Stress-Corrosion Cracking

Materials Performance and Evaluation

Russell H. Jones, Editor

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Stress-Corrosion Cracking

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CHAPTER 4

Stress-Corrosion Cracking of Stainless Steels

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Stainless steels are iron alloys that contain a minimum of approximately 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres (hence the designation "stainless"). Today there are more than 180 different alloys that belong to the stainless steel group. The chromium content of some steels now approaches 30%, and many other alloying elements are added to provide specific properties or ease of fabrication (Ref 1). Figure 1 provides a useful summary of some of the compositional and property linkages in the stainless steel family. Because the susceptibility to stress-corrosion cracking (SCC) of stainless steels depends on alloy composition, structure, and thermal history (Ref 1), the alloys shown in Fig. 1 exhibit widely varying susceptibilities in different environments. For example, the austenitic (300 series) stainless steels can be susceptible to SCC in certain chloride environments, whereas the ferritic and martensitic grades (400 series) can be susceptible to hydrogen embrittlement. However, there is still lack of agreement about the mechanisms of cracking in many stainless steel/environment systems (Ref 2). In fact, the multiplicity of proposed mechanisms and the disagreement as to which mechanisms are operative (Ref 2), have led to the evolution of a simplistic nomenclature that describes SCC in terms of the environments that cause it. The terms "chloride SCC," "caustic SCC," and "polythionic acid SCC" are often used to describe SCC of stainless steels in those types of environments. The term "high-temperature water SCC" usually denotes SCC in simulated boiling water reactor (BWR) and pressurized water reactor (PWR) coolant environments. The term "irradiation-assisted SCC" refers to SCC in nuclear power station core components that are subjected to heavy doses of radiation within the core as well as to coolant water. The term "sulfide SCC" usually denotes hydrogen embrittlement, with the sulfide ion acting as a hydrogen ion recombination poison, promoting entry of hydrogen into the metal.

The extent to which these variously described forms of SCC are manifestations of the same process remains a matter of continuing debate that is not likely to be settled in the near future. Accordingly, in this chapter the various forms of SCC are discussed under the environment-related descriptors noted above. When considering the SCC of stainless steels, it is also useful to distinguish between cracking in sensitized and nonsensitized materials. Sensitization is particularly detrimental to the stress-corrosion resistance of austenitic stainless steels in a variety of environments, and in many cases the elimination of sensitization will eliminate SCC susceptibility. In view of the importance of sensitization to SCC, it is worthwhile to describe it here in some detail.

Sensitization

It is evident from Fig. 1 that in the development of the 300 series, considerable effort has gone into producing grades that resist sensitization. It is now widely accepted that this phenomenon is related to the precipitation of carbide at austenite grain boundaries. To understand this phenomenon in terms of microstructure, it is in-

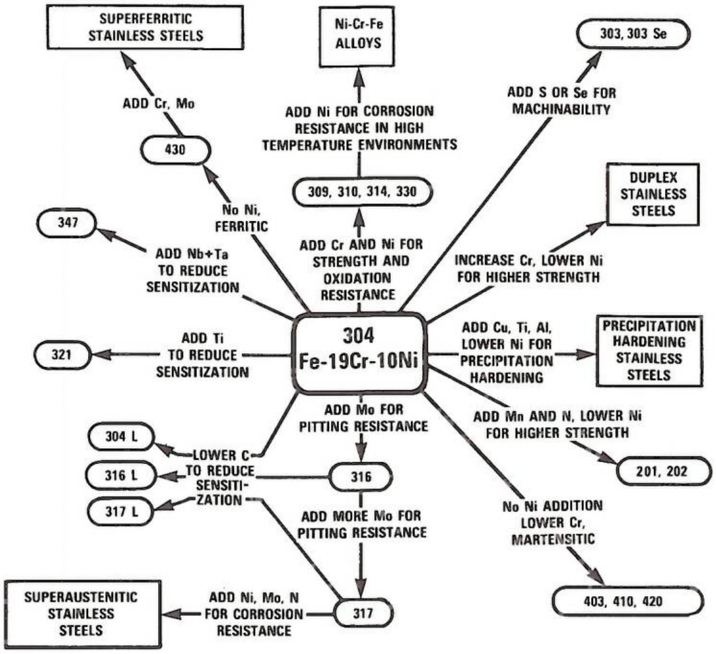

Fig. 1 Compositional and property linkages in the stainless steel family of alloys

structive to examine the equilibrium relationships and carbon solubility in the Fe-18Cr-8Ni alloy, illustrated in Fig. 2 (Ref 3). This figure shows that in alloys containing between about 0.03 and 0.7% C, the equilibrium structure should contain austenite, α-ferrite, and carbide ($M_{23}C_6$) at room temperature. In commercial alloys containing various austenite stabilizers, the reaction $\gamma + M_{23}C_6 \rightarrow \gamma + \alpha + M_{23}C_6$ (at line SK) is too sluggish to take place at practical rates of cooling from elevated temperatures. The same applies to the reaction $\gamma \rightarrow \alpha + M_{23}C_6$ at carbon contents below approximately 0.03%.

For commercial-purity materials, the transformation of austenite to α-ferrite is ignored in practice, and in considering carbon solubility in austenite, the simplified diagram (Ref 4) shown in Fig. 3 is often regarded as representative of real (*i.e.*, nonequilibrium) situations. In terms of this simplified diagram, up to 0.03% C should be soluble in austenite at temperatures up to 800 °C (1470 °F). Austenite that contains more than 0.03% C should precipitate $M_{23}C_6$ on cooling below the solubility line. However, at relatively rapid rates of cooling, this reaction is partially suppressed. This is the case in practice when type 304 stainless steel containing more than 0.03% C is heat treated at 1050 °C (1920 °F) to remove effects of cold working or hot working and cooled at a fairly rapid rate to room temperature. While some carbide may have precipitated on cooling, the room-temperature austenite is still largely supersaturated with respect to carbon.

If this supersaturated austenite is reheated to elevated temperatures within the $\gamma + M_{23}C_6$ field, further precipitation of the chromium-rich $M_{23}C_6$ will take place at the austenite grain boundaries. Certain time-temperature combinations will be sufficient to precipitate this chromium-rich carbide, but insufficient to rediffuse chromium back into the austenite near the carbide. This will result in the formation of envelopes of chromium-depleted austenite around the carbide (Ref 5, 6). Because the carbides precipitate along grain boundaries, the linking of the chromium-depleted envelopes provides a continuous path of lower corrosion resistance along the grain boundaries for the propagation of SCC. This type of structure is known as "sensitized," irrespective of whether the chromium depletion has been caused by slow

