 304. Duplex 2205 would have higher resistance to SCC and is regarded as being suitable for pressure vessels.

Stainless steel clad carbon steel requires to be carefully specified, including intergranular corrosion testing specified for all plates, to detect carbon contamination of the stainless steel surface from the cladding manufacturing process.

Intergranular corrosion of 316L and 304L stainless steel cladding can occur in sulphite and Kraft digesters due to carbon contamination of the surface, and is made more severe if vessels are stress relieved at 650°C.

Carbon steel digesters can also be protected from corrosion by weld overlay with ferrite-containing 310 SS welding consumable by automatic submerged arc welding.

Kraft and Bisulphite digesters of solid 2205 duplex stainless steel have been used successfully, commencing in 1988. This material has high resistance to SCC and has high corrosion resistance.

Pulp bleaching uses liquors containing chlorine and chlorine compounds and high chloride content recycled washing liquids. Corrosion resistance of stainless steels to chlorine and its compounds is proportional to the molybdenum content. Active chlorine of 150 ppm or chlorine dioxide of 50 ppm requires 6% molybdenum stainless steels, but in-plant corrosion testing should be carried out first.

For resistance to residual chloride with lower active chlorine, 904L with 4.5% molybdenum or 317L with 3 to 4% molybdenum can be satisfactory.

For corrosive environments which are near the limit of the parent metal alloy, the welding consumable should be one grade higher in alloying elements. e.g. 4.5% molybdenum stainless steel should be welded with 6% molybdenum consumables to match corrosion resistance.

Other particular features include:

Selection of L Grades of Stainless Steel.

Low carbon grades of stainless steel (L grades) are necessary if the welding process heats the plate in the temperature range (600 to 750°C) for a sufficiently long time to cause intergranular carbide precipitation. This may be 0.5 minute for 304 with 0.08% carbon. Practically 304 thicker than 3 mm thick for use in a corrosive environment should be specified as 304L if it is to be welded.

Surface Condition For Corrosion Resistance

Stainless steels are reliant for their corrosion resistance on a passive surface layer, which is of monomolecular thickness, for optimum corrosion resistance. In practical terms, for optimum corrosion resistance, the surface must be clean and of bright appearance. The corrosion resistance of stainless steel is severely down-graded by the presence of thicker oxide films from welding, or iron oxide from contamination of the surface with carbon steel. Oxide on stainless steel produced by welding should be removed by buffing or by pickling with solution or paste. This paste contains toxic amounts of nitric acid and hydrofluoric acid, and must be used with appropriate safety measures. The inside surface of pipe at butt welds should be protected from formation of deleterious oxide films by purging the pipe with argon gas to bring the oxygen content of the gas in the pipe down to about 100 ppm.

The thickness of the oxide film is shown by its colour, and this should be no darker than light brown for optimum corrosion resistance. Blue or black colours will decrease corrosion resistance.

Stainless steel equipment such as flow boxes and wire pits are usually buffed or electropolished to produce a bright finish to prevent deposits of pulp adhering, and thus are in their optimum condition for corrosion resistance.

Microbiologically Influenced Corrosion

MIC occurs when microbial slimes form on surfaces, and sulphate reducing bacteria can form active colonies in the chemically reducing conditions beneath the slime. Corrosion testing has shown that MIC corrosion can commence within 10 days of equipment being placed in service, and corrosion can perforate 3 mm wall pipe in a few months.

More information on corrosion resistance of stainless steel in the Pulp and Paper Industry is available (7, 57, 58), and stainless steel manufacturer pamphlets.

8.2 Corrosion of Stainless Steels in the Food Processing Industry

Although environmental conditions are often less severe in the food processing industry than those encountered in other industries, the issue of contamination from the corrosion is of paramount importance. This can arise either from direct dissolution resulting in a metallic aftertaste in a food product and/or through microbiological spoilage due to the presence of micro-organisms that may accumulate in cavities formed as a result of the corrosion process(es). As in other industries, corrosion can also result in expensive downtime and unnecessary cost. The corrosion of stainless steel in this industry has been well documented and reviewed over recent years (59, 60, 61, 62).

The number of stainless steel grades available for the fabrication of food processing plant has increased substantially in recent times. Duplex (austenitic/ferritic) stainless steels and "super-austenitic" stainless steels which have greater corrosion resistance than Grade 304 and Grade 316 are readily available. Alloys such as Grade 304 and Grade 316 stainless steel have effectively been reformulated to possess narrower concentration limits of chromium, molybdenum and carbon, lower impurity levels (e.g. non-metallic inclusions), and some specific alloying additions (e.g. nitrogen). Stainless steels are highly differentiated in cost and performance, and are selected to operate within relatively narrow environmental domains.

