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

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Nickel is an ideal base for corrosion-resistant alloys. Not only is it inherently resistant to certain chemicals, but also it can be highly alloyed with elements known to enhance corrosion performance, such as chromium, copper, and molybdenum, while retaining its ductile face-centered cubic structure. Iron is not as accommodating; thus high levels of such elements are not possible in the stainless steels without structural instability.

In addition to commercially pure nickel, three binary alloy systems also provide exceptional corrosion resistance. These include nickel-chromium (Ni-Cr), nickel-copper (Ni-Cu), and nickel-molybdenum (Ni-Mo). Chromium enhances the resistance of nickel to oxidizing acids by encouraging the formation of passive films. Copper is very helpful in seawater, brackish water, and reducing acids, in particular hydrofluoric. Molybdenum is extremely beneficial in all reducing acids.

This article focuses on the effects on various nickel alloys of industrially important acids, bases, and salts. These include nitric acid, phosphoric acid, sulfuric acid, and caustic alkalis.

Nitric acid
Unlike the three halogen acids discussed last month, nitric acid causes a high potential (oxidizing) cathodic reaction that readily induces passive films on high-chromium stainless steels. In fact, the stainless steels are very resistant to nitric acid and the nickel alloys are not needed unless there are extenuating circumstances, such as the additional presence of halogen acids or halide salts.

Some nickel alloys exhibit good resistance to nitric acid, notably those Ni-Cr and Ni-Cr-Mo materials with high chromium contents. Nitric acid iso-corrosion diagrams are shown for C-2000 and G-35 alloys in Fig. 1 and 2. From these, the strong influence of chromium content can be deduced. The G-35 alloy, with a chromium content of 33 wt%, exhibits corrosion rates of less than 0.1 mm/y at all temperatures up to the boiling point curve, at acid concentrations up to 70 wt%.

Phosphoric acid
About ten million tons of phosphoric acid are produced annually in the United States, 80% of which is used in the production of agricultural fertilizers. Most of this acid is made by the “wet process,” which involves a reaction between sulfuric acid and phosphate rock.

Iso-corrosion diagrams do not exist for fertilizer-grade phosphoric acid. This is partly because impurity contents vary from country to country...
and from plant to plant due to variations in the composition of phosphate rock. In addition, the corrosivity of a particular solution can vary with time of storage, as a result of impurity interactions. Impurities include fluoride ions, chloride ions, silica, aluminum, iron (which serves to increase the oxidizing potential of the acid), calcium, and sodium.

Instead, it is customary to test alloys at specific concentrations and temperatures typical of the production process. Within the fertilizer industry it is also customary to define phosphoric acid concentrations in terms of P₂O₅ content. Corrosion rates for G-30 and G-35 alloys in several concentrations of P₂O₅ (supplied by plants in Florida) at 121°C are shown in Fig. 3.

Pure phosphoric acid, which is added to foods, is made by oxidizing elemental phosphorus derived from phosphate rock, then adding water. This type of phosphoric acid is much less corrosive than the fertilizer grade, as indicated by the iso-corrosion diagrams for B-3 and C-2000 alloys in Fig. 4 and 5. Indeed, only at high concentrations and temperatures do the Ni-Mo, Ni-Cr, and Ni-Cr-Mo alloys exhibit corrosion rates in excess of 0.1 mm/y in pure phosphoric acid.

Sulfuric acid

Sulfuric acid is one of the most important industrial chemicals. Not only is it used in the manufacture of fertilizer-grade phosphoric acid, but also it serves as a catalyst in the petroleum industry and as a reagent in the production of detergent, polymers, and pigments.

Provided that the acid is pure, the Ni-Mo materials are the most resistant nickel alloys; second best are the Ni-Cr-Mo alloys. Impurities of an oxidizing nature are extremely detrimental to the function of the Ni-Mo materials, whereas the Ni-Cr-Mo alloys generally benefit from such impurities. Iso-corrosion diagrams for B-3, C-2000, 400, and 625 alloys are shown in Fig. 6 to 9. A 0.1 mm/y line comparison between C-2000 alloy, 316L, 254SMO alloy, and 20Cb-3 alloy (designed especially for service in sulfuric acid) is shown in Fig. 10.

Sulfuric acid is reducing to the nickel alloys at concentrations up to about 60 wt%(meaning that the cathodic reaction is hydrogen evolution). At higher concentrations, other cathodic reactions are possible, and some materials exhibit sharp dips in performance. Concentrated, industrial-grade sulfuric acid is known to contain impurities of an oxidizing nature; indeed, at temperatures in excess of about 90°C (194°F), the oxidizing potential of this acid is beyond the scope of the chromium-bearing nickel alloys.
A nickel alloy designed for such situations is a high-silicon Ni-Cr material known as D-205 alloy. However, the mechanical properties of D-205 weldments are such that it can only function safely in the form of plate heat exchangers.

Caustic alkalis
Sodium hydroxide (known also as caustic soda) and potassium hydroxide (known also as caustic potash) are widely used chemicals. Applications include the manufacture of soap, paper, and aluminum. They also serve to neutralize acids, especially in the petrochemical industries. Molten sodium hydroxide functions to descale stainless steels and other alloys in the metals industry.

As indicated earlier, the commercially pure nickels are the premier materials for service in caustic alkalis. They are resistant over very wide ranges of concentration and temperature. Alloys 400 (from the Ni-Cu group) and 600 (from the Ni-Cr group) are also favored in caustic alkalis. For situations involving caustic alkalis on the one hand and chlorinated compounds on the other, the Ni-Cr-Mo alloys are candidates. However, it has recently been discovered that high-molybdenum nickel alloys are susceptible to “caustic dealloying” in strong, hot, caustic solutions. This means that elements other than nickel are selectively leached from surfaces. Field testing is therefore important prior to placing Ni-Cr-Mo materials into service in caustic alkalis.

Welding nickel alloys
Three processes are typically chosen to weld the nickel alloys. For sheets and plate root passes, gas tungsten arc (TIG) welding is favored. For plate welds, the gas metal arc (MIG) process is preferred. For field welding, the shielded metal arc process with coated electrodes is favored.

To minimize the precipitation of second phases in regions affected by the heat of welding, a maximum interpass temperature of 90°C is recommended for the nickel alloys. Also, welding of cold-worked materials is strongly discouraged, since they sensitize more quickly and induce residual stresses. A full solution anneal, followed by water quenching, is recommended for cold-worked structures prior to welding.

Applications
While the corrosion-resistant nickel alloys are used primarily in the chemical process industries, several other industries take advantage of their corrosion behavior. These include Food: Commercially pure nickels are easy to form and provide inherent resistance to mild corrosives; Marine: Ni-Cu alloys enable resistance to corrosion and cavitation erosion; Power: Ni-Cr-Mo alloys line flue gas desulfurization systems; and Metal finishing: Ni-Cr and Ni-Cr-Fe alloys serve as pickling fixtures.

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