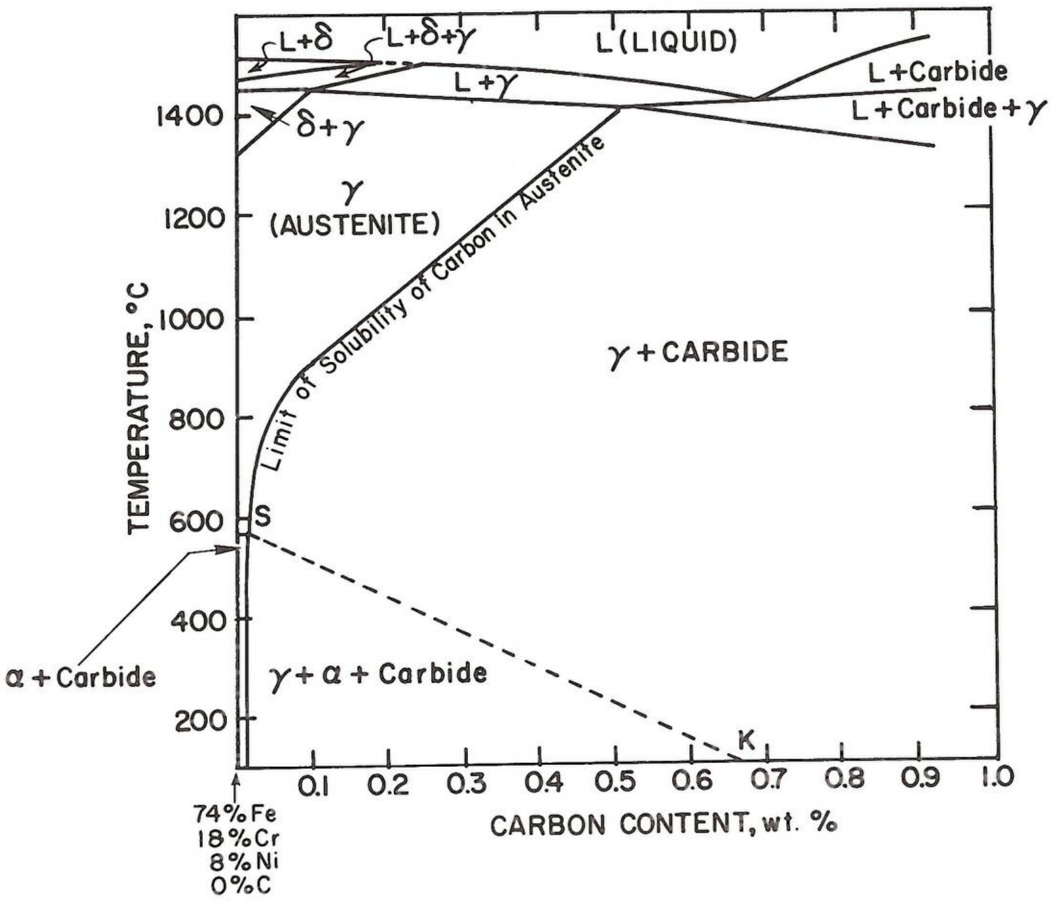

Fig. 2 Pseudo-binary phase diagram for an Fe-18Cr-8Ni alloy with varying carbon content. After Ref 3

cooling, heat treatment, elevated-temperature service, or welding. Sensitization also occurs in ferritic and martensitic stainless steels (Ref 1). The metallurgical remedies for reducing sensitization in austenitic stainless steels include (1) the use of low-carbon (0.03% maximum) grades of stainless steel (for example, types 304L, 316L, and 317L), (2) postweld heat treatment to rediffuse chromium back into the impoverished austenite, and (3) addition of titanium (type 321) or niobium plus tantalum (type 347) to precipitate the carbide at higher temperatures so that little carbon is left to precipitate as the chromium-rich grain-boundary carbide during cooling. Types 321 and 347 are sometimes given a stabilizing treatment at 900 to 925 °C (1650 to 1695 °F) to ensure maximum precipitation of carbon as titanium or niobium carbide. All of these remedies have certain advantages and disadvantages. Thus, postweld heat treatment is not always practicable in large structures, the stabilized grades can suffer another form of corrosive attack known as knife-line attack (Ref 1), and the low-carbon grades have lower strength.

To compensate for the lower strength of the low-carbon (L) grades, the nuclear power industry has supported the development of nitrogen-strengthened nuclear grade (NG) stainless steels (Ref 7). These are designated as types 304NG and 316NG and have the low carbon levels of the L-grades (that is, less than 0.03 wt% C), but contain added nitrogen at levels of $0.06 < N < 0.1$ wt% to increase strength. Sensitized types 304NG and 316NG have exhibited resistance to intergranular SCC when tested in high-purity water at elevated temperatures (Ref 7). However, other studies

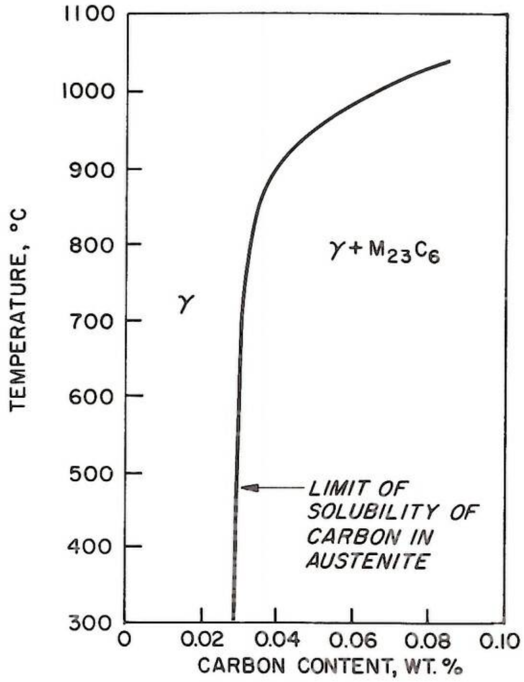

Fig. 3 Solid solubility of carbon in an Fe-18Cr-8Ni alloy. After Ref 4

(Ref 8) have shown that sensitized type 316NG exhibits transgranular SCC when tested in simulated BWR environments that contain sulfate ions as an impurity.

Other recent sensitization studies related to the nuclear power industry suggest that at BWR operating temperatures of about 288 °C (550 °F), radiation itself can cause chromium depletion at the grain boundaries in type 304 stainless steel and nickel-base alloys (Ref 9). In this radiation-induced phenomenon, described in greater detail in Chapter 6, there is no precipitation of chromium carbide and the chromium depletion is thought to occur by a process known as radiation-induced segregation. During the irradiation of an alloy, some constituents of the alloy migrate toward point defect sinks, such as grain boundaries or dislocation lines, and other constituents migrate away. This nonequilibrium segregation during irradiation was predicted in 1971 (Ref 10) and has subsequently received considerable attention. In austenitic steels, this segregation causes a depletion in the chromium levels and an enhancement in the nickel levels near grain boundaries during irradiation. Minor alloying elements are also redistributed; for example, silicon and phosphorus migrate toward the grain boundaries (Ref 9). These compositional changes occur in narrow regions close to grain boundaries. For example, the chromium depletion profiles suggest that the depletion widths are less than 20 nm (Ref 11). Cracking associated with this radiation-induced segregation is known as irradiation-assisted stress-corrosion cracking (IASCC) (Ref, 12, 13) and has been shown to be dependent on temperature and radiation fluence. IASCC of solutionized stainless steel is reported (Ref 9) to occur in service at fluences above 0.3×10^{21} n/cm^2 and at temperatures above 150 °C (300 °F) (Ref 14). Maximum radiation-induced segregation is reported to occur in the temperature range of 400 to 500 °C (750 to 930 °F) (Ref 12).

Chloride SCC

Chloride SCC in stainless steels was first widely studied using austenitic stainless steels in boiling magnesium chloride solutions. Nickel-free ferritic stainless steels are highly resistant to SCC in boiling magnesium chloride and sodium chloride solutions. Hence, a misleading impression has emerged that all ferritic stainless steels are immune to all chloride environments. As will be shown in later discussion, there is no immunity associated with the body-centered cubic (bcc) ferrite lattice, and, as in the case of austenitics, susceptibility of ferritic and duplex stainless steels to chloride SCC depends on alloy composition and structure and on environmental parameters. Also, the danger of chloride SCC in austenitic stainless steels should not be minimized; it is reassuring to see the supplier literature (*e.g.*, Ref 15) using the caution "may be susceptible to chloride stress-corrosion cracking" when describing all variants of the austenitic types 304, 316, 317, 321, 347, and 348 and the austenitic high-manganese/high-nitrogen grades UNS S21904 and S20910.

Austenitic Stainless Steels

The Magnesium Chloride Test. Because chloride SCC was first noted in the more widely used austenitic stainless steels, these materials have received the greatest amount of study. Most early evaluations employed boiling magnesium chloride solutions, which are very severe environments. Nevertheless, the magnesium chloride test has continued to be used because of its severity and the belief among end-users that stainless alloys that can survive lengthy periods of exposure to concentrated boiling magnesium chloride are not likely to exhibit chloride cracking in service. It is also used by researchers because it is simple and rapid, and allows comparison among tests performed in different laboratories.

The boiling magnesium chloride test was first described in 1945 (Ref 16). It has now been standardized as ASTM G 36. The boiling point of magnesium chloride solution is strongly dependent on concentration, as shown in Fig. 4 (Ref 17), and ASTM G 36 recommends the use of a test solution that boils at 155 °C ± 1 °C. It is important to make alloy comparisons under the same conditions, since significant differences in the relative susceptibilities of types 304 and 316 are found at different temperatures or concentrations (Ref 18).