The general corrosion of stainless steel is largely confined to a number of acids; organic acids such acetic, citric, lactic and tartaric, which can attack the 18-8 grades (such as Grade 304) at temperatures above about 70-80°C and inorganic acids (which may be used to clean equipment or disinfect equipment) including uninhibited hydrochloric and sulphuric acids. In contrast dilute nitric acid is often recommended for use for this purpose as it assists the formation of a thin protective "passive" film on stainless steel. However it can attack other materials. Sulphamic acid, which can be used as a descalent, is not recommended for use at elevated temperatures as it can decompose releasing ammonium hydrogen sulphate.

Localised corrosion processes such as pitting, stress corrosion cracking (SCC) and crevice corrosion are in general more troublesome than uniform corrosion in the food processing industry (62). A number of factors can contribute to the onset of such processes, including increased chloride levels through some concentration mechanism, low flow velocities (stagnant conditions), elevated temperatures and low solution pH typical of many food products (see Table 12) in conjunction with low solution buffer capacity. In addition an increased electrochemical corrosion potential arising from either the presence of a strong oxidant such as a hypochlorite or peroxide or resulting from galvanic coupling or stray current, may also make a stainless steel component susceptible to attack.

Table 12: Approximate pH Values of Selected Foods

Food	pH	Food	pH
Apples	2.9 - 3.3	Peaches	3.4 - 3.6
Beans	4.0 - 6.0	Pears	3.6 - 4.0
Beers	4.0 - 5.0	Peas	5.8 - 6.4
Butter	6.1 - 6.4	Pickles	3.0 - 3.6
Cheese	4.8 - 6.4	Plums	2.8 - 3.0
Cider	2.9 - 3.3	Potatoes	5.6 - 6.0
Eggs, fresh white	5.5 - 6.5	Raspberries	3.2 - 3.6
Flour, wheat	5.5 - 6.5	Shrimp	6.8 - 7.0
Grapes	3.5 - 4.5	Soft drinks	2.0 - 4.0
Jams, fruit	3.5 - 4.0	Strawberries	3.0 - 3.5
Jellies, fruit	2.8 - 3.4	Tomatoes	4.0 - 4.4
Lemons	2.2 - 2.4	Tuna	5.9 - 6.1
Milk, cows	6.3 - 6.6	Vinegar	2.4 - 3.4
Oranges	3.0 - 4.0	Water, drinking	6.5 - 8.0
Oysters	6.1 - 6.6	Wines	2.8 - 3.8

It is generally held that stainless steels are more prone to localised corrosion in solutions containing high levels of chloride. Levels of chloride in food processing can range from a few parts per million (ppm) in supply waters up to hundreds of thousands of ppm in some products such as sauces, Table 13. Concentration mechanisms can increase these levels markedly. Evaporative concentration of chloride solutions on exposed surfaces or within insulation materials and under scale deposits can all lead to localised attack and ultimately cause premature component failure.

Some products such as sauces and dressings are multiphase in nature (e.g. oil/water emulsion) and consequently aqueous phase chloride concentrations can be over 10%. Another source of chloride often encountered in these industries is certain of the cleaning/sanitising chemicals which can contain hypochlorite or organo-chlorine compounds whose decomposition results in increased chloride ion levels. However, provided such products are used strictly in accordance with documented procedures and the time of exposure is kept relatively brief, then such potential problems may be avoided.

Surface roughness can also influence the corrosion performance of a stainless steel. A smooth surface finish offers better pitting and crevice corrosion resistance than a rough finish. However, one of the chief benefits of stainless steel in the food processing industry is its ability to be mechanically ground and polished either through abrasion or electropolishing. Stringent hygiene requirements which require relatively smooth surfaces to ensure poor adhesion of micro-organisms also assist the corrosion performance of these alloys. Thus in general surface finish requirements are more exacting in this industry, a 2B (general purposes cold-rolled) or better often being required for adequate corrosion performance.

Stresses, either from applied loads, or residual stresses resulting from manufacture or fabrication procedures are obviously an important component in stress corrosion cracking (SCC). Whilst it is often difficult to avoid them in practice, good design, good materials selection (i.e. use of SCC-resistant materials) and careful operating procedures may help overcome this problem. Chloride ions, and some sulphur-containing compounds are well known agents of SCC, which is a problem with austenitic stainless steels above 50°C (65). The modern duplex stainless steel alloys however are highly resistant to this type of attack.

