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The Influence of Post-Weld Heat Treatments (PWHT) upon the Resistance of Ni-Mo and Ni-Cr-Mo alloys to Chloride-Induced Stress Corrosion Cracking, Pitting, and Crevice Attack

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ABSTRACT

The wrought, nickel-molybdenum (Ni-Mo) and nickel-chromium-molybdenum (Ni-Cr-Mo) alloys are very important materials of construction in the chemical process, pharmaceutical, petrochemical, and oil and gas industries. The objective of this study is to compare the resistance of “as welded” and PWHT samples of several alloys to chloride-induced stress corrosion cracking (SCC), pitting, and crevice corrosion, using standard ASTM test procedures. Commercial alloys HASTELLOY® B-3® (UNS N10675)*, C-22® (UNS N06022)*, C-276 (UNS N10276)*, C-2000® (UNS N06200)*, G-35® (UNS N06035)* and HYBRID-BC1® (UNS N10362)* were selected in this study. The gas tungsten arc (GTAW/TIG) welding process was used in sample preparation. The primary conclusion from this study is that no benefit appears to accrue from PWHT regarding resistance to SCC and pitting corrosion. However, there are some distinct advantages of PWHT with regard to crevice attack for UNS N06200, UNS N06035 and UNS N10362 alloys.

Key words: stress corrosion cracking, pitting and crevice corrosion, corrosion resistant alloys, hydrochloric acid, sulfuric acid, sensitization

INTRODUCTION

The wrought, nickel-molybdenum (Ni-Mo) and nickel-chromium-molybdenum (Ni-Cr-Mo) alloys are very important materials of construction in the chemical process, pharmaceutical, petrochemical, and oil and gas industries.¹ They provide greatly enhanced performance over the stainless steels in hydrochloric acid, sulfuric acid, hydrofluoric acid, hydrobromic acid, and chloride-bearing solutions; also, they are not subject to the limitations of the reactive metal alloys (i.e. alloys based on titanium, zirconium, etc.) in solutions which induce oxide film breakdown.

An important attribute of the Ni-Mo and Ni-Cr-Mo alloys is their excellent weldability, which, combined with their high ductilities, enables ease of component fabrication.

* Trade name

Like most metallic materials, the wrought, Ni-Mo and Ni-Cr-Mo alloys undergo some structural changes at temperatures above about 1200°F (650°C), where the diffusion of elements becomes appreciable. These can be due to carbon and silicon impurities, which are kept low by sophisticated melting techniques, but can cause problems due to their extremely low solubilities in nickel and its alloys. They can also be due to overalloying, whereby greater corrosion resistance is possible, but with some sacrifice in high temperature thermal stability. To overcome these limitations, the Ni-Mo and Ni-Cr-Mo alloys are normally used in the solution annealed and rapidly quenched condition. The solution annealing treatment serves to dissolve any second phases due to carbon, silicon, or overalloying; the quenching treatment serves to “lock-in” the fully face-centered cubic (FCC) structure created during the anneal.²

Since the wrought, Ni-Mo and Ni-Cr-Mo alloys normally experience service temperatures below 500°F(260°C), and only rarely to 800°F(427°C), metallurgical changes during operation are generally not an issue. However, thermal cycles during welding can cause the precipitation of second phases in heat-affected zones (HAZ), particularly at the grain boundaries, which tend to act as nucleation sites. Such precipitation can induce preferential grain boundary attack, especially if it is continuous within the boundaries, as opposed to discontinuous, with “clean” boundary sections separating discrete second phase particles.^{2,3}

The alloys with which this paper is concerned were all designed for use in the “as welded” condition, that is they are melted using procedures that minimize carbon and silicon contents, and are not excessively overalloyed. In addition, they each have solution annealing temperatures (in the 1950°F(1065°C) to 2100°F(1149°C) range) that ensure complete dissolution of second phase precipitates generated during wrought processing.

