

Corrosion Performance of Various Types of Welded and Seamless Tubulars of Ni-Mo and Ni-Cr-Mo Alloys in Standard Acids and Other Selected Environments

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ABSTRACT

The Ni-based corrosion resistant alloys are known to exhibit high resistance to hydrochloric and sulfuric acids over wide concentration and temperature ranges. Pipe and tube materials are widely used in chemical process industry (CPI) and various other industries. The common tubing forms include seamless, as-welded, welded bead-worked, and welded fully cold-reduced. Many of the Ni-Based product types are produced according to ASTM and ASME (B622, B626, B619) ⁽¹⁾ specifications. Commercial UNS N10675 (HASTELLOY® B-3®) ⁽²⁾, UNS N10276 (HASTELLOY® C-276) ⁽²⁾, UNS N06200 (HASTELLOY® C-2000 ®) ⁽²⁾, UNS N06022 (HASTELLOY® C-22®) ⁽²⁾ and UNS N10362 (HASTELLOY® HYBRID-BC1®) ⁽²⁾ alloys with the above-mentioned forms of tubing materials were studied in this paper. UNS N10362 tubes showed excellent general corrosion and pitting resistance compared to other C-type alloy tubes in selected test environments. C-type alloy welded tubes sensitization behavior was studied in ASTM standard G28A⁽³⁾ and G28B ⁽³⁾ solutions. From testing it was concluded that welded and fully cold-reduced tubing has similar corrosion resistance to that of seamless tubing, while as-welded and welded bead-worked tubing underwent localized corrosion.

Key words: tubes, pitting corrosion, intergranular corrosion, corrosion resistant alloys, hydrochloric acid, sulfuric acid, sensitization

⁽¹⁾ ASTM and ASME Specification for Seamless, Welded Nickel and Nickel Cobalt Alloy Tube

⁽²⁾ Trade Name

⁽³⁾ ASTM Standard Test Methods for Detecting Susceptibility to Intergranular Corrosion in Wrought, Nickel-Rich, Chromium-Bearing Alloys

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INTRODUCTION

Nickel-based corrosion-resistant alloys are vitally important materials in chemical processing, petrochemical, agrichemical and pharmaceutical industries. When aggressive process streams are involved, corrosion-resistant alloys are selected for applications such as heat exchangers, reactors, pressure vessels and/or other process equipment in various industry sectors.¹ The Ni-Mo alloys provide excellent resistance to reducing hydrochloric and sulfuric acids over large ranges of concentration and temperature. They also resist pure hydrobromic acid, hydrofluoric acid and other non-oxidizing halide salt solutions.¹ The primary limitation of the Ni-Mo alloys is that they cannot tolerate either oxidizing acids, such as nitric, or acids that contain oxidizing species. Such species include oxygen, hydrogen peroxide, chlorine, bromine, ferric ions and cupric ions.¹

The Ni-Cr-Mo alloys provide both excellent general corrosion and localized corrosion resistance, such as stress corrosion cracking, pitting and crevice corrosion, when they are exposed to highly corrosive reducing or oxidizing acids. Chromium induces passivation in oxidizing acids, Molybdenum provides resistance to reducing acids, in particular hydrochloric acid.¹

Many fluid process designs require tubular products for use as piping for heat exchanger systems.² The common tubing materials include seamless tubes and welded tubes. Seamless tubing is produced from billets by trepanning or extrusion followed by pilgering and/or drawing process.³ Welded tubing is made from strip by forming, welding, sizing or cold-working, solution heat treating, and testing in accordance with the applicable specifications. Class I is as-welded, sized and solution-annealed tubes; Class II is welded, cold worked, solution annealed. Class III is welded, cold worked, solution annealed, and nondestructively tested according to ASTM B626 ⁽⁴⁾ and ASME SB626 ⁽⁴⁾ specifications.³ For Class II and Class III tubes, the cold work could be on both the weld seam and base metal or on the weld seam only, usually referred to welded and fully cold-reduced tube or welded and bead-worked tube. The welded and fully cold-reduced tubing encompasses the cold reduction of both the weld seam and base metal (parent material). The minimum reduction is generally 20% of the total area and achieves optimum metallurgical properties after solution annealing. Bead-worked tubing encompasses the cold reduction of the weld seam only, generally reducing the weld seam by 2-10%.

Seamless tubing usually has higher ASME B31 ⁽⁵⁾ allowable stresses compared to welded tubing of the same material and size due to not having a welded seam. Another advantage of seamless tubing is that it can offer superior corrosion resistance because it has less potential for failure compared to welded tubing. Using seamless tubing allows customers to avoid the potential for defects and differences in malleability that may be associated with the welded area in welded tubes. Unlike welded tubes, seamless tubes do not require testing for weld integrity.

Welded tubing has its own advantages. Because fewer cold working and annealing steps are needed in the manufacture of tubing. The cost of welded tubing is typically less expensive than seamless tubing. Welded tubing can be typically procured quicker than seamless tubing. Cost considerations steer the user toward the selection of welded tubing that has been cold worked and annealed rather than to seamless tubing. Usually manufacturing has the guideline to fabricate different types of tubing according to tube/pipe dimension and OD/wall thickness ratio requested by customer; which can help customer make the correct selection for their application.

Cold work plus solution annealing is designed to achieve complete recrystallization and substantial homogenization of the seam weld. This approach could provide similar performance to that of the wrought seamless tubing.² For optimum corrosion performance, Ni-Cr-Mo materials should have

⁽⁴⁾ ASTM and ASME Specification for Welded Nickel and Nickel Cobalt Alloy Tube

⁽⁵⁾ ASME process piping code

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“optimum” metallurgical structure. The goal of alloy producers is to achieve a homogeneous single-phase alloy to avoid setting up permanent anodic and cathodic sites.¹ However, if an alloy is single-phase in the annealed and quenched condition but supersaturated with elements such as Cr and Mo, then the driving force for grain boundary intermetallic precipitation during welding solidification is high in the as-welded condition; with the risk of preferential grain boundary attack in service.¹ If there is severe banding structure in base metal or the weld is partially recrystallized it may result in premature failure in service as shown in the literature.² For non-optimum metallurgical structures such as “