Table 13. Typical Chloride Contents

Fluid	Approximate Chloride Concentration (ppm)
Potable Water	10-50
Gelatine	2,000
Refrigerant Brine	300,000
Sauces	20,000
Sugar Juice	2,000-10,000

Vibration resulting in constant cyclical loadings can cause fatigue, either in the presence (corrosion-assisted fatigue) or absence of an initiating corrodent. Pitting and crevice corrosion of stainless steels are far more likely to occur in quiescent liquids than those in which there is a significant flow of fluid past the metal surface. One of the reasons often cited for this is the constant replenishment of the protective surface film that results from interaction of the stainless steel with dissolved oxygen in the fluid. However, erosion-corrosion can be a problem at higher flow rates when solid particles are present in a corrosive environment. Attack, which invariably manifests itself in a highly directional pattern, is most often found in elbows, or T-junctions in piping and on impeller blades in pumps. Solutions to this problem lie in the use of harder, more corrosion-resistant stainless steels, such as duplex (austenitic-ferritic) grades, changes in design (e.g. through lessening the severity of the bend), removal of suspended solids and process temperature reduction (where appropriate).

Crevices such as those found in flanges, weld spatter, mechanically-produced indentations and under fasteners as well as under deposits such as scale and dirt, are particularly significant in the food processing industries, as they can lead to the onset of crevice corrosion problems. Microbes including bacteria and other organisms can also thrive in such environments, making strict hygiene and sanitation procedures necessary. In addition, these organisms may lead to microbiological influenced corrosion (MIC). Removal of scale and other surface deposits (such as iron contaminants) from grinding or weld spatter serves to mitigate against corrosion, as does sealing of crevices. Again good design and materials selection (e.g. use of molybdenum-bearing stainless steel and certain gasket materials) generally helps alleviate the problem.

In summary stainless steels are a material ideally suited to the food processing industry. However, their limitations and capabilities need to be recognised and understood, where a combination of alloy grade, fabrication methods, surface and environmental treatments can have a marked influence on their successful implementation. Alloy selection in the food processing industry is particularly dependent on environmental factors.

Within the constraints of existing plant, plant operators can ensure the successful performance of stainless steel plant through their operating and control practices. Stainless steels commonly fail by a localised corrosion mechanism arising from transient environmental conditions. Conditions outside the threshold limits of alloy performance (often defined by temperature, chloride level, and exposure time) can rapidly cause corrosion initiation and propagation which result in product contamination or component failure.

Careful consideration and control of all process modifications is necessary, particularly those involving sanitising agents, brine solutions, soft unbuffered water, and start-up/shut-down procedure (e.g. hydro-testing).

8.3 Use of Stainless Steels in the Upstream Petroleum Industry

The higher grades of stainless steels are finding increasing use in the control of corrosion in the production of oil and gas, particularly in fields containing higher amounts of the corrosive gases, carbon dioxide and hydrogen sulphide. Typical grades of stainless steel used start with the 9% Cr and 13% Cr martensitic steels, progress through the 22% Cr duplex steels up to the 25% Cr super duplex steels. Higher temperatures and concentrations of chlorides and hydrogen sulphide may require the use of nickel-based alloys.

The selection of an appropriate grade of stainless steel is not straight forward and users must carefully consider the following:

- Carbon dioxide - a minimum grade of stainless steel (13% Cr) is resistant to corrosion caused by CO_2 by itself at low to moderate temperatures. However, at higher temperatures, and in the presence of H_2S and sodium chloride, higher grades of stainless steel are required;
- Hydrogen sulphide - stainless steels in general are extremely sensitive to stress cracking caused by H_2S. Resistance increases with increasing grade of steel, and for a given grade of steel, susceptibility to H_2S induced stress corrosion cracking is at a maximum at a temperature of around 80°C. Use of stainless steels in sour (H_2S) environments is discussed in NACE MR-0175 (63);
- Chloride ion concentration - most produced fluids contain sodium chloride, and thus the material used must be resistant to chloride induced stress corrosion cracking. Susceptibility to sulphide stress cracking also increases with increasing chloride ion concentration;
- Service temperature - as a general rule, corrosion rate increases with increasing temperature;
- Weldability - if the material is to be welded, care must be taken to select correct welding procedures that do not lead to cracking or to weld sensitisation.