Other studies (Ref 19) using a 40% $MgCl_2$ solution have shown that keeping the solution at or near the boiling point for long periods of time causes it to become more alkaline. This increased alkalinity is reported to cause changes in the chloride SCC susceptibility of type 304, with different behaviors observed in freshly prepared and in aged (preboiled) solutions (Ref 19). The increased alkalinity reduces the transgranular crack-propagation rate and changes the potential dependence of the cracking process (Ref 19).

ASTM G 36 notes that any type of stress-corrosion test specimen can be used in the magnesium chloride test. For a comprehensive discussion of the various types of test specimens, consult Ref 20. One of the most popular is the U-bend specimen (described in ASTM G 30), which contains large elastic and plastic strains and provides one of the most severe configurations available for smooth (as opposed to notched or fatigue precracked) specimens. It is also simple and relatively inexpensive to make and use.

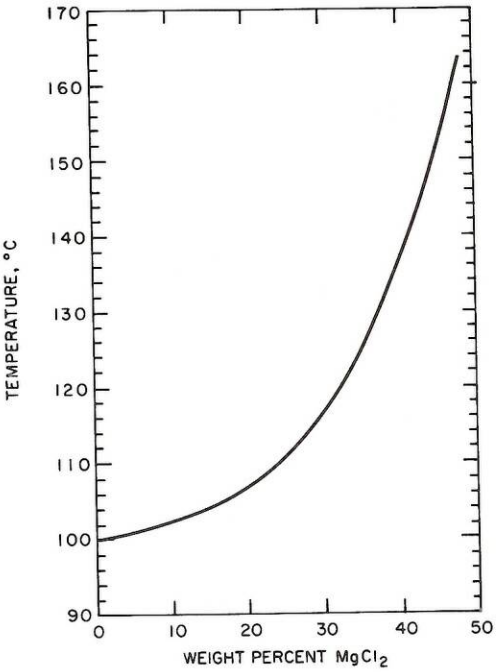

Fig. 4 Boiling points of aqueous magnesium chloride solutions at 1 atm as a function of concentration. After Ref 17

Effects of Composition. As noted before, there has been extensive research, often employing boiling magnesium chloride environments, on the effects of alloying additions on the chloride SCC resistance of stainless steels. The results, summarized in Fig. 5, have been taken largely from Ref 21 and 22. It is evident from Fig. 5 that many alloying additions appear to be detrimental to chloride SCC, but there are also those that can be categorized as "beneficial" and "variable." Those designated beneficial in Fig. 5 are nickel, cadmium, zinc, silicon, beryllium, and copper. It should be emphasized that the beneficial effect of nickel relates only to austenitic stainless steels. When present in relatively small quantities in ferritic stainless steels, nickel is detrimental to chloride SCC resistance. The beneficial effect of nickel on chloride SCC resistance of austenitic stainless steels and higher alloys has been extensively studied and is well documented (Ref 23-26).

Figure 6 (Ref 23) shows the effect of nickel content on the susceptibility to chloride SCC of stainless steel wire specimens tested in boiling magnesium chloride. The data of Fig. 6 suggest

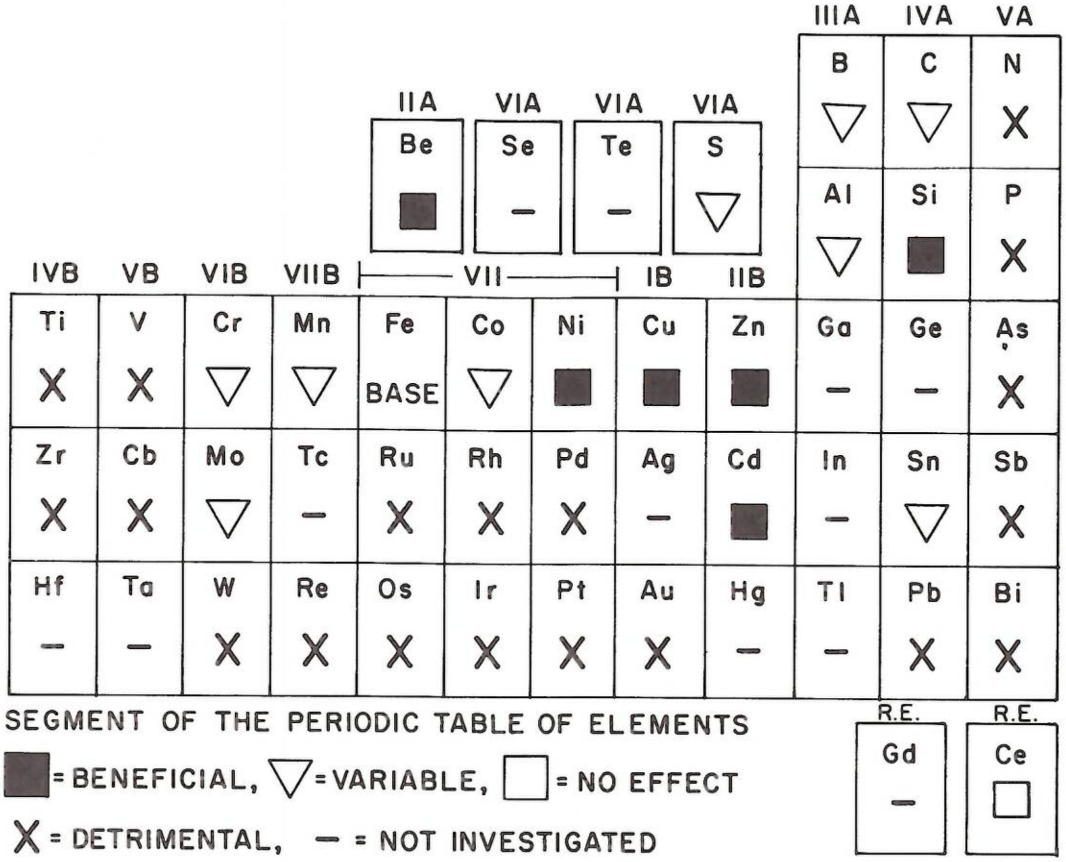

Fig. 5 Effect of various elements on resistance of austenitic stainless steels to SCC in chloride solutions

that very high nickel contents (about 50%) would be required for resistance to chloride SCC. This is at variance with general industrial experience, which is that chloride SCC is not usually observed at nickel contents at or above 42%. In fact, alloy 825 (42% Ni), Alloy G (44% Ni), and 20Cb3 (33% Ni) are often specified for applications requiring resistance to chloride SCC. Recent evaluations (Ref 27) using precracked fracture-mechanics specimens support the view that magnesium chloride is a much more severe environment than sodium chloride (Fig. 7), and suggest that the nickel level required for lack of susceptibility to SCC in sodium chloride may be between 30 and 40% (Fig. 8). In these tests, absence of crack propagation at a stress intensity of 60 $\text{MPa}\sqrt{\text{m}}$ (55 $\text{ksi}\sqrt{\text{in.}}$) is equated with resistance to SCC.

Additions of cadmium and zinc are also designated as beneficial (Fig. 5). Actually, there is very little information about the effects of these alloying elements. A 0.2% Cd addition to type 304 inhibited cracking in a vapor test that readily cracked type 304 (Ref 28), and a 1% Zn addition to an Fe-20Cr-15Ni alloy led to a fivefold improvement in SCC resistance (Ref 29). Therefore, the designation of these elements as beneficial must be regarded as tentative.

Alloying with silicon has been shown to be beneficial to chloride SCC resistance in boiling 42% $MgCl_2$ (Ref 30). However, other studies (Ref 31), summarized in Table 1, have shown that the beneficial effect of silicon noted in magnesium chloride tests is barely detectable, if at all, in sodium chloride solutions at higher temperatures. Beryllium and copper alloying additions have

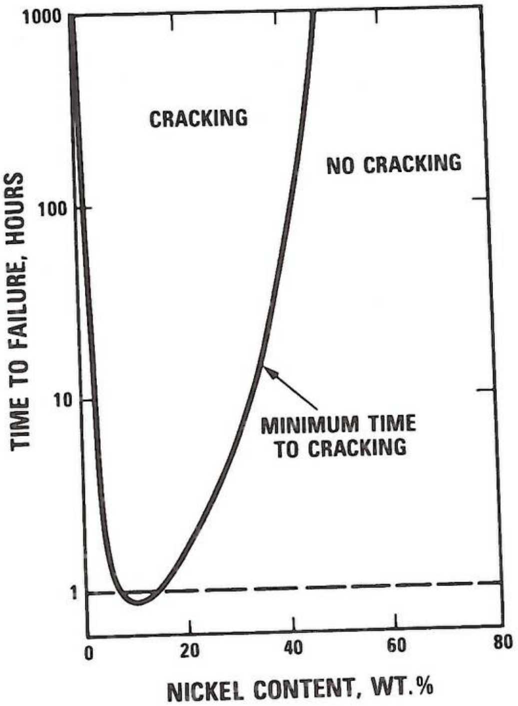

Fig. 6 Effect of nickel content on SCC susceptibility of stainless steel wires containing 18 to 20% Cr in a magnesium chloride solution boiling at 154 °C (309 °F). After Ref 23

been shown to be beneficial (Ref 32), although the effect of copper is slight.

