Corrosion Resistance of a New Ni-Cr-Mo Alloy

Corrosion Resistance of a New, Wrought Ni-Cr-Mo Alloy

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A new, nickel-based alloy resistant to a very wide range of corrosive media is described.

The main alloying additions are chromium and molybdenum; however, the alloy also contains -1.6% copper, which significantly enhances its resistance to dilute sulfuric and hydrochloric acids. The safe operating regimes for the alloy in these two acids are defined, as are its current and potential applications in the chemical process industries.

Of the materials available to chemical process industry engineers, the wrought NiCr-Mo alloys are among the most versatile. Not only do they resist uniform attack in a wide range of acidic and alkaline environments, but they also withstand stress corrosion cracking, pitting, and crevice corrosion. In addition, they can be formed and welded, without difficulty, into complex components.

Many of the attractive properties of the wrought Ni-Cr-Mo alloys stem from the physical properties of nickel. First, it is more noble than iron; second, it exhibits a ductile, face-centered cubic structure at all temperatures; and third, it is very tolerant of useful solutes, such as chromium and molybdenum, which enhance passivity and nobility.

The chromium contents of the wrought Ni-Cr-Mo alloys range from 16 wt% to 23 wt% (Table 1). The higher the chromium content, the better is the performance in oxidizing acids. The performance of the wrought Ni-Cr-Mo alloys in reducing acids, on the other hand, is largely a function of the levels of molybdenum and tungsten, which range from -13 wt% to 16.5 wt% and 0 wt% to 4 wt%. Reducing acids include hydrochloric, hydrofluoric, phosphoric, and dilute sulfuric; however, when these acids contain sufficient quantities of ferric ions, cupric ions, or dissolved oxygen they become oxidizing. Nitric acid and concentrated sulfuric acid are naturally oxidizing to nickel-based alloys, although the relationship between chromium content and resistance to corrosion do not hold in the case of concentrated sulfuric.

Solubility constraints at the solution annealing temperatures define how much chromium, molybdenum, and tungsten can be retained in solution, assuming that the materials are quenched after annealing. For a given amount of chromium, only certain quantities of molybdenum and tungsten can be added; further additions then partition to primary precipitates. The same is true if the molybdenum and tungsten levels are fixed, and chromium is added. Thus, only certain levels of resistance to both oxidizing and reducing acids can be attained using only chromium, molybdenum, and tungsten additions. The compositions of the existing alloys reflect the type of media for which they were designed, since none span the entire Ni-Cr-Mo alloys capability range, as illustrated using corrosion rate reciprocals in strong oxidizing and reducing solutions (Figure 1).

| Table 1: Typical Compositions of New and Existing Wrought Ni-Cr-Mo alloys (weight %) |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|
| Alloy  | Nickel | Chromium | Molybdenum | Tungsten | Iron | Manganese | Silicon | Carbon | Others          |
| C-276  | Balance | 16    | 16    | 4     | 5    | 0.5     | 0.02    | 0.002  | Vanadium 0.15, Aluminum 0.25 |
A new, wrought Ni-Cr-Mo alloy was designed along slightly different lines. The technical objective during development was a wider application range, i.e., increased versatility. The development goal was to equal the performance of the existing high chromium alloys in oxidizing acids, and to equal the high molybdenum and tungsten alloys in reducing acids. To achieve this, a combination of molybdenum and copper was used. Copper was found not only to be more effective than tungsten in enhancing nobility under active corrosion conditions, but also it allowed the use of a high chromium content.\(^1\) The success of this approach is evident in comparing the application range of the new material with those of the existing alloys, as defined by the same two media (Figure 1). The composition of the new material, which is known commercially as alloy C-2000\(^\circledR\), and designated UNS N06200 is given in Table 1.

### Resistance to Corrosion

In common with the existing, wrought Ni-Ti-Cr-Mo materials, alloy C-2000\(^\circledR\) is very resistant to pitting, crevice corrosion, and stress corrosion cracking, in the presence of chlorides. As part of the assessment of its uniform corrosion resistance, alloy C-2000\(^\circledR\) was tested extensively in sulfuric and hydrochloric acids, since these are among the most corrosive and common compounds encountered in the chemical process industries. The results of the tests in sulfuric acid are summarized in the iso-corrosion diagram (Figure 2). This diagram, which indicates the "very safe," "moderately safe," and "unsafe" regimes, was constructed from 80 data points, i.e., two test results at each of 40 concentration and temperature combinations. The tops of the bars represent the boiling points. This diagram shows that alloy C-2000\(^\circledR\) is usable in pure sulfuric acid up to -100°C at concentrations up to 70 wt%, this being a significant advance over the most widely used Ni-Cr-Mo material, alloy C-276 (UNS N10276). The new alloy also possesses advantages over other existing Ni-Cr-Mo alloys in sulfuric acid.\(^1\)

