

CORROSION- RESISTANT PART 3 NICKEL ALLOYS

Nickel alloys provide levels of corrosion resistance not possible with other alloys. This is part three of a four-part series about corrosion-resistant nickel alloys.

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The corrosion-resistant nickel alloys are vitally important industrial materials. In most aggressive environments, they represent a significant improvement over the stainless steels, and their higher initial costs are offset by longer life, hence reduced equipment downtime. They are also easy to form and weld into complex industrial components.

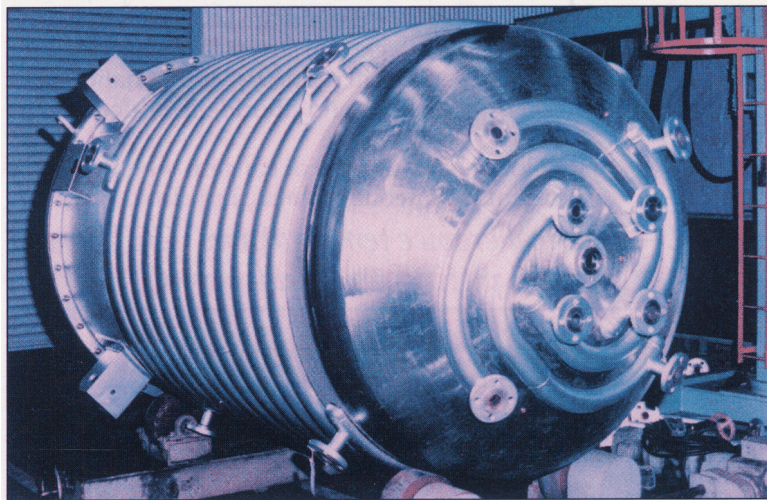
This article describes nickel alloy corrosion behavior in sea water and various salt solutions, as well as hydrochloric, hydrobromic, and hydrofluoric acids. Where sufficient data are available, 0.1 mm/y line charts provide comparisons with the stainless steels. To define the resistance of some of the nickel alloys to chloride-induced pitting and crevice attack, their Critical Pitting Temperatures (CPT's) and Critical Crevice Temperatures (CCT's) in acidified ferric chloride are given, alongside those for some of the more common stainless steels. To complement these data, previously published information on the crevice corrosion resistance of the same alloys in seawater are provided. To demonstrate the relative resistance of the nickel alloys and stainless steels to stress corrosion cracking (SCC), test results for U-bend samples in boiling magnesium chloride are given.

Next month's final article in the series will cover nickel alloy performance in sulfuric, phosphoric, and nitric acids. The welding and fabrication characteristics of the corrosion-resistant nickel alloys will be discussed, and some of their uses within the chemical process industries will be defined.

Sea water

Sea water is encountered by marine vessels, oil rigs, and coastal structures and facilities (which typically use sea water as a coolant). As a chlo-

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A reactor built for service in the chemical industry must be built of alloys that resist acids at high temperatures.

ride, it can induce pitting, crevice attack, and stress corrosion cracking of metallic materials, as well as uniform attack. Furthermore, marine equipment can become encrusted, leading to a form of crevice attack known as "under-deposit" corrosion. Biofouling is also an issue in sea water.

Fortunately, the nickel alloys possess good sea water resistance. In particular, those with high copper contents, such as alloy 400, resist biofouling (copper is a poison to microbes). For stagnant or low-velocity conditions, chromium- and molybdenum-bearing nickel alloys provide higher resistance to pitting and crevice attack.

Some recent crevice corrosion data for seawater, generated as part of a U.S. Navy study at the LaQue Laboratories in Wrightsville Beach, North Carolina, are presented in Table 1. Crevice tests were carried out in both still (quiescent) and flowing seawater, at 29°C, plus or minus 3°C. Two samples of each alloy were tested in still water for 180 days, and two samples of each alloy were tested in flowing water for 180 days. Each sample contained two possible crevice sites. In quiescent seawater, the results mirror those generated in acidified ferric chloride, with C-22 and C-2000 alloys as the most resistant. In flowing seawater, crevice attack of the stainless steels was shallower, and none of the Ni-Cr-Mo alloys exhibited crevice corrosion.