The elements designated in Fig. 5 as having a variable effect on chloride SCC can be divided into the three categories shown in Table 2. Boron, aluminum, and cobalt appear to be detrimental in small quantities but beneficial in larger amounts (Ref 29, 32-36); tin and manganese appear to have no effect in certain ranges and beneficial or detrimental effects in other ranges (Ref 21, 36); carbon and chromium show minimal effect on chloride SCC resistance (Ref 21, 37). The effect of molybdenum appears to depend on the test environment. The magnesium chloride data suggest that molybdenum additions first decrease and then increase resistance to cracking, with a minimum resistance at about 1.5% Mo (Ref 37). No such pattern is in evidence in sodium chloride tests (Fig. 9) (Ref 27), which show cracking resistance increasing with increasing molybdenum content.

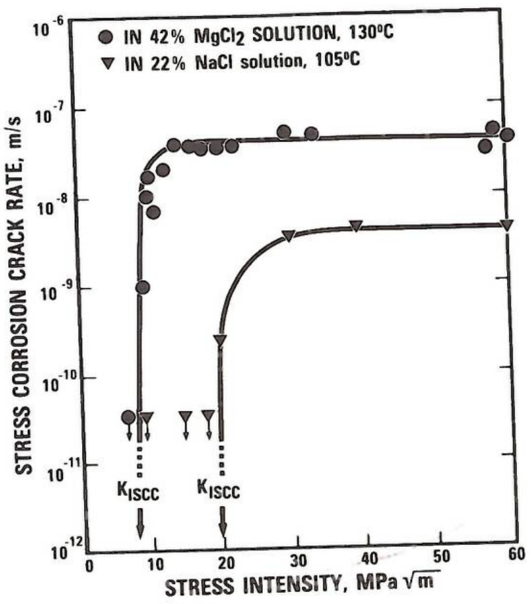

Fig. 7 Effect of stress intensity on the growth rate of stress corrosion cracks in type 304L stainless steel exposed to magnesium chloride and sodium chloride solutions. After Ref 27

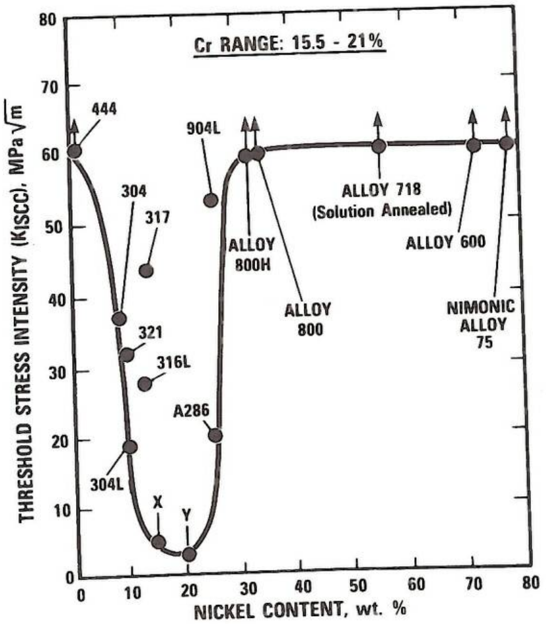

Fig. 8 Effect of nickel content on the stress-corrosion threshold stress intensity of various alloys in an aerated aqueous 22% NaCl solution at 105 °C (220 °F). Alloys X and Y are German heat-resistant grades. After Ref 27

Table 1 Effect of Silicon on SCC Resistance of Austenitic Stainless Steels in Various Chloride Media

Analysis, wt%(a)							Time to failure, h		
C	Si	Mn	Cr	Ni	N	Ferrite content, %	42% $MgCl_2$ at boiling point(b)	100 ppm NaCl at 250 °C (480 °F)	1000 ppm NaCl at 250 °C (480 °F)
0.020	0.46	0.83	18.28	15.10	0.07	0.5	219	28	10
0.022	0.80	0.77	18.54	15.20	0.08	0.5	292	24	5
0.031	2.48	0.83	18.58	15.23	0.07	1	1000 NF	92	32
0.031	3.69	0.88	18.46	15.20	0.07	1	1000 NF	81	15
0.031	4.53	0.86	18.42	15.28	0.08	2.5	1000 NF	54	50

(a) Balance iron. (b) 1000 NF, no failure in 1000 h
After Ref 31

Table 2 Effects of Various Elements on Resistance of Austenitic Stainless Steels to Chloride Cracking

Element	Beneficial	Detrimental
Boron	>0.1%	0.01%
Aluminum	0.1%	0.04%
Cobalt	>1.8%	1.50%
Tin	0.001–0.02%	No effect at 0.4%
Manganese	No effect at 0–2%	>2%
	Minimum in cracking resistance at:	
Carbon	0.06–0.1%	
Molybdenum	~1.5%	
Chromium	12–25%	

The foregoing survey of the effects of alloying additions on the chloride SCC resistance of austenitic stainless steels pertains to materials made by conventional melting practice, which contain many impurities. In this regard it has been shown that austenitic (as well as ferritic) stainless steels of very high purity are highly resistant to SCC in boiling magnesium chloride. Two examples are Fe-16Cr-20Ni (Ref 36) and Fe-18Cr-14Ni (Ref 38) high-purity alloys. In the latter case, the total metallic impurities were quoted at 1 ppm and the total nonmetal impurities (oxygen, nitrogen, sulfur, and phosphorus) at 10 ppm, the material having been prepared by plasma furnace melting. Other studies (Ref 39) have shown that decreasing the phosphorus content of an Fe-18Cr-10Ni stainless steel down to 0.003 wt% produces a material that is highly resistant to chloride SCC in a magnesium chloride solution boiling at 154 °C (309 °F) (Fig. 10). It has been suggested (Ref 40) that these high-purity alloys are resistant because their corrosion potentials are outside the potential range where SCC occurs.

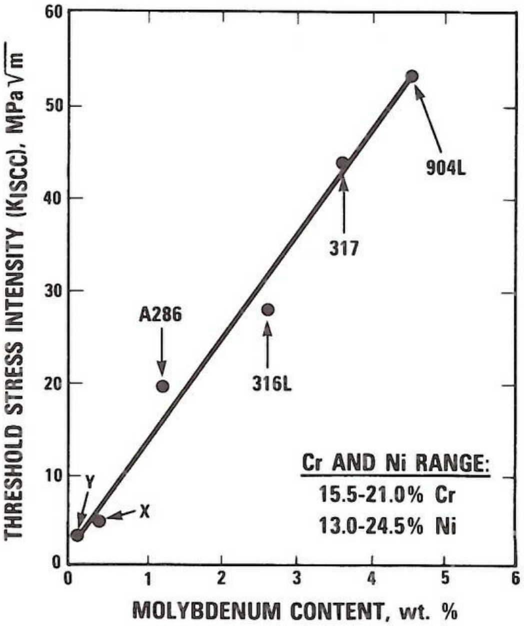

Fig. 9 Effect of molybdenum content on the stress-corrosion threshold stress intensity of Fe-Cr-Ni-Mo alloys in an aerated aqueous 22% NaCl solution at 105 °C (220 °F). Alloys X and Y are German heat-resistant grades. After Ref 27

Effects of Stress. As shown in Fig. 11 (Ref 41), decreasing the applied stress increases time to failure, and at low stresses a runout (threshold) stress is indicated. Careful studies (Ref 42) using

