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Re: Stress Corrosion Cracking (SCC) Induced by a Halide (i.e., Typically Chloride)

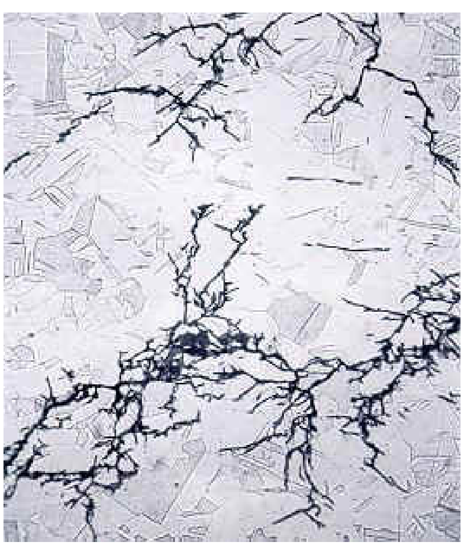
DEFINTION

Stress Corrosion Cracking (SCC) is the cracking induced from the combined influence of tensile stress and a corrosive environment due to halides. A *halide* is a binary compound of which one part is a halogen atom and the other part is an element or radical that is less electronegative than the halogen, to make a fluoride, chloride, bromide, iodide, or astatide compound. Many salts are halides.

The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. The problem itself can be quite complex.

Chloride stress corrosion is a type of intergranular corrosion and occurs in austenitic stainless steel under tensile stress in the presence of oxygen, chloride ions, and high temperature. It is thought to start with chromium carbide deposits along grain boundaries that leave the metal open to corrosion. This form of corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and use of low carbon steels.

Usually, most of the surface remains unattacked, but with fine cracks penetrating into the material. In the microstructure, these cracks can have an intergranular or a transgranular morphology. Macroscopically, SCC fractures have a brittle appearance. SCC is classified as a catastrophic form of corrosion, as the detection of such fine cracks can be very difficult and the damage not easily predicted. Experimental SCC data is notorious for a wide range of scatter. A disastrous failure may occur unexpectedly, with minimal overall material loss.



The photo on the left (X300) illustrates stress corrosion cracking in a 316 stainless steel chemical processing piping system. ***Chloride stress corrosion* cracking** in austenitic stainless steel is characterized by the multi-branched "lightning bolt" transgranular crack pattern. Photo by Metallurgial Technologies.

GENERAL PROPERITES

One of most familiar and most frequently used alloys in the stainless steel family are 302, 304, 304L, 305 based on variations of the 18 percent chromium – 8 percent nickel austenitic alloy. These alloys may be considered for a wide variety of applications where one or more of the following properties are important:

1) Resistance to corrosion
2) Prevention of product contamination
3) Resistance to oxidation
4) Ease of fabrication
5) Excellent formability
6) Beauty of appearance
7) Ease of cleaning
8) High strength with low weight
9) Good strength and toughness at cryogenic temperatures
10) Ready availability of a wide range of product forms

Each alloy represents an excellent combination of corrosion resistance and fabricability. This combination of properties is the reason for the extensive use of these alloys which represent nearly one half of the total U.S. stainless steel production. Type 304 represents the largest volume followed by Type 304L. Types 302 and 305 are used in smaller quantities. The 18-8 stainless steels, principally Types 304 and 304L, are available in a wide range of product forms including sheet, strip, foil and plate. The alloys are covered by a variety of specifications and codes relating to, or regulating, construction or use of equipment manufactured from these alloys for specific conditions. Food and beverage, sanitary, cryogenic, and pressure-containing applications are examples.

Type 304L is typically used for welded products which might be exposed to conditions which could cause intergranular corrosion in service.

CHEMICAL COMPOSITION

The following table shows the chemical composition per ASTM A240 and AMSE SA-240.

Element	Percentage by Weight Maximum Unless Range is Specified			
	302	304	304L	305
Carbon	0.15	0.08	0.030	0.12
Manganese	2.00	2.00	2.00	2.00
Phosphorus	0.045	0.045	0.045	0.045
Sulfur	0.030	0.030	0.030	0.030
Silicon	0.75	0.75	0.75	0.75
Chromium	17.00 / 19.00	18.00 / 20.00	18.00 / 20.00	17.00 / 19.00
Nickel	8.00 / 10.00	8.00 / 10.50	8.00 / 12.00	10.50 / 13.00
Nitrogen	0.10	0.10	0.10	--

GENERAL CORROSION

The Types 302, 304, 304L and 305 austenitic stainless steels provide useful resistance to corrosion on a wide range of moderately oxidizing to moderately reducing environments. The alloys are used widely in equipment and utensils for processing and handling of food, beverages and dairy products. Heat exchangers, piping, tanks and other process equipment in contact with fresh water also utilize these alloys. Building facades and other architectural and structural applications exposed to non-marine atmospheres also heavily utilize the 18-8 alloys. In addition, a large variety of applications involve household and industrial chemicals.

The 18 to 19 percent of chromium that these alloys contain provides resistance to oxidizing environments such as dilute nitric acid. Other laboratory data for Types 304 and 304L illustrate that these alloys are also resistant to moderately aggressive organic acids such as acetic, and reducing acids such as phosphoric. The 9 to 11 percent of nickel contained by these 18-8 alloys assists in providing resistance to moderately reducing environments. The more highly reducing environments such as boiling dilute hydrochloric and sulfuric acids are shown to be too aggressive for these materials. Boiling 50 percent caustic is likewise too aggressive.