Salt solutions

Although many salts cause few problems for

Table 1 — Seawater crevice corrosion results

Alloy	Quiescent seawater		Flowing seawater	
	Number of attack sites	Depth, mm	Number of attack sites	Depth, mm
316L	2	1.80	2	0.32
254SMO	2	1.25	2	0.01
625	2	0.11	2	<0.01
C-22	0	0	0	0
C-276	1	0.12	0	0
C-2000	0	0	0	0

nickel alloys, some can induce insidious and unpredictable forms of attack. For example, water solutions of chloride salts are known to cause pitting, crevice attack, and stress-corrosion cracking of stainless steels in particular. Other halide salts (notably bromides and fluorides) induce similar effects.

Not only anions are of concern when salts are present in aqueous systems, but also cations can

be influential. For example, ferric ions and cupric ions can substantially alter the electrochemistry of acid systems, resulting in cathodic reactions of higher potential, and significant corrosion of alloys that would otherwise be inert. The Ni-Cu and Ni-Mo materials are particularly susceptible to such effects.

Fortunately, the nickel alloys in general are very resistant to chloride-induced stress corrosion cracking and some (notably the Ni-Cr-Mo materials) possess high resistance to pitting and crevice attack. In fact, much of their success in chemical industry applications is due to these attributes.

To assess the resistance of alloys to crevice attack and pitting, it is customary to measure their Critical Crevice Temperatures (CCT's) and Critical Pitting Temperatures (CPT's) in acidified 6 wt% ferric chloride, in accordance with the procedures defined in ASTM Standard G 48. These values represent the lowest temperatures at which crevice attack and pitting are encountered in acidified ferric chloride in a 72-hour time frame. CCT and CPT values for several nickel alloys and stainless steels are given in Table 2. These data clearly show the superiority of the chromium-bearing nickel alloys over the stainless steels.

A common solution for evaluating the resistance to chloride-induced stress corrosion cracking of metallic materials is boiling 45 wt.% magnesium chloride. Typically, U-bend samples are tested in this environment for periods up to 1008 hours, with interruptions to check for cracking. Data for several nickel alloys and stainless steels are presented in Table 3. The table shows that low-iron nickel alloys, such as the Ni-Cr-Mo materials, offer the highest resistance to stress corrosion cracking.

Table 2 — Critical crevice temperatures (CCT's) and critical pitting temperatures (CPT's)*

Alloy	CCT		CPT	
	°C	°F	°C	°F
316L	0	32	15	59
254SMO	30	86	60	140
28	17.5	64	45	113
31	42.5	109	72.5	163
G-30	37.5	100	67.5	154
G-35	45	113	95	203
625 40	104	100	212	
725 (Age-Hardened)	25	77	85	185
C-22	80	176	>120	>248
C-22HS (Annealed)	100	212	>120	>248
C-22HS (Age-Hardened)	75	167	110	230
C-276	55	131	>120	>248
C-2000	80	176	>120	>248

*Nickel alloys and stainless steels in acidified 6% ferric chloride (ASTM G 48, Methods C and D)

Table 3 — Time required to induce stress corrosion cracking*

Alloy	Time to cracking, hours
316L	2
254SMO	24
28	36
31	36
G-30	168
G-35	No Cracking in 1008 h
625	No Cracking in 1008 h
C-22	No Cracking in 1008 h
C-276	No Cracking in 1008 h
C-2000	No Cracking in 1008 h

*In U-bend samples of nickel alloys and stainless steels in boiling 45% magnesium chloride (ASTM G 30 and G 36)

Hydrobromic acid

Hydrobromic is one of the strongest mineral acids. Indeed, it is a more effective solvent for some ore minerals than hydrochloric acid because of its higher boiling point and stronger reducing action. One of the primary functions of hydrobromic acid is for the production of inorganic bromides for applications such as some medicines, adhesives, and photosensitive emulsions.

Of the nickel alloys, those with high molybdenum contents possess the highest resistance to hydrobromic and the other halogen acids. Iso-corrosion diagrams for B-3 and C-2000 alloys (as representatives of the Ni-Mo and Ni-Cr-Mo groups) are shown in Figures 1 and 2, respectively.

