

# CORROSION- RESISTANT PART 2 NICKEL ALLOYS

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

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**T**he most versatile of the ternary alloy nickel systems is the nickel-chromium-molybdenum (Ni-Cr-Mo) system. Not only do the chromium and molybdenum provide resistance to oxidizing and reducing acids, respectively, but also they act synergistically to provide outstanding resistance to the chloride-induced phenomena of pitting, crevice attack, and stress-corrosion cracking. The remaining two families, nickel-chromium-iron (Ni-Cr-Fe) and nickel-iron-chromium (Ni-Fe-Cr), were designed to bridge the performance and cost gaps between the Ni-Cr alloys and the austenitic stainless steels. Their benefits over the stainless steels include enhanced resistance to stress corrosion cracking.

## **Ni-Cr-Mo alloys**

The Ni-Cr-Mo alloys are particularly resistant to the insidious and unpredictable forms of corrosion caused by chlorides: pitting, crevice attack, and stress corrosion cracking. Chromium induces passivation in oxidizing acids, as it does in the stainless steels. Molybdenum provides resistance to reducing acids, in particular to hydrochloric acid. In heat exchangers, not only is the process stream important, but also the cooling medium must be taken into account. Cooling waters are often chlorinated to combat biofouling, and seawater (perhaps the most common chloride solution) serves as a coolant at many coastal locations.

Just as the Ni-Cr-Mo alloys resist hydrochloric acid and associated salts, they also resist the corresponding compounds of bromine and fluorine. Indeed, the Ni-Cr-Mo alloys are among the few metallic materials that withstand warm hydrofluoric acid. Among their other attributes, the Ni-Cr-Mo alloys resist sulfuric and phosphoric acids,

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*Offshore oil rig structures must be built of alloys that resist seawater corrosion. Image courtesy Rolls Royce.*

and certain concentrations of caustic soda and caustic potash.

- **Hastelloy C:** The first Ni-Cr-Mo material was Hastelloy C, introduced in the early 1930's in cast form. Wrought products became available in the 1940's, notably with a lower carbon limit. Post-weld annealing was necessary with Hastelloy C, due to the fact that, prior to the 1960's, carbon and silicon contents could not be minimized during melting.

- **Hastelloy C-276:** Wrought Hastelloy C-276 (1960's) was the first low-carbon, low-silicon version. It was made possible by the advent of argon-oxygen decarburization (AOD) during melting.

- **Hastelloy C-22:** Wrought C-22 (1980's) alloy contains higher chromium content, to cope better with industrial environments containing oxidizing impurities.

- **Hastelloy C-2000:** Copper was added to the C-2000 alloy (1990's), improving resistance to sulfuric and hydrofluoric acids.

The nominal compositions of the Ni-Cr-Mo alloys are given in Table I. From this table, the lower chromium contents of the early alloys are evident. The effects of tungsten, which is present in several Ni-Cr-Mo alloys, are similar to those of molybdenum, if the atomic weight differences between the two elements are taken into account.

## **Ni-Cr-Mo microstructure**

The atomic structure of the Ni-Cr-Mo alloys is predominantly face-centered cubic (fcc). In this respect, they are similar to the austenitic stainless steels. Also like the stainless steels, they are not completely stable, and are therefore susceptible

*Table 1 — Nickel-chromium-molybdenum alloys resistant to aqueous corrosion*

Family	Alloy	UNS No.	Form	Composition, wt.% (values denoted with * are maxima, and ** are minima)											
				Ni	Cu	Mo	Cr	Fe	W	Mn	Si	C	Al	Ti	Other
Ni-Cr-Mo	C-4	N06455	Wrought	65	0.5*	16	16	3*	—	1*	0.08*	0.01*	—	0.7*	—
	C-22	N06022	Wrought	56	0.5*	13	22	3	3	0.5*	0.08*	0.01*	—	—	V 0.35*
	C-22HS	—	Wrought	61	0.5*	17	21	2*	1*	0.8*	0.08*	0.01*	0.5*	—	—
	C-276	N10276	Wrought	57	0.5*	16	16	5	4	1*	0.08*	0.01*	—	—	V 0.35*
	C-2000	N06200	Wrought	59	1.6	16	23	3*	—	0.5*	0.08*	0.01*	0.5*	—	—
	59	N06059	Wrought	BAL.	—	16	23	1.5*	—	0.5*	0.1*	0.01*	0.25	—	—
	686	N06686	Wrought	BAL.	—	16	21	5*	3.7	0.75*	0.08*	0.01*	—	0.15	—
	CW-2M	N26455	Cast	BAL.	—	16.25	16.25	2*	1*	1*	0.8*	0.02*	—	—	—
	CW-6M	N30107	Cast	BAL.	—	18.5	18.5	3*	—	1*	1*	0.07*	—	—	—
	CW-12MW	N30002	Cast	BAL.	—	17	16.5	6	4.5	1*	1*	0.12*	—	—	V 0.3
	CX-2MW	N26022	Cast	BAL.	—	13.5	21.5	4	3	1*	0.8*	0.02*	—	—	V 0.35*

*Table 2 — Nickel-chromium-iron alloys resistant to aqueous corrosion*

Family	Alloy	UNS No.	Form	Composition, wt.% (values denoted with * are maxima, and ** are minima)											
				Ni	Cu	Mo	Cr	Fe	W	Mn	Si	C	Al	Other	
Ni-Cr-Fe	G-3	N06985	Wrought	44	2	7	22	19.5	1.5*	1*	1*	0.015*	—	Co 5*, Nb 0.5*	
	G-30	N06030	Wrought	43	2	5.5	30	15	2.5	1.5*	0.8*	0.03*	—	Co 5*, Nb 0.8	
	G-50	N06950	Wrought	50**	0.5*	9	20	17	1*	1*	1*	0.02*	0.4*	Co 2.5*, Nb 0.5*	