Extensive testing programs have been carried out to define the exact service limits of the various grades of stainless steel, and selection criteria tables, listing the suitability of the various grades of stainless steel are available from manufacturers.

In selecting the material for a particular service, requirements for conditions other than the service conditions need to be considered. For example, conditions under hydrotest, when oxygenated sea water may be used, or conditions downhole, when the tubular may be in contact with a high salinity brine may present very different hazards to normal service conditions. In addition, the external environment conditions must be considered, for example, steels resistant to chloride induced pitting attack and SCC must be used in an offshore environment.

Highly alloyed stainless steels are also being used increasingly for seawater service, for example, in seawater fire deluge systems. In this application, stainless steels are resistant to the corrosion suffered by carbon steel, and are also resistant to the corrosion-erosion attack experienced by copper-nickel, the other material commonly used for this service.

8.4 Cryogenics

Austenitic stainless steels because of their superior low temperature mechanical properties are used for cryogenic application (10). Grade 304 and 304L (S30403) are the most widely used grades. Other grades commonly used are 316, 316L and 321. Where superior strength is required the high nitrogen grades such as S30453 and S31653 find favour whilst more highly alloyed grades such as 310 may be used where maximum stability and a high degree of toughness are demanded. When these steels are welded the ferrite content of the weld metal may be restricted to 3-7% or fully austenitic filler metal employed to ensure adequate low temperature toughness.

The above grades, when correctly fabricated, are unlikely to be susceptible to corrosion with cryogenic applications.

8.5 Specific Industry Problems - Heat Exchangers

Heat exchangers come in a wide variety of sizes and designs, ranging from large steam turbine condensers and air-conditioning plant, to small oil coolers. Many different fluids may be cooled or heated, usually by treated water circulated through a cooling tower or by river or sea water. Heat exchangers also include associated pipe systems, water boxes, pumps, valves, screens and filters.

The traditional material for heat exchanger tubes in Australia is copper alloy, with titanium being used for more critical applications. However, because of problems with impingement and erosion of copper alloys, stainless steels have been used in America and Europe.

Important factors to be considered when using stainless steels in heat exchangers include:

- The maximum temperature in the system. With temperatures commonly above 35°C Grade 304 and 316 stainless steels may well have insufficient pitting resistance. High alloy austenitics such as AL-6XN or 254 SMO have been used extensively for condenser tubing, while the duplex alloys are gaining acceptance for heat exchangers and associated systems. Austenitic alloys may suffer Stress Corrosion Cracking at temperatures above 60°C (see section 4.5);
- Stainless steels must be kept free of deposits and marine growth to maintain their pitting resistance. Large heat exchangers usually have an online tube cleaning system to remove deposits and maintain heat transfer.

Finally, when using stainless steels in heat exchangers it is important to consider the system as a whole and select compatible materials with appropriate corrosion resistance.

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LIST OF WTIA TECHNICAL NOTES

These Technical Notes may be obtained from the WTIA:
Welding Technology Institute of Australia
PO Box 6165, Silverwater NSW 2128
Phone (02) 9748 4443 Fax (02) 9748 2858
http://www.wtia.com.au

1. **The Weldability of Steels - TN1-96**
   Gives guidance on the preheat and heat input conditions (run size, current, voltage) required for acceptable welds and to avoid cold cracking in a wide variety of steels. The Note is applicable to a wide range of welding processes.

2. **Successful Welding of Aluminium - TN2-97**

   This note covers the major welding processes as they are used for the welding and repair of aluminium and its alloys. Information is given on the processes, equipment, consumables and techniques. It also provides information on the range of alloys available and briefly covers safety, quality assurance, inspection and testing, costing and alternative joining processes.

3. **Care and Conditioning of Arc Welding Consumables - TN3-94**
   Gives the basis and details for the correct care, storage and conditioning of welding consumables to control hydrogen and to ensure high quality welding.

4. **The Industry Guide to Hardfacing for the Control of Wear - TN4-96**
   Describes wear mechanisms and gives guidance on the selection of hardfacing consumables and processes for a wide range of applications.
   Includes Australian Hardfacing Suppliers Compendium 1998.

5. **Flame Cutting of Steels - TN5-94**
   Gives a wealth of practical guidance on flame cutting including detailed procedures for efficient cutting, selection of equipment and gases, practices for identifying and curing defective cutting, methods of maximising economy and other important guidance on the use of steels with flame cut surfaces.
   Flame Cut Surface Replicas
   These have been developed to complement Technical Note Number 5 by defining three qualities of flame cut surface. Each set of three is contained in a convenient holder with a summary sheet of main flame cutting data.