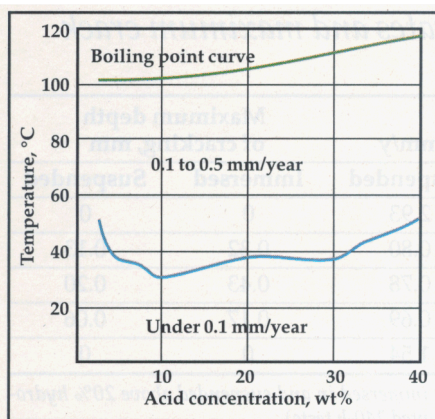


Fig. 1 — Iso-corrosion diagram for B-3 alloy in hydrobromic acid.

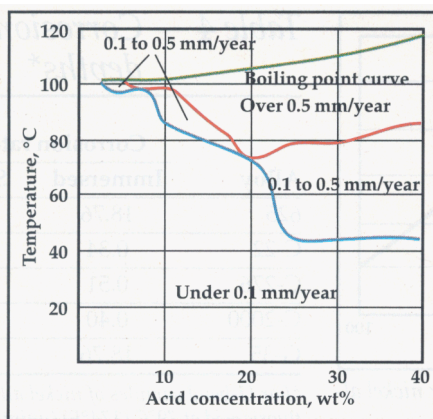


Fig. 2 — Iso-corrosion diagram for C-2000 alloy in hydrobromic acid.

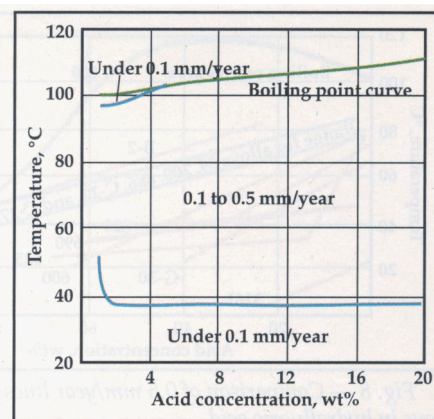


Fig. 3 — Iso-corrosion diagram for B-3 alloy in hydrochloric acid.

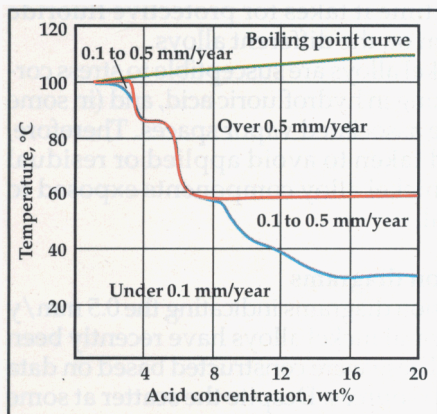


Fig. 4 — Iso-corrosion diagram for C-2000 alloy in hydrochloric acid.

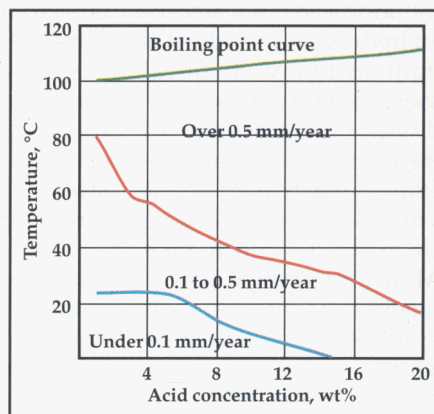


Fig. 5 — Iso-corrosion diagram for Alloy 400 in hydrochloric acid.

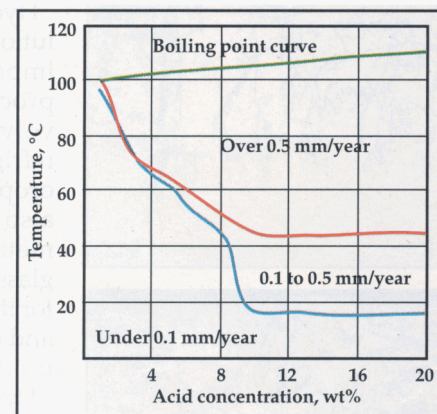


Fig. 6 — Iso-corrosion diagram for Alloy 625 in hydrochloric acid.

Figure 1 indicates that B-3 alloy can function up to the boiling-point curve in hydrobromic acid, although corrosion rates in excess of 0.1 mm/y are expected at temperatures above about 40°C (100°F). The diagram for C-2000 alloy is quite different. On a positive note, corrosion rates of less than 0.1 mm/y (the accepted limit for thin structures) are expected over a larger range. On the other hand, rates over 0.5 mm/y (the accepted limit for thick structures) are anticipated within a significant area below the boiling-point curve.

