316L Stainless Steel Today - Is it a questionable choice for use in certain process systems?

The processing industries are experiencing unexpectedly short service life with equipment and piping fabricated from 316L stainless steel. It is speculated that the alloy is being produced with the concentrations of chromium, nickel and molybdenum at the low end of the range specified for the 316L stainless steel. Consequently the present 316L alloy is less resistant to corrosion, particularly to crevice corrosion. The situation raises several questions. How aware is the steel industry of the uncertainty with respect to the 316L alloy? Would simply increasing the concentration of molybdenum in the alloy, to the high end of the specified range, improve the resistance to localized corrosion? Is it possible to produce a 316L stainless steel (a “new” alloy) with the highest specified concentrations of chromium, nickel and molybdenum to obtain performance equivalent to the earlier 316L alloy? Assuming that sanitary tubing and the associated fittings in this “new” alloy became readily available, does it represent a cost effective alternative to the 904L, 2205 and AL6XN alloys?

There is a concern in the processing industries, particularly in the food industry, that a significantly shorter service life is presently obtained from the 316L stainless steel equipment and piping. The industries use the stainless steels to meet the standards established for sanitary or hygienic processes, e.g., “3-A Accepted Practices for Product and Solution Pipelines.” The austenitic stainless steels, 304, 304L, 316 and 316L, have become the workhorses of the food, beverage and dairy industries, representing a highly versatile and cost effective choice for the fabrication of process systems.

Properties of the stainless steels.

Stainless steels all contain iron and chromium, with other elements such as nickel, manganese, molybdenum nitrogen and copper, introduced to further modify the physical properties of the material. Advances in the techniques used in the manufacture of stainless steels have resulted in cleaner, purer products, the compositions of which can be closely controlled. Chromium imparts the unique corrosion properties to the stainless steel, properties that are significantly different from those of carbon steels, low alloy steels and cast iron. For example, at concentrations of chromium above 11% by weight, the rate of general corrosion of a stainless steel is practically negligible. This corrosion resistance is attributed to the formation of a thin, passive film, generally considered to be chromium oxide, at the surface of the stainless steel. The addition of nickel stabilizes the austenite crystal structure in the steel, making it more weldable, less brittle and easier to shape and bend than the other crystal structures in which a stainless steel may exist. Manganese also stabilizes the crystal structure of the stainless steel and this metal is frequently used as a partial substitute for nickel. Molybdenum and nitrogen both enhance the resistance to pitting and crevice corrosion and nitrogen also tends to stabilize the austenite crystal structure. The carbon content of the 304L, 316L and 317L stainless steels is specified to be 0.03% (maximum), reduced from 0.08% in the 304,316 and 317 steels. This is important since carbon reacts to form chromium carbide during annealing, welding and forming processes and the presence of carbide at grain boundaries leads to the onset of intergranular corrosion when the alloy is in service.

The concentrations of carbon, chromium, nickel and molybdenum in the stainless steels that are used extensively in the fabrication of process equipment, process piping and process systems are shown below as Table 1.

Table 1 The Composition of Stainless Steels

Stainless Steel	Carbon	Chromium	Nickel	Molybdemum	Magnanese	Nitrogen	Copper
304	0.08	18-20	8-15	---	2	---	---
304L	0.03	18-20	8-15	---	2	---	---
316	0.08	16-18	10-14	2-3	2	---	---
316L	0.03	16-18	10-14	2-3	2	---	---
317	0.08	18-20	11-15	3-4	2	---	---
317L	0.03	18-20	11-15	3-4	2	---	---
904L	0.02	19-23	23-28	4-5	---	---	1.5
AL6XN	0.03	20-22	25	6-7	0.4	0.2	0.2
2205	0.03	21-23	4.5-6.5	2.5-3.5	---	0.15	---

*Data shows percentages (%)

The alloys also contain 0.03% sulfur, 1% silicon, 0.045% phosphorus, with the balance being iron.

The alloys all have the austenitic crystal structure, except for 2205, which contains both austenitic and ferritic structures and is referred to as a duplex alloy.

What is meant by “localized corrosion?”

“Localized corrosion” refers to pitting and crevice corrosion, which are very similar and occur at specific sites rather than over a large area, as does general corrosion. It is difficult to predict the incidence of localized corrosion, particularly as the corrosive environment becomes more complex and fluctuations occur in the temperature, pH and the concentration of chloride ions or other aggressive ionic species. Pitting is the result of attack at minor discontinuities in the passive film, arising from inclusions, defects in the substrate, dirt and other contaminants on the surface of the steel. Crevices are formed at joints and gaskets, as well as at scale, deposits and where there is overlap of materials. To function as a site for corrosion, the crevice has to be wide enough to allow the corrosive fluid to enter, but sufficiently narrow to ensure stagnant conditions. Unlike pitting, with crevice corrosion it is essential that there is no movement of the corrosive environment (process fluid, foodstuff) out of the crevice. This type of corrosion is often regarded as a more severe form of pitting corrosion, being initiated at lower temperatures.

How is crevice corrosion measured?

There are several measures of the resistance to crevice corrosion. One approach is described in the ASTM Procedure G-48, in which a sample of the metal or alloy, with artificial crevices attached, is immersed in an aqueous solution containing chloride ions for a specified period of time. The tests are carried out at various temperatures to establish the onset of crevice corrosion. The so-called “critical crevice corrosion temperature (CCCT)” -- the temperature at which crevice corrosion is first detected -- for a series of stainless steel alloys, is shown as Table 2.