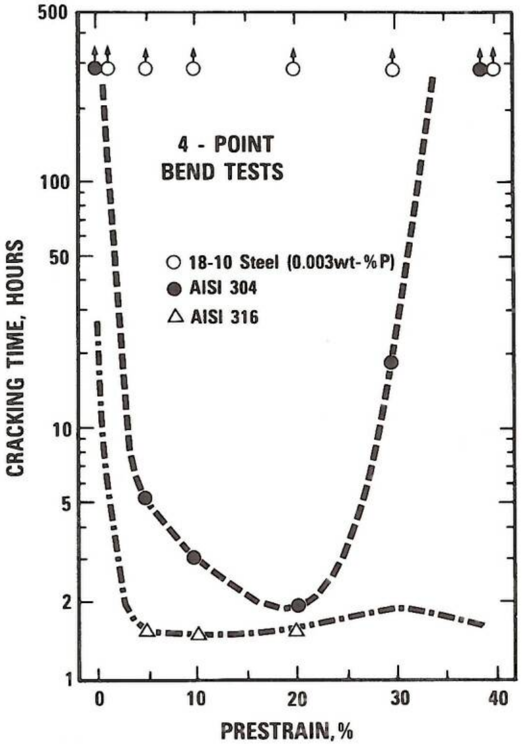

Fig. 10 Effect of cold work on the cracking time of a low-phosphorus (0.003% P) 18Cr-10Ni stainless steel and types 304 and 316 in magnesium chloride solutions boiling at 154 °C (309 °F) under an applied tensile stress of 196 MPa (28 ksi). After Ref 39

solution-annealed type 347 electropolished tensile specimens have established a threshold stress for this material at approximately 160 MPa (23 ksi), as indicated in Fig. 12. Threshold stress intensities (K_{ISCC}) obtained using precracked fracture-mechanics specimens in boiling magnesium chloride and sodium chloride solutions have been measured for various stainless steels, as shown in Fig. 7 to 9 (Ref 27). These threshold stress intensities should be regarded as stress-intensity factors below which the rate of cracking in a given environment is very low, rather than as absolute thresholds.

The method of increasing resistance to chloride SCC by reducing stress level has been studied. Stress, however, is a difficult parameter to control, and while it is obviously good practice to minimize applied (design) stresses, the presence of tensile residual stresses in the material can negate any benefit. The only sure way to control stresses is by stress-relief annealing the fully assembled structure. Full stress relief can be attained by annealing in the range of 800 to 900 °C (1470 to 1650 °F), since this causes a recrystallization of the deformed (internally stressed) grains. Unfortunately, this is often an option only for small components. For larger components, it is sometimes possible to achieve partial stress-relieving by heating to 400 to 600 °C (750 to 1110

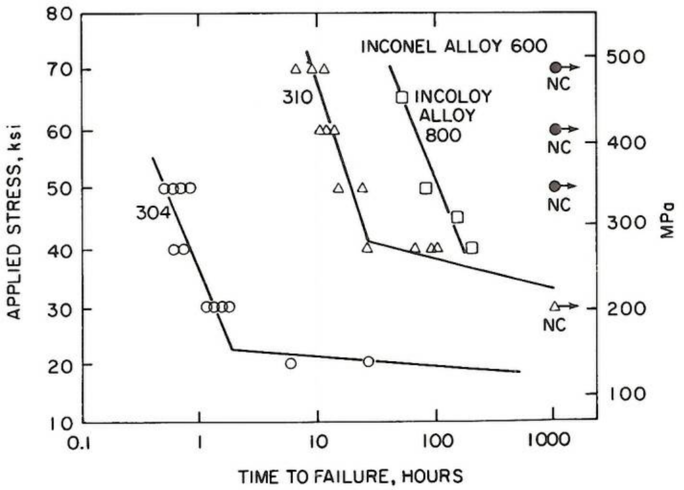

Fig. 11 Effect of applied stress on the times to failure of various alloys tested in a magnesium chloride solution boiling at 154 °C (309 °F). After Ref 41

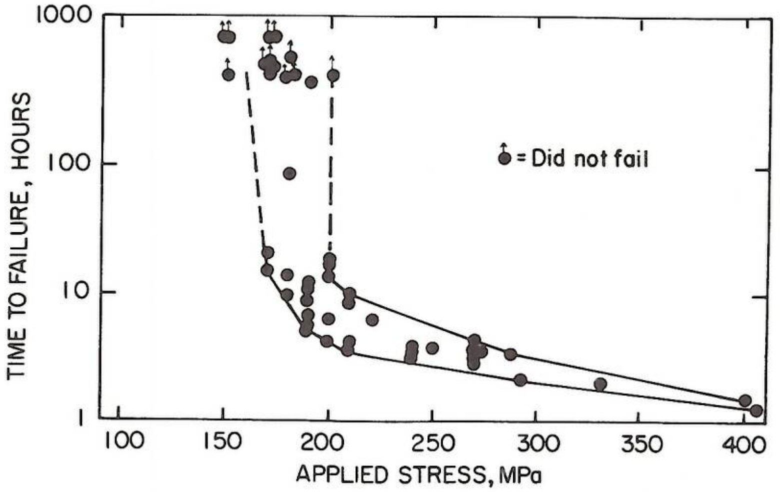

Fig. 12 Effect of applied stress on the time to failure of solution-annealed and electropolished type 347, tested in a magnesium chloride solution boiling at 145 °C (293 °F). After Ref 42

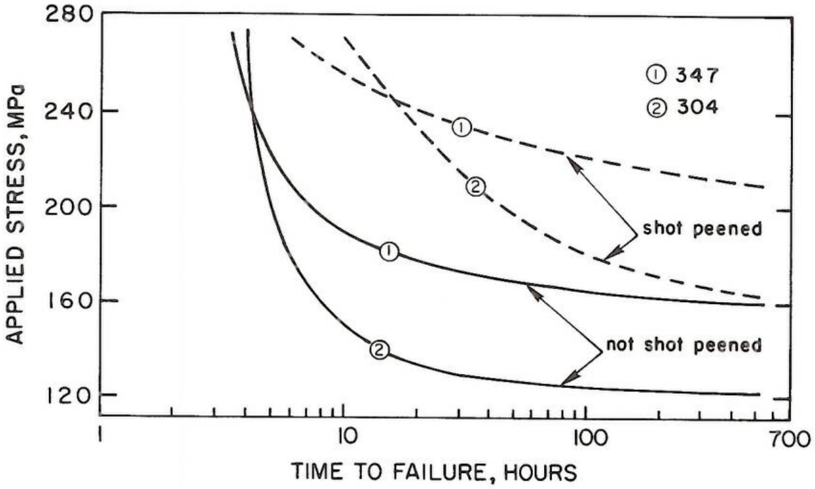

Fig. 13 Effect of peening with 40 to 80 μm glass shot on the times to failure of types 304 and 347 in a boiling 42% $MgCl_2$ solution . After Ref 43

°F), and it is believed, particularly in Europe, that even such partial stress-relieving can significantly improve resistance to chloride SCC. However, the benefits of any such procedure should be carefully weighed against potential sensitization problems. Compressive residual stresses, such as may be introduced by careful shot peening, have been shown to increase resistance to chloride SCC (Fig. 13) (Ref 43).

The effects of various surface finishes, which can produce stress variations due to local work hardening, martensitic transformation, residual stresses, and embedded material from abrasives and machining equipment, or provide stress raisers such as deep grooves or notches, are virtually impossible to quantify. All that can be said is that comparative evaluation of chloride SCC resistance should be carried out with nominally identical surface finishes. In particular, predictive laboratory evaluations should be performed using surface finishes identical to those encountered in service.

Effects of Microstructure. A schematic of the microstructural features found in stainless steels is shown in Fig. 14 (Ref 44), and many of these features have an effect on chloride SCC, as noted below.