These diagrams were created by analyzing numerous corrosion rates generated in pure hydrobromic acid in the laboratory. With regard to the impurities and residuals often present in industrial process streams, if these are of an oxidizing nature, then they are detrimental to the Ni-Mo materials. The Ni-Cr-Mo alloys, on the other hand, are tolerant of species of an oxidizing nature, and even benefit from them. Such species include ferric ions, cupric ions, oxygen, chlorine, and hydrogen peroxide.

Hydrochloric acid

Hydrochloric acid is by far the most important chemical for corrosion-resistant nickel alloys in the chemical process industries. Not only is it widely encountered, but also it is very aggressive to the stainless steels. Furthermore, hydrochloric acid is indirectly responsible for the insidious effects of chloride salts on metallic materials.

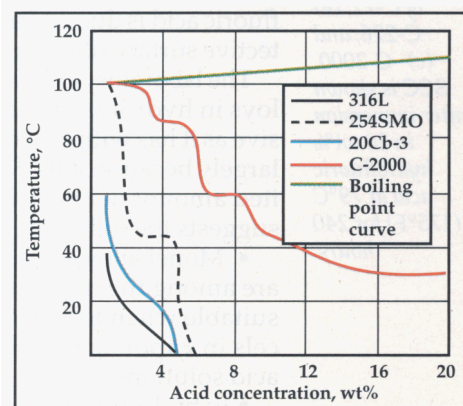
Iso-corrosion diagrams for alloys representing

the Ni-Mo, Ni-Cu, Ni-Cr, and Ni-Cr-Mo groups are shown in Figures 3 to 6. Figure 3 indicates that the Ni-Mo alloys can function in 0 to 20 wt% hydrochloric acid up to the boiling-point curve, without the corrosion rates exceeding 0.5 mm/y. Indeed, rates of 0.3 mm/y or less are typical above 40°C (100°F).

The Ni-Cr-Mo alloys are the next best option for hydrochloric acid, service, and are preferred at low concentrations and elevated temperatures. High-molybdenum Ni-Cr alloys, such as alloy 625 (Figure 6) also offer considerable resistance to hydrochloric acid.

For perspective, a comparison between the performance of the Ni-Cr-Mo materials (represented by C-2000 alloy) and three types of austenitic stainless steel is given in Figure 7. This indicates the concentration/temperature combinations at which a corrosion rate of 0.1 mm/y would be expected, based on laboratory tests in hydrochloric acid. Not surprisingly, the stainless steel with the highest molybdenum content (254SMO alloy) is the most resistant of the stainless steels. However, this falls well short of the C-2000 alloy.

Fig. 7 — Comparison of 0.1 mm/year lines in hydrochloric acid.



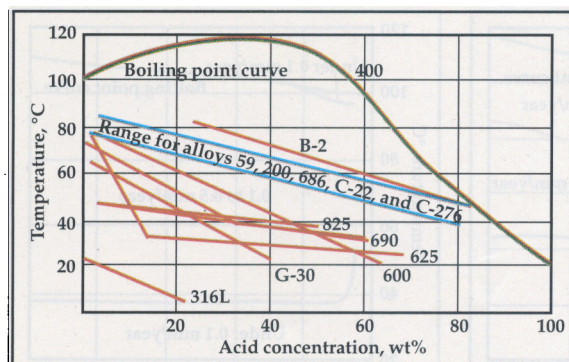


Fig. 8 — Comparison of 0.5 mm/year lines for nickel alloys in hydrofluoric acid.

Table 4 — Corrosion rates and maximum crack depths*

Alloy	Corrosion rate, mm/y		Maximum depth of cracking, mm	
	Immersed	Suspended	Immersed	Suspended
625	18.76	2.93	0	0
C-22	0.34	0.80	0.32	0.13
C-276	0.51	0.78	0.43	0.20
C-2000	0.40	0.69	0.17	0.06
G-35	18.76	1.54	0	0

*For U-bend samples of nickel alloys immersed in and suspended above 20% hydrofluoric acid at 79°C (174°F) (uninterrupted 240-h tests).