In some industrial circles and with some metallic materials, post-weld heat treatment has been used to counter the effects of second phase precipitation in the HAZ, and ostensibly optimize the resistance of welded components to preferential HAZ attack in corrosive solutions. However, major concerns of this approach (as related to the Ni-Mo and Ni-Cr-Mo alloys) have been identified, as follows:

1. Not all commercial heat treatment facilities have furnaces which will reach the (re-solution annealing) temperatures required for PWHT, of the Ni-Cr-Mo alloys in particular; nor do all possess means of accomplishing a sufficiently rapid quench.
2. The use of lower temperatures can result in more extensive precipitation (hence greater potential for preferential attack).
3. There is a risk that the base metal will be negatively affected, if the solution annealing temperature is incorrect, and/or the quench is not sufficiently rapid.
4. Wide differences in section thickness within components can result in different heating rates, annealing times, and cooling rates (during quenching).
5. Components can suffer distortion during quenching.

With these facts in mind, the primary objective of this study was to compare the resistance of “as welded” and “welded plus post-weld heat treated” samples of several materials to chloride-induced stress corrosion cracking, pitting, and crevice corrosion, using standard ASTM[†] test procedures. Such a comparison should enable improved risk/benefit analyses, as they relate to PWHT.

The following Ni-Mo and Ni-Cr-Mo alloys were chosen for study:

1. UNS N10675 alloy
2. UNS N06022 alloy

[†] ASTM international standards

3. UNS N10276 alloy
4. UNS N06200 alloy
5. UNS N06035 alloy
6. UNS N10362 alloy

The nominal compositions of these alloys are shown in Table 1.

Table 1: Nominal Compositions of Test Alloys

Alloy	Composition, wt. %										
	Ni	Cr	Mo	W	Fe	Mn	Si	C	Al	Cu	Other
N10675	Balance	1.5	28.5	3*	1.5	3*	0.1*	0.01*	0.5*	0.2*	-
N06022	Balance	22	13	3	3	0.5*	0.08*	0.01*	-	0.5*	V: 0.35*
N10276	Balance	16	16	4	5	1*	0.08*	0.01*	-	0.5*	V: 0.35*
N06200	Balance	23	16	-	3*	0.5*	0.08*	0.01*	0.5*	1.6	-
N06035	Balance	33	8	-	2*	0.5*	0.6*	0.05*	0.4*	-	-
N10362	Balance	15	22	-	2*	0.25	0.08*	0.01*	0.5*	-	Co: 1*

*Maximum

Within this group of nickel-based materials, the most influential elemental additions are chromium and molybdenum. Chromium enables the formation of passive (protective) films in so-called oxidizing, aqueous solutions. Molybdenum ennobles nickel, and greatly enhances its resistance to so-called reducing solutions, which include the key industrial chemical, hydrochloric acid. Reducing solutions are those which induce a cathodic reaction that results in hydrogen evolution. Oxidizing solutions are those that induce a cathodic reaction of higher potential, and support the growth of oxide and/or hydroxide surface films.

This group of alloys covers a large range of chromium/molybdenum ratios, from N10675 alloy (1.5/28.5) to N06035 alloy (33/8). N10675 alloy excels in pure hydrochloric and sulfuric acid, whereas N06035 alloy excels in nitric acid, and acids containing oxidizers such as ferric ions and dissolved oxygen, especially in the presence of halides. The other alloys offer outstanding versatility as a result of their balanced chromium/molybdenum ratios.

EXPERIMENTAL PROCEDURE

Most of the experimental procedures used in this work are defined in ASTM Standards G30 (Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens), G36 (Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride Solution), and G48 (Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution) ⁷. For ASTM G48, Methods C (Critical Pitting Temperature Test for Nickel-Base and Chromium-Bearing Alloys) and D (Critical Crevice Temperature Test for Nickel-Base and Chromium-Bearing Alloys) were used.

All samples were prepared using 0.125 in/3.2 mm thick sheets of material. To form the welds, an autogenous (no filler metal) gas tungsten arc (GTA/TIG) process was used; subsequent filler metal passes (using identical alloy wires) were required to ensure parallel, ground surfaces (prior to U-bending), in the case of the stress corrosion cracking test specimens.

As to the post-weld heat treatments, these involved the solution annealing temperatures in Table 2. The coupons were annealed for 20mins at each individual temperature then followed by air quench. The pitting samples were blasted with fine alumina powder to remove the oxide on the surface. The crevice and SCC samples were reground to remove the oxide surface.