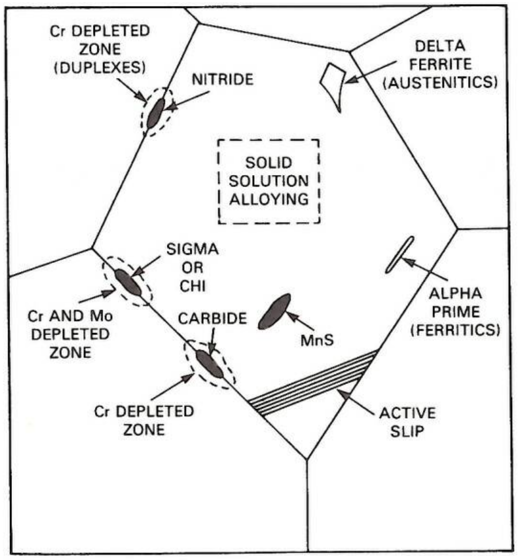

Fig. 14 Schematic of microstructural features found in stainless steels. After Ref 44

The presence of δ ferrite in austenitic stainless steels generally improves resistance to chloride SCC. An example of this for several cast austenitic stainless steels is shown in Fig. 15 (Ref 45). The beneficial effect of δ ferrite is generally attributed to its interference with the propagation of cracks across the austenite matrix. To obtain significantly improved resistance, however, considerable quantities of ferrite must be present, such as those found in duplex stainless steels. These are discussed in the section "Duplex Stainless Steels" in this chapter.

Regarding σ phase, few attempts have been made to evaluate its effect on chloride SCC resistance. A metallographic study (Ref 46) has shown that the transgranular cracks produced in boiling 42% $MgCl_2$ avoid or bypass σ phase produced in high-silicon types 316 and 317 by heating for 4 h at 871 °C (1600 °F).

Studies (Ref 46, 47) have failed to identify any relationship between sulfide stringers and the transgranular cracks produced in boiling magnesium chloride environments. The cracks appear to ignore the sulfide stringers. Other studies suggest

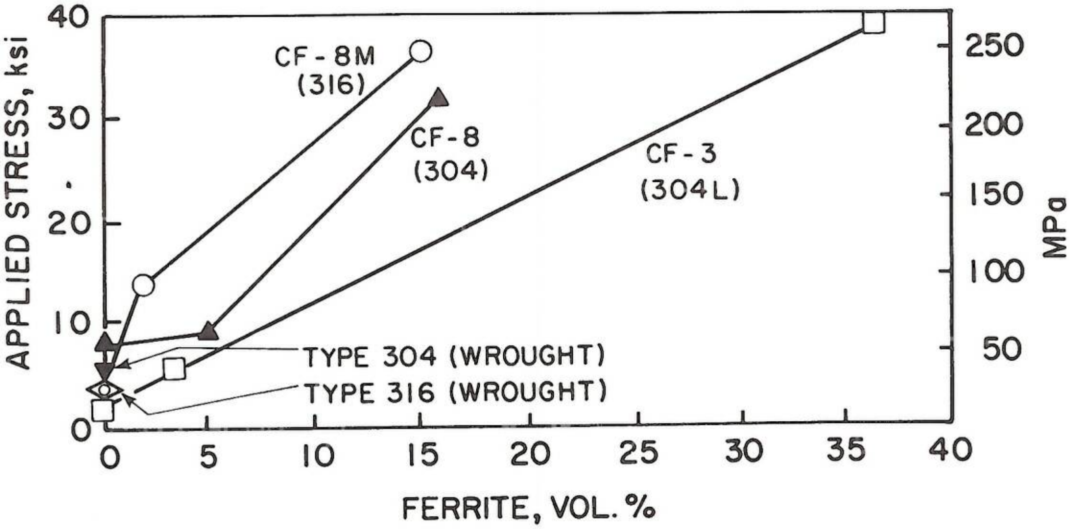

Fig. 15 Effect of ferrite content on the stress required to induce chloride SCC in various cast stainless steels. Materials exposed for 8 h in condensate from a 875 ppm chloride solution at 204 °C (400 °F). After Ref 45

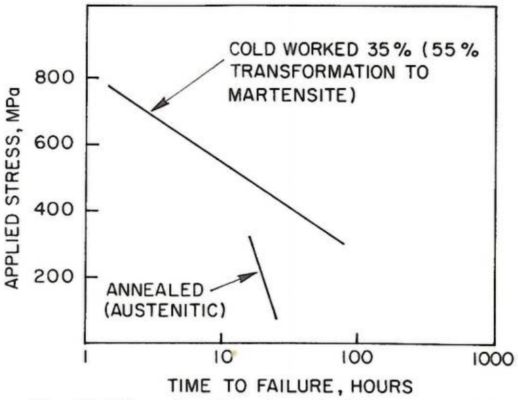

Fig. 16 Effect of cold work on the SCC susceptibility of type 301 in a boiling 40% $CaCl_2$ *solution. After Ref 49*

that there may be an association between crack initiation and sulfides (Ref 48).

Plastic deformation of austenitic stainless steels results in both work hardening and partial transformation to α and ε martensites. Therefore, it is very difficult to separate effects caused by cold work (slip) from those caused by transformation to martensites. Studies (Ref 49) using type 301, which readily transforms to martensites on cold working, show that at comparable applied stresses (*e.g.*, 300 MPa, or 43.5 ksi) the cold-worked and partially transformed material exhibits longer times to failure than the untransformed material (Fig. 16). However, the deformed material has a higher yield stress. Studies (Ref 50) using prestrained wires of type 310, which shows little tendency for transformation to martensites, suggest a minimum at 10% prestrain (Fig. 17). Other reports of the observation of such minima have been compiled in Ref 21. An exception appears to be type 316 (Fig. 10), which shows a sharp decrease with strain but no increase at higher strains (Ref 39). Current understanding of this phenomenon can be summarized by stating that, in general, significant cold work (*e.g.*, 35%) increases time to failure, as shown by the data for type 321 in Fig. 18 (Ref 49).

Sensitization is very detrimental to chloride SCC resistance, and in many cases it appears to cause SCC. As shown in Table 3 (Ref 51), sensitization can cause many stainless steels to become susceptible to intergranular cracking in chloride environments such as marine atmosphere. Sensitization is also reported (Ref 52) to cause intergranular chloride SCC of types 304 and 316 in synthetic seawater and in 0.1 M NaCl solutions at 80 °C (175 °F). More quantitative tests using fracture-mechanics test specimens have shown that the threshold stress-intensity factor for SCC susceptibility, K_{ISCC}, of type 304 stainless steel tested in a 22% NaCl solution at 105 °C (220 °F) is decreased from a value above 35 MPa$\sqrt{m}$ (32 ksi$\sqrt{in.}$) to a value below 9 MPa$\sqrt{m}$ (8 ksi$\sqrt{in.}$) as a result of sensitization (Ref 27).

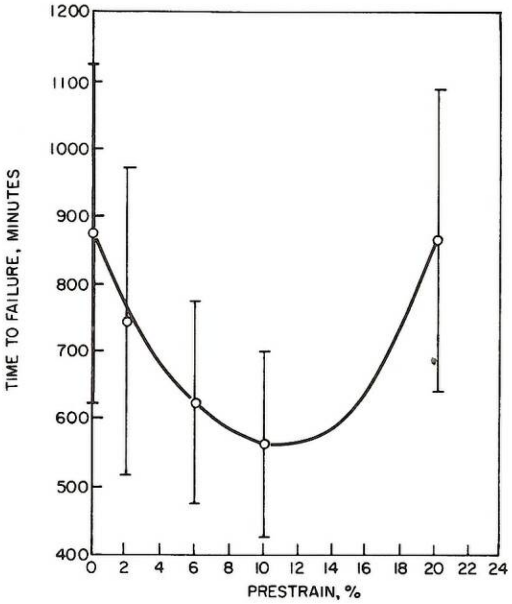

Fig. 17 Effect of prestrain on the time to failure of type 310 exposed to a magnesium chloride solution boiling at 154 °C (309 °F) and stressed at 90% of the yield stress. After Ref 50

Stress-corrosion cracking in sensitized stainless steels generally propagates along an intergranular crack path, whereas nonsensitized materials exhibit predominantly transgranular cracking in environments such as boiling magnesium chloride. However, exceptions occur, and the factors determining the selection of a crack path require further research. Sensitization-induced SCC in the high-temperature water environments of nuclear light-water reactors is discussed later in this chapter.