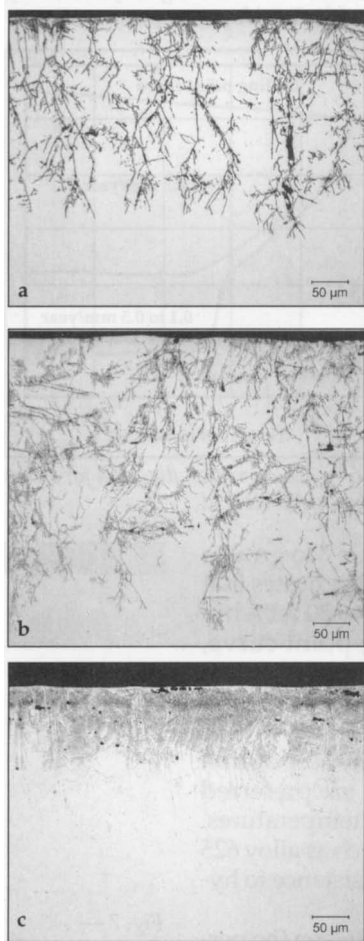


Fig. 9 — (a) Stress corrosion cracking in U-bend samples of C-22; (b) C-276; and (c) C-2000. SCC is shown after immersion in 20 wt% hydrofluoric acid at 79°C (175°F) for 240 hours.

Hydrofluoric Acid

Hydrofluoric acid is a water solution of hydrogen fluoride. It is important in many chemical processes, notably those involved with the production of refrigerants, adhesives, and fluoropolymers (such as PTFE). It also works to pickle various metallic materials and to etch glass. More important, it is used for the acid treatment of oil wells and the alkylation of petroleum products.

Hydrofluoric acid is among the most dangerous of chemicals, as it is highly corrosive to skin and mucous membranes. Containment of the acid is also a problem, especially at elevated temperatures and intermediate concentrations. The reactive metals (notably titanium, zirconium, niobium, and tantalum), for example, are readily attacked by hydrofluoric acid, and the stainless steels generally exhibit high corrosion rates.

Fortunately, the nickel alloys exhibit low to moderate corrosion rates in hydrofluoric acid, over wide ranges of concentra-

tion and temperature, and are thus suitable for many types of equipment involved in the manufacture and application of the acid. It is believed that the resistance of the nickel alloys to hydrofluoric acid is due, in part, to the formation of protective surface films, in particular nickel fluoride.

The laboratory characterization of the nickel alloys in hydrofluoric acid has not been as extensive as it has with other common inorganic acids, largely because of its dangerous nature. The limited amount of information available, however, suggests the following:

- Monel alloy 400 and Hastelloy C-2000 alloy are among the most resistant. Alloy 400 is most suitable when fully immersed; C-2000 alloy excels in vapor spaces above warm hydrofluoric acid solutions.
- In hydrofluoric acid laboratory tests, the du-

ration of testing is important. This probably relates to the time it takes for protective fluoride films to form on the different alloys.

- The nickel alloys are susceptible to stress corrosion cracking in hydrofluoric acid, and (in some cases) in the associated vapor spaces. Therefore, care should be taken to avoid applied or residual stresses in nickel alloy components exposed to the chemical.

Iso-corrosion diagrams

Iso-corrosion diagrams indicating the 0.5 mm/y lines for several nickel alloys have recently been published. These were constructed based on data from several sources. Despite the scatter at some concentrations and temperatures, undoubtedly due to different test times and conditions, the workers were able to provide a good, general guide to the performance of the nickel alloys in hydrofluoric acid. A reproduction of their summary plot is presented in Figure 8.

Stress corrosion cracking in hydrofluoric acid is a fascinating subject, because the cracks are unlike those caused by chloride salt solutions. Rather than individual deep cracks, hydrofluoric acid tends to induce fine craze-cracking that progresses in broad-front fashion.

Table 4 shows the results of a recent study involving an acid concentration of 20 wt%, a temperature of 79°C (175°F), and a test duration of 240 hours. The cracks observed in immersed U-bend samples of C-22, C-276, and C-2000 alloys are shown in Figure 9. Interestingly, those alloys that lost considerable weight during the tests (namely 625 and G-35) did not exhibit stress corrosion cracking, suggesting that the uniform corrosion front was propagating more rapidly than the crack front. Of those materials that did exhibit cracking, C-2000 alloy was the least susceptible, in terms of depth of cracking and crack width. In fact, it was difficult to resolve the cracks optically.

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