*Table 3 — Nickel-iron-chromium alloys resistant to aqueous corrosion*

Family	Alloy	UNS No.	Form	Composition, wt.% (values denoted with * are maxima, and ** are minima)											
				Ni	Cu	Mo	Cr	Fe	Mn	Si	C	Al	Ti	Other	
Ni-Fe-Cr	825	N08825	Wrought	42	2.2	3	21.5	30	0.5	0.2	0.05*	0.1	0.9	—	
	925	N09925	Wrought	44	2.2	3	21	28	1*	0.5*	0.03*	0.3	2.2	Nb 0.5*	

to the formation of second phases when exposed to temperatures in the approximate range 650 to 1100°C (the sensitizing range).

The Ni-Cr-Mo alloys are normally supplied in the solution-annealed condition; the annealing temperature for most alloys is about 1120°C. They are typically quenched in water from their annealing temperatures, to "lock in" their high temperature fcc microstructures. However, they are quenched in gas if they are annealed in hydrogen.

Concerns over structural instability are greatest during welding, since weld heat-affected zones (HAZ) are exposed to temperatures in the sensitizing range. The second phases of most concern are  $M_6C$  carbides, which develop in the range 650 to 1040°C, and  $\mu$  ( $\mu$ ) phase, which occurs in the range 760 to 1090°C. Both of these phases form rapidly and heterogeneously, typically within the alloy grain boundaries, rendering them susceptible to preferential attack.

At lower temperatures, a homogeneous, long-range ordering reaction is possible, but this is slow and of no concern during welding. That said, Hastelloy C-22HS alloy was designed specifically to take advantage of the long-range ordering reaction. Its yield strength can be doubled by this reaction, in a period of 48 hours, with only a moderate reduction in its corrosion performance.

The development of cast Ni-Cr-Mo alloys has

followed a similar path, with initial efforts aimed at improving thermal stability, and, where possible, enhanced corrosion resistance. Notable among early developments was Chlorimet 3, which is also known as CW-6M. Apart from Hastelloy C alloy, the composition of which is still sold as CW-12MW, and Chlorimet 3, only two other casting alloys have found commercial success, namely CW-2M (a cast counterpart to wrought C-4 alloy) and CX-2MW (a cast counterpart to wrought C-22 alloy).

Although undesirable from a thermal stability standpoint, silicon is important in casting alloys, since it influences fluidity. Silicon maxima are therefore much greater in Ni-Cr-Mo casting compositions. Higher carbon contents are also common in castings, unless special precautions are taken to avoid its pickup. Along with slow cooling from the molten state, a necessary result of pouring such materials into ceramic molds, these factors result in significant grain boundary precipitation, which must be dissolved by solution annealing if optimum corrosion properties are to be attained.

#### Ni-Cr-Fe alloys

The nickel-chromium-iron alloys were originally designed to fill the performance gap between the high-molybdenum stainless steels and the

nickel-chromium-molybdenum alloys. Thus, they possess good resistance to chloride-induced phenomena, such as pitting, crevice corrosion, and stress corrosion cracking, and exhibit moderate resistance to the halogen acids, in particular hydrochloric. Significant applications of the Ni-Cr-Fe alloys include oil and gas well tubes and evaporators for the concentration of fertilizer-grade phosphoric acid.

Nominal compositions of three such alloys are given in Table 2. These evolved from Hastelloy G alloy developed in the 1950's before the advent of argon-oxygen decarburization (AOD). Application of this melting technology allowed the introduction, in the 1970's, of Hastelloy G-3 alloy, which became established in two major applications. First, cold-reduced tubes of G-3 alloy became standard for moderately sour oil and gas wells. Second, G-3 alloy was applied in evaporators for concentrating fertilizer-grade phosphoric acid.

The success of the G-3 alloy in these applications led, in the 1980's, to the introduction of the G-30 and G-50 alloys. The G-30 alloy was a high-chromium variant with enhanced resistance to phosphoric acid. G-50 was a high-molybdenum variant with enhanced resistance to stress corrosion cracking in elevated temperature environments containing hydrogen sulfide, such as those in oil and gas wells. Notable in Table 2 are the relatively high chromium content of G-30 alloy and the relatively high molybdenum content of G-50 alloy. It should also be noted that G-3 and G-30

alloys contain copper, to enhance their resistance to sulfuric and hydrofluoric acids. Incidentally, the original G alloy was conceived as a copper-bearing variant of a prior Ni-Cr-Fe alloy, Hastelloy F.

#### **Ni-Fe-Cr alloys**

Incoloy alloy 825 and its age-hardenable cousin Incoloy alloy 925 contain significantly more iron than chromium, and thus constitute a separate grouping, shown in Table 3. With iron contents of 30 and 28 wt% respectively, they are compositionally close to the high-nickel austenitic stainless steels. The negative aspects of such high iron contents are reduced solubilities of key elements such as molybdenum, and reduced resistance to environmental cracking. On the other hand, high iron contents reduce the cost of making the alloys.

One of the main applications of 825 alloy is downhole tubing in the oil and gas industries. It is a common material for wells that are only moderately sour. For wells with higher hydrogen sulfide contents, Ni-Cr-Fe and (in extreme cases) Ni-Cr-Mo materials (G-3, G-50, and C-276 alloys, in particular) are more suitable.

One of the key additions to alloy 825 is copper. As in other materials, it provides enhanced resistance to sulfuric acid.

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