Effects of Environmental Variables. Temperature is an important variable in determining

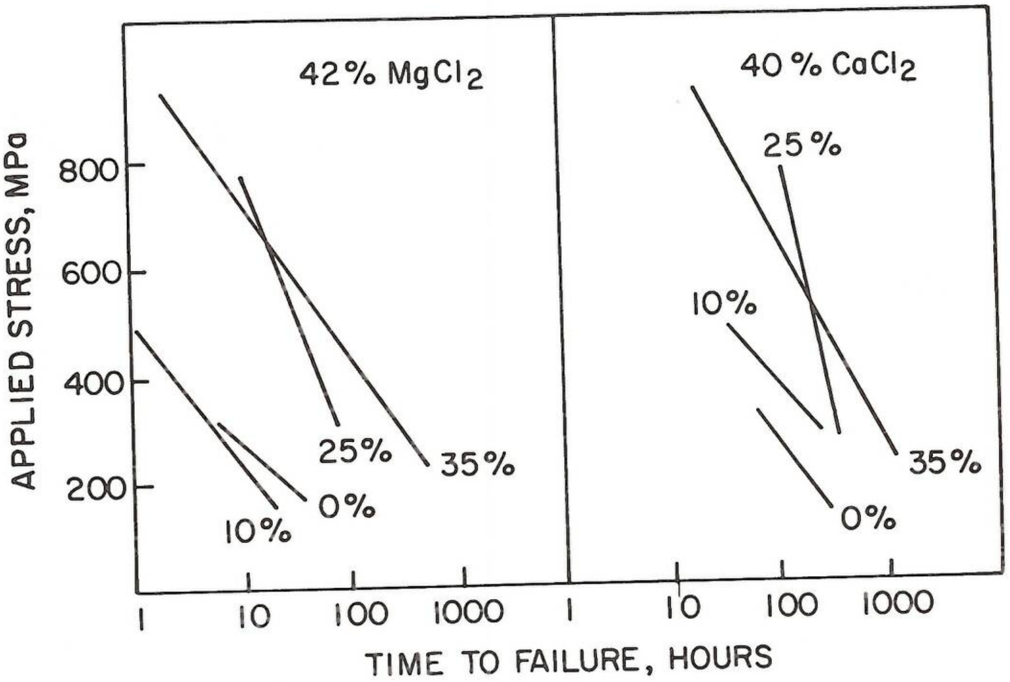

Fig. 18 Effect of cold work (%) on the SCC susceptibility of type 321 in boiling magnesium chloride and calcium chloride solutions. After Ref 49

Table 3 Results of SCC Tests in Which U-Bend Specimens Were Exposed for 5 Years to Marine Atmosphere in the 80-Ft Lot at Kure Beach

	Condition(a)			
Material	**Annealed**	**Welded**	**Cold worked, 1/4 hard**	**Sensitized, 650 °C/1.5 h/FC**
201	NF	NF	NF	IGA
301	NF	IGA	NF	IGA
302	NF	NF	NF	IGA
304	NF	NF	NF	IGA
304L	NF	NF	NF	NF
309	NF	NF	...	IGA
310	NF	NF	...	NF
316	NF	NF	NF	IGA
Carpenter 20Cb3	NF	NF	...	NF
Incoloy alloy 825	NF	NF	...	NF
Incoloy alloy 800	NF	NF	...	NF
Inconel alloy 600	NF	NF	...	NF

(a) NF, no failure in 5 years; IGA, intergranular attack; FC, furnace cooled
After Ref 51

whether chloride SCC will occur. The traditional engineering viewpoint, based on practical experience (Ref 53), has been that chloride SCC does not occur in nonsensitized austenitic stainless steels at temperatures below about 60 °C (140 °F) in near-neutral chloride solutions. Under the severe conditions encountered in a fracture-mechanics SCC test, this minimum temperature can

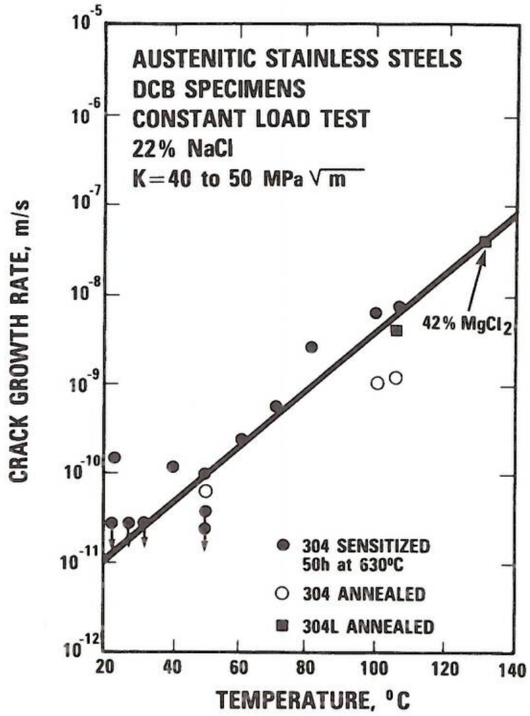

Fig. 19 Effect of temperature on SCC velocity for austenitic stainless steels in concentrated chloride solutions. After Ref 27

be lowered to 50 °C (120 °F) for annealed type 304 and to temperatures approaching ambient for sensitized type 304 (Fig. 19) (Ref 27).

Instances of transgranular chloride SCC in service in nonsensitized austenitic stainless steels at ambient temperature have been reported to occur in atmospheres above indoor swimming pools (Ref 54, 55) and in the marine atmosphere (Ref 56, 57). The swimming pool atmospheres have caused chloride SCC in ceiling support rods made from type 304, type 316, and a German titanium-stabilized type 316 (DIN 1.4571). The mechanism of these swimming pool atmosphere failures is not understood, and their occurrence was not predicted (Ref 54).

Marine atmospheres have caused transgranular chloride SCC in type 303 (free-machining grade) nuts after 14 years of service (Ref 56), in type 304L heater sheaths and dished ends (Ref 57), and in type 304 pipe for an emergency cooling system (Ref 57). Common factors in the marine atmosphere failures were the presence of a hot, humid coastal atmosphere, contamination of the stainless steel by iron that rusted, and residual stresses from fabrication and fit-up. Reference 58

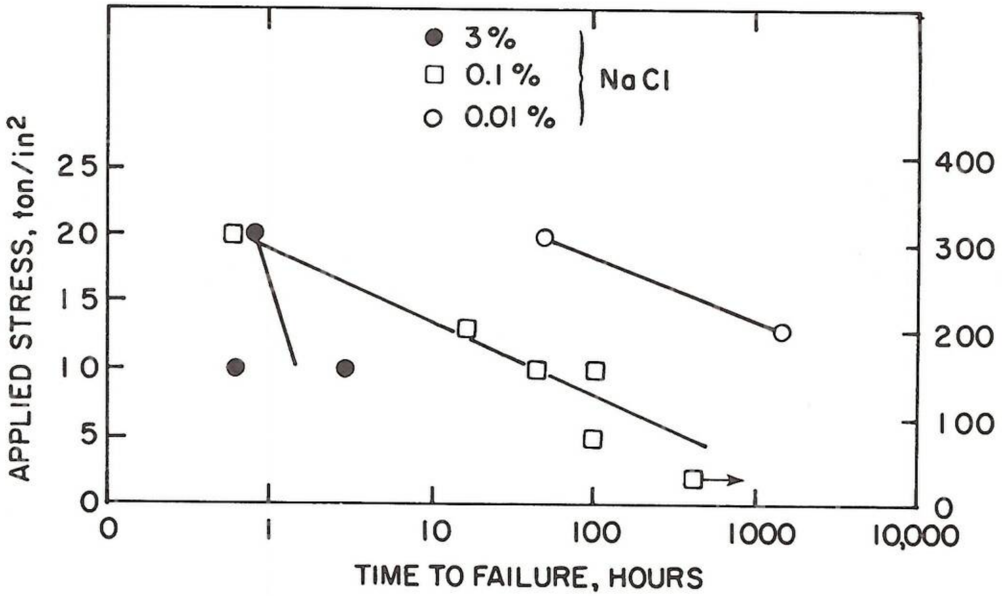

Fig. 20 Effect of chloride concentration on the SCC susceptibility of type 347 in oxygen-containing sodium chloride solutions at 250 °C (480 °F). After Ref 64