<table>
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<th></th>
<th>Balance</th>
<th>16</th>
<th>16</th>
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<tr>
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<tr>
<td>C-2000(^\circledR)</td>
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<td>16</td>
<td>-</td>
<td>0.5</td>
<td>0.2</td>
<td>0.02</td>
<td>0.002</td>
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</tbody>
</table>

### References

1. M. Raghavan, B.J. Berkowitz, J.C. Scanlon, Metallurgical
2. P. Crook, CORROSION /96, paper no. 412 (Houston, 1996)
3. Haynes International, 1020 West Park Ave., P.O. Box 9013, Kokomo, IN 46904-9013
4. Material Data Sheet No. 4030, NICROFER 5923
The performance of alloy C-2000® in hydrochloric acid is depicted by the iso-corrosion diagram (Figure 3). This chart was constructed from 90 data points, i.e., two test results at each of 45 concentration and temperature combinations. From this chart, it is evident that the alloy can be used in boiling solutions up to a concentration of 3 wt%, which is beyond the capability of existing Ni-Cr-Mo alloys, and up to a temperature of 60°C in the concentration range 7 wt% to 20 wt%. Concentrations in excess of 20 wt% were not studied because of the volatility of hydrochloric acid, i.e., it is not possible to maintain a boiling solution at concentrations >20 wt% in a flask/condenser system, due to the evolution of hydrogen chloride gas.

Alloy C-2000® is also resistant to hydrofluoric acid, phosphoric acid, nitric acid, organic acids, mixed inorganic adds, and sodium hydroxide.

### Physical Metallurgy

The wrought Ni-Cr-Mo alloys are typically used in the solution annealed and water quenched condition.

At the solution annealing temperature, which is normally in the range 1, 20°C to 150°C, secondary phases dissolve in the fcc structure. The effect of the quench is to "freeze in" the high-temperature structure. Only when the alloys are subsequently raised to a temperature sufficient to cause appreciable diffusion, e.g., during welding is there need for concern.

Several precipitates can occur in alloy C-276, for example, when it is exposed to elevated temperatures. In the range 300°C to 650°C, an ordered phase of the type Ni²(Cr,Mo) can form homogeneously throughout the microstructure, although the reaction kinetics are slow. At temperatures above 650°C, precipitates of α phase, M6C carbide, and P phase can form heterogeneously at the grain boundaries and twin boundaries in the microstructure. Of these precipitates, α phase is the most abundant, and M6C the second most abundant. They are both rich in molybdenum and can quickly form continuous grain boundary networks, which render the alloy prone to intergranular attack, since they possess different compositions from the alloy solid solution, and in forming, deplete the surrounding matrix of molybdenum. To reduce the tendency of the wrought Ni-Cr-Mo alloys to form such precipitates, special melting procedures are used to minimize the contents of carbon and silicon (a known promoter of intermetallics).

The issues of thermal stability and intergranular attack are complex. Not only are the kinetics of the precipitation reactions important, but also the nature of the corrosive environment, and the electrochemical effects of the precipitates must be taken into account.

To determine the effects of elevated temperature precipitation on alloy C-2000®, samples were held (aged) for three minutes at temperatures ranging from 760°C to 982°C, then tested according to the ASTM G 28A. These procedures were designed specifically to detect the susceptibility of wrought nickel-based chromium-bearing alloys to intergranular corrosion, which have been used before to
establish the time-temperature-sensitization characteristics of the wrought Ni-Cr-Mo alloys.\textsuperscript{3-4} The heating cycle in each case was 13 min (10 min to reach the precipitation temperature, and 3 min at this temperature, followed by water quenching). To assess the level of grain boundary attack at each temperature, the samples were studied metallographically, in section, and the maximum depths of attack recorded. For comparison, similar tests were performed on alloys C-276, 59 (N06059), and 686 (N06686). The results of these tests are shown in Figure 4. Those alloys with the highest chromium contents (alloys C-2000\textsuperscript{®} and 59) exhibit the highest resistance to intergranular corrosion after aging.

Applications
As a result of its ease of forming and welding, alloy C-2000\textsuperscript{®} is suitable for many types of hardware, including reaction vessels, heat exchangers, piping and fittings, valves, and pumps. ASME approval, for use in pressurized systems, has been applied for. Its superiority over alloy C-276 has so far led to two chemical process industry applications, one involving the handling of sulfuric acid over a wide range of acid concentrations, the other involving a mixture of acids, including hydrofluoric. Field tests also indicate alloy C-2000\textsuperscript{®} possesses advantages in brominated water and in chloride-containing acid mixtures.

Summary
The wrought Ni-Cr-Mo alloys are extremely versatile materials, resistant to many forms of corrosive attack. By using copper in alloy C-2000\textsuperscript{®}, this versatility has been extended significantly. Copper provides greatly enhanced nobility in certain reducing acids, and allows the use of a high chromium content, for optimum passivity in oxidizing media.

References
1. P. Crook, CORROSION /96, paper no. 412 (Houston, TX: NACE, 1996).