In some cases, the low carbon Type 304L alloy may show a lower corrosion rate than the higher carbon Type 304 alloy. The data for formic acid, sulfamic acid and sodium hydroxide illustrate this. Otherwise, the Types 302, 304, 304L and 305 alloys may be considered to perform equally in most corrosive environments. A notable exception is in environments sufficiently corrosive to cause intergranular corrosion of welds and heat-affected zones on susceptible alloys. The *Type 304L alloy is preferred for use in such media in the welded condition since the low carbon level enhances resistance to intergranular corrosion.*

INTERGRANULAR CORROSION

Exposure of the 18-8 austenitic stainless steels to temperatures in the 800°F to 1500°F (427°C to 816°C) range may cause precipitation of chromium carbides in grain boundaries. Such steels are “sensitized” and subject to intergranular corrosion (i.e, corrosion occurring between the grains, or crystals, that form the metal) when exposed to aggressive environments.

The carbon content of Types 302, 304, and 305 may allow sensitization to occur from thermal conditions experienced by autogenous welds and heat-affected zones of welds. For this reason, the *low carbon Type 304L alloy is preferred for applications in which the material is put into service in the as-welded condition. Low carbon content extends the time necessary to precipitate a harmful level of chromium carbides, but does not eliminate the precipitation reaction for material held for long times in the precipitation temperature range*.

STRESS CORROSION CRACKING

The Type 302, 304, 304L and 305 alloys are the most susceptible of the austenitic stainless steels to stress corrosion cracking (SCC) in halides because of their relatively low nickel content. *Conditions that cause SCC are:*

(1) presence of halide ions (generally chloride),
(2) residual tensile stresses, and
(3) temperatures in excess of about 120°F (49°C).

Stresses may result from cold deformation of the alloy during forming, or by roller expanding tubes into tubesheets, or by welding operations that produce stresses from the thermal cycles used. Stress levels may be reduced by annealing or stress relieving heat treatments following cold deformation, thereby reducing sensitivity to halide SCC. *The low carbon Type 304L material is the better choice for service in the stress relieved condition in environments which might cause intergranular corrosion.*

Halide (Chloride) Stress Corrosion Tests		
Test	U-Bend (Highly Stressed) Samples	
	302, 304, 304L, 305	
42% Magnesium Chloride, Boiling	Base Metal	Cracked, 1 to 20 hours
	Welded	Cracked, ½ to 21 hours
33% Lithium Chloride, Boiling	Base Metal	Cracked, 24 to 96 hours
	Welded	Cracked, 18 to 90 hours
26% Sodium Chloride, Boiling	Base Metal	Cracked, 142 to 1004 hours
	Welded	Cracked, 300 to 500 hours
40% Calcium Chloride, Boiling	Base Metal	Cracked, 144 Hours
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Ambient Temperature Seacoast Exposure	Base Metal	No Cracking
	Welded	No Cracking

The data to the left illustrate that various hot chloride solutions may cause failure after differing lengths of time. The important thing to note is that failure eventually occurs under these conditions of chloride presence, high stresses and elevated temperatures.

PITTING/CREVICE CORROSION

The 18-8 alloys have been used very successfully in fresh waters containing low levels of chloride ion. Although Type 304 tubing has been used in power plant surface condenser cooling water with as much as 1000 ppm chloride, this performance can only result from careful cleaning of the tubes during use and care to avoid stagnant waters from remaining in contact with the tube. *Generally, 100 ppm chloride is considered to be the limit for the 18-8 alloys, particularly if crevices are present.* Higher levels of chloride might cause crevice corrosion and pitting.

For the more severe conditions of higher chloride levels, lower pH and/or higher temperatures, alloys with higher molybdenum content such as Type 316 or AL-6XN® alloy should be onsidered. Interestingly, Types 304 and 304L stainless steels pass the 100 hour, 5 percent neutral salt spray test (ASTM B117) with no rusting or staining of samples. However, Type 304 building exteriors exposed to salt mists from the ocean are prone to pitting and crevice corrosion accompanied by severe discoloration. The 18-8 alloys are not recommended for exposure to marine environments.

The reader is invited to consult the steel manufacturer with questions concerning the suitability of the 18-8 alloys for specific environments.

WELDING

The austenitic stainless steels are considered to be the most weldable of the high-alloy steels and can be welded by all fusion and resistance welding processes. The Types 302, 304, 304L and 305 alloys are typical of the austenitic stainless steels. Two important considerations in producing weld joints in the austenitic stainless steels are:

1) preservation of corrosion resistance, and
2) avoidance of cracking.

A temperature gradient is produced in the material being welded which ranges from above the melting temperature in the molten pool to ambient temperature at some distance from the weld. The higher the carbon level of the material being welded, the greater the likelihood that the welding thermal cycle will result in the chromium carbide precipitation which is detrimental to corrosion resistance.

To provide material at the best level of corrosion resistance, low carbon material (Type 304L) should be used for material put in service in the welded condition. Alternately, full annealing dissolves the chromium carbide and restores a high level of corrosion resistance to the standard carbon content materials. Weld metal with a fully austenitic structure is more susceptible to cracking during the welding operation. For this reason, Types 302, 304, and 304L alloys are designed to re-solidify with a small amount of ferrite to minimize cracking susceptibility. Type 305, however, contains virtually no ferrite on solidification and is more sensitive to hot cracking upon welding than the other alloys. If filler metal is required, Type 308 (20% Cr-11% Ni) is generally used. This enriched composition avoids martensite that might otherwise form in multi-pass welds. Chemistry is controlled to allow a small amount of ferrite in the deposit to limit hot cracking tendency.

Sincerely,

Shipco® Marketing and Sales Department