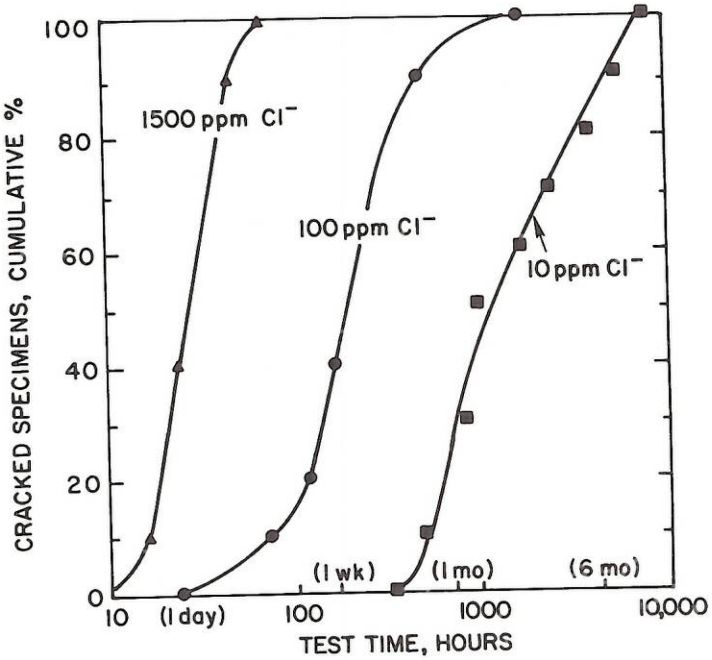

Fig. 21 Effect of chloride concentration on the SCC susceptibility of type 304 exposed at 100 °C (212 °F) under the concentrating conditions of the wick test. After Ref 65

outlines procedures for identifying and removing iron contaminants from stainless steel equipment.

Ambient-temperature chloride SCC of type 304 stainless steel has also been reported in solutions containing sulfuric acid and sodium chloride (Ref 59-61), and in hydrochloric acid solutions (Ref 59, 62). Type 304 U-bend specimens exposed to a 10 N H_2SO_4 + 0.5 N NaCl solution at 28 °C (82 °F) for 300 h exhibited primarily intergranular cracking, with only short transgranular cracks developing (Ref 59). However, type 316 tested under similar exposure conditions showed entirely transgranular cracking (Ref 59). Exposure of U-bend specimens of types 304 and 316 to a 5% HCl solution held at –5 °C (23 °F) for 742 h resulted in transgranular cracking (Ref 59). This form of acid-induced SCC occurs at potentials in the active region (Ref 62). Chloride SCC of stainless steels has also been reported (Ref 55) to occur on exposure to hydrogen chloride vapor at – 4 °C (25 °F).

Under immersion conditions, chloride SCC is facilitated by increased chloride concentrations, presence of oxygen, and lowered pH. The relationship between chloride concentration and SCC susceptibility is not simple, and in elevated-temperature environments it is linked with oxygen concentration. The presence of oxygen is not necessary to cause SCC in concentrated chloride solutions boiling at atmospheric pressure, since their oxygen contents should approach zero. However, the introduction of oxygen into such solutions by bubbling accelerates SCC (Ref 63).

There is some evidence to suggest that in oxygen-containing higher-temperature sodium chloride solutions, susceptibility to SCC decreases with decreasing chloride concentration, as indicated in Fig. 20 (Ref 64). However, the maintenance of low chloride levels cannot ensure freedom from SCC under conditions in which chloride can concentrate in crevices or shielded areas. The effect of temperature on chloride SCC susceptibility of type 304 under concentrating conditions is shown in Fig. 21 (Ref 65). In the wick test used to obtain the data of Fig. 21, a porous insulating material was used to draw the salt solution to the heated surface of a stressed speci-

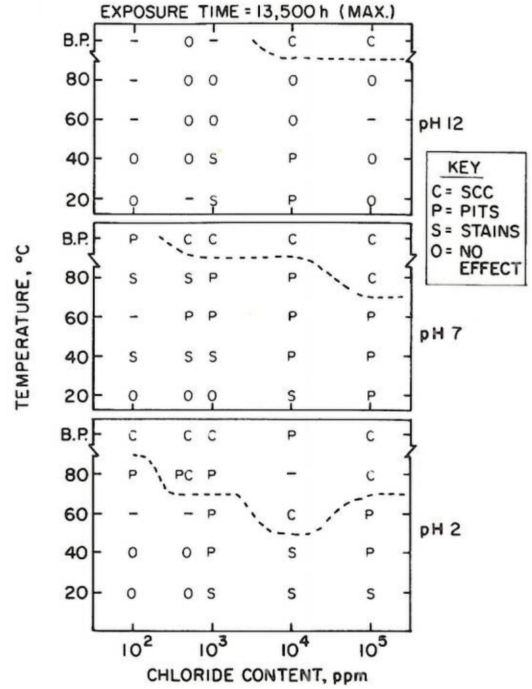

Fig. 22 Effect of pH on the chloride content and temperature required to produce SCC of type 304 in sodium chloride solutions. After Ref 69

men, where chloride can concentrate (Ref 20, 65, 66).

Regarding pH, it has been determined (Ref 67) that the pH of the solution at the tip of a crack in type 304 undergoing SCC in magnesium chloride is between 1.2 and 2.0. This suggests that, as in the case of pitting and crevice corrosion, acidification may be occurring by the hydrolysis of metal ions. In the case of pitting, increase in the bulk pH of the solution increases pitting resistance (Ref 68), and a similar improvement with increasing pH has been reported for chloride SCC resistance [see Fig. 22 (Ref 69) and Table 4 (Ref 70)]. However, as noted later, caustic SCC may occur in stronger caustic solutions. Acidity may also explain (Ref 55) why magnesium chloride and calcium chloride, which dissolve to form acidic solutions (Ref 19), cause chloride SCC.

Electrode potential has a major effect on susceptibility to chloride SCC. Detailed studies (Ref 71), summarized in Fig. 23, have established the relationships among applied potential, applied stress, and time to failure for type 304 stainless steel in boiling 42% $MgCl_2$. Increasing the potential in the noble direction facilitates cracking, whereas increasing the potential in the active direction reduces susceptibility until a cathodic protection potential is attained.

Regarding cathodic protection, it has been shown (Ref 72) that both impressed currents and sacrificial anodes can be used to prevent chloride SCC of type 304 in boiling 42% $MgCl_2$. Cathodic protection is also effective for preventing crack initiation in sensitized type 304 in NaCl solutions at 80 °C (175 °F) (Ref 73). Some researchers regard the cathodic protection potential as a critical cracking potential and equate it with the repassivation potential for crevice corrosion (Ref 74).

Inhibitors of chloride SCC have been extensively studied (Ref 72, 75-80). Silicates, nitrates, phosphates, carbonates, iodides, and sulfites have all proved to effectively inhibit chloride SCC if present in certain concentrations. Cadmium sulfate effectively inhibits chloride SCC of sensitized type 304 in 4 *N* NaCl solution acidified to a pH 2.3 with HCl at 100 °C (212 °F) (Ref 81).

Ferritic Stainless Steels

The high resistance to chloride SCC of types 405 and 430 ferritic stainless steels was first demonstrated in 1945 (Ref 16) and was confirmed in subsequent studies (Ref 72, 82). More recent studies have also demonstrated the SCC resistance of some of the newer ferritic grades tested as U-bend specimens (Ref 83) and precracked fracture-mechanics specimens (Ref 27). In the fracture-mechanics tests (Ref 27), the ferritic grades UNS S44400 (Remanit 4522) and S44800 (Remanit 4575) were fully resistant to chloride SCC at stress-intensity levels of 60 $MPa\sqrt{m}$ (55 $ksi\sqrt{in.}$) in 22% NaCl solutions at 105 °C (220 °F). The U-bend test data are shown in Table 5 (Ref 83), with types 409, 439, and 444 exhibiting resistance to chloride SCC in all three test environments.

The tests noted above have led to the misleading impression that all ferritic stainless steels are immune to SCC in all chloride environments. However, SCC of the ferritics has been reported in several instances: for type 434, type 430, and Fe-18Cr-2Mo in lithium chloride solutions (Ref 84), for sensitized type 446 in boiling magnesium