Table 2 Critical Crevice Corrosion Temperatures for Slelected Stainless Steel

Stainless Steel	CCCT (ºF)	Test Solution
316	<27.5	2
317	35	3
304L	40	3
316L	60	1
904L	65	1
AL6XN	113	1
2205	125	3

*Solution 1	6% Ferric Chloride
*Solution 2	10% Ferric Chloride
*Solution 3	6% Sodium Chloride

The conditions used in ASTM tests are deliberately severe, the steels being exposed to a weakly acidic solution containing a high concentration of chloride ions, in order to obtain a result in a practical period of time. However, it can be seen that several of the stainless steels may be susceptible to crevice corrosion if the process requires an elevated temperature, particularly if the product being processed contains chloride ions.

A simple model for crevice corrosion

Crevice corrosion may be considered as a process that occurs in two stages;

(i) An “incubation period,” during which the process fluid or foodstuff enters the crevice and corrosion is initiated.
(ii) The corrosion in the crevice penetrates into the alloy, continuing until a hole results.

The “incubation period” is independent of the composition of the alloy, being determined by such factors as the temperature, the depth and width of the crevice, the compressive forces exerted at the connection, and the nature of both the alloy surface and the process fluid. The site at which the corrosion starts can be a defect, inclusion or contaminant at the alloy surface. In contrast, the rate at which the crevice grows is largely controlled by the composition of the alloy, but is also dependent upon the temperature, pH and concentration of chloride ions.

Which processes have a problem with 316L?

The extent of the problem with 316L stainless steel in food processing is becoming larger as more field performance data is obtained. Food processors are experiencing shorter lifetimes for the process piping systems and equipment, resulting in higher operational maintenance budgets to replace these items. This situation prompted one major food producer to undertake a study (1) in an effort to identify the corrosion processes that were involved. The food product used in this study was tomato ketchup, which is weakly acidic and contains chloride ions from a salt source. It was found that the failures in the equipment were mainly due to crevice corrosion in the flange areas that experience temperatures above 140º F. This type of accelerated corrosion has also been observed, though not formally documented, on the flanges and piping in the hot processing areas of the production of Taco sauce. Again the product is weakly acidic and contains chloride ions.

The study cited above was also designed to evaluate other alloys in the particular environment and identify, if possible, an alternative material in terms of corrosion resistance, cost and availability. In a series of laboratory tests that simulated the conditions experienced in the ketchup process, coupons of 304L, 316L, 317L, 2205, 904L and AL6XN showed no visible corrosion. It was therefore recommended that in-plant tests be carried out. The exposure of several samples of stainless steels (with crevices attached) to the hot ketchup process established that both 316L and 317L were susceptible to crevice corrosion within a period of 16 weeks, while the alloys 2205, 904L and AL6XN did not show any signs of corrosion under the same test conditions and over the same length of time.

Sanitary tubing and the associated flange fittings are currently not readily available in either the 2205 or the 904L alloy and it would require special arrangements with the manufacturers to fabricate the products from these alloys. The required tubing and fittings can be obtained in the alloy AL6XN, but at a cost which is significantly higher than the equivalent 316L products.

The results of the study of the ketchup process system did lead to changes being recommended in (i) the process piping, (ii) the gasket material at the flanges, (iii) the clamps being used at the connections in the system and (iv) the maintenance program.

"Why is crevice corrosion occurring so much earlier in the service life of today's 316L?"

The specifications for the concentrations of the alloying elements in the 316L stainless steel are 16-18% chromium, 10-14% nickel and 2-3% molybdenum. Analyses showed that the 316L steel in the flange areas of the process system used to produce tomato ketchup contained 17% chromium, 10% nickel and 2% molybdenum, all the concentrations being at the low end of the specified range. It is recognized that advances in steel-making technology now allow the industry to closely control the composition of the stainless steel alloys. With the recent escalations in the prices of the alloying elements (the nickel, molybdenum, chromium and manganese) it would certainly be cost effective to produce the stainless steels containing the lowest, acceptable concentrations of these metals. Two questions follow and both are of interest to the food, beverage and dairy industries:

1. Would concentrations of one (molybdenum) or all of the alloying elements at the high end of the range specified for the 316L steel improve its' resistance to crevice corrosion?

2. Would this "new" 316L stainless steel be a cost effective alternative to 904L or AL6XN?

Some Final Thoughts

Reference to Table 1 shows that the concentrations of chromium, nickel and molybdenum, at the high end of the specified range for the 316L alloy, overlap the lower concentrations for the 317L alloy. Therefore, the observed corrosion of the samples of both the 316L and 317L alloys (1) suggests that small increases in the concentrations of chromium, nickel and molybdenum would not significantly improve its' resistance to crevice corrosion. On the other hand, the alloys 904L and AL6XN have very different compositions from the 316L stainless steel, with higher concentrations of chromium, nickel and molybdenum. The AL6XN alloy also contains nitrogen and copper. The 2205 stainless steel has a duplex structure and its' composition is different again, with an unusually low concentration of nickel (4.5-6.5%).

Based upon composition alone, increasing the concentrations of chromium, nickel and molybdenum, to the high end of the range specified for the 316L stainless steel, may not improve the resistance to crevice corrosion. However, the physical properties of an alloy is sensitive to the metallurgical history of that alloy. Stress relieving, normalizing and annealing are heat treatments that prepare the alloy for processing and for the intended service conditions. These heat treatments may be used to (i) control the ability of the stainless steel to be machined and/or formed, and (ii) optimize corrosion resistance. This aspect, together with the changes in composition, may be worthy of further consideration, in the efforts to identify an acceptable alloy.

Reference

1. "Corrosion. Ketchup Process Piping," Steven Ament, Heinz North America. June 10, 2004.