6. **Control of Lamellar Tearing - TN6-85**
   Describes the features and mechanisms of this important mode of failure and the means of controlling tearing through suitable design, material selection, fabrication and inspection. Acceptance standards, repair methods, specification requirements and methods of investigation are proposed. Four appendices give details on the mechanism, material factors, tests for susceptibility and the important question of restraint.

7. **Health and Safety in Welding - TN7-98**
   Provides information on all aspects of health and safety in welding and cutting. Designed to provide this information in such a way that it is readily useable for instruction in the shop and to provide guidance to management. Recommendations are given for safe procedures to be adopted in a wide variety of situations found in welding fabrication.

8. **Economic Design of Weldments - TN9-79**
   Principles and guidance are given on methods and procedures for optimising design of weldments and welded joints and connections to maximise economy in welding fabrication. Factors influencing the overall cost of weldments which need to be considered at the design stage are discussed.

9. **Welding Rate in Arc Welding Processes: Part 1 MMAW - TN9-79**
Gives practical guidance and information on the selection of welding conditions to improve productivity during manual metal arc welding (MMAW). Graphs are provided showing rates as a function of weld size. The graphs enable a direct comparison of different types of welding electrodes when used for butt and fillet welds in various welding positions.

10. **Fracture Mechanics - TN10-80**
Provides theory and gives practical guidance for the design and fabrication of structures, planning of maintenance and assessment of the likelihood of brittle or ductile initiation from flaws in ferrous and non-ferrous alloys. Engineering critical assessment case histories are discussed.

11. **Commentary on the Structural Steel Welding Standard AS/NZS 1554 - TN11-98**
(A joint publication with AISC)
The Note complements AS/NZS 1554 Parts 1 to 5, by presenting background information which could not be included in the Standard. It discusses the requirements of the Standard with particular emphasis on new or revised clauses. In explaining the application of the Standard to welding in steel construction, the commentary emphasises the need to rely on the provisions of the Standard to achieve satisfactory weld quality.

12. **Minimising Corrosion in Welded Steel Structures - TN12-96**
(A joint publication with the Australasian Corrosion Association Inc)
Designed to provide practical guidance and information on corrosion problems associated with the welding of steel structures, together with possible solutions for minimising corrosion.

13. **Stainless Steels for Corrosive Environments - TN13-98**
Provides guidance on the selection of stainless steels for different environments. Austenitic, ferritic and martensitic stainless steels are described together with the various types of corrosive attack. Aspects of welding procedure, design, cleaning and maintenance to minimise corrosion are covered.

14. **Design and Construction of Welded Steel Bins - TN14-84**
Written because of the widely expressed need for guidance on the design and fabrication of welded steel bulk solids containers, this Technical Note gathers together relevant information on functional design, wall loads, stress analysis, design of welded joints and the fabrication, erection and inspection of steel bins. It also contains a very comprehensive reference list to assist in a further understanding of this very broad subject.

15. **Welding and Fabrication of Quenched and Tempered Steel - TN15-96**
Provides information on quenched and tempered steels generally available in Australia and gives guidance on welding processes, consumables and procedures and on the properties and performance of welded joints. Information is also provided on other important fabrication operations such as flame cutting, plasma cutting, shearing and forming.

16. **Welding Stainless Steels - TN16-85**
This Technical Note complements Technical Note Number 13 by detailing valuable information on the welding of most types of stainless steels commonly used in industry.

17. **Automation in Arc Welding - TN17-86**
Provides information and guidance on all the issues involved with automation in arc welding. The general principles are applicable to automation in any field.

18. **Welding of Castings - TN18-87**
Provides basic information on welding procedures for the welding processes used to weld and repair ferrous and non-ferrous castings. It also provides information on the range of alloys available and briefly covers non-destructive inspection, on-site heating methods and safety.

19. **Cost Effective Quality Management for Welding - TN19-95**
Provides guidelines on the application of the AS/NZS ISO 9000 series of Quality Standards within the welding and fabrication industries. Guidance on the writing, development and control of Welding Procedures is also given.

20. **Repair of Steel Pipelines - TN20-94**
Provides an outline of methods of assessment and means of repair available to a pipeline whilst allowing continuity of supply.

Binder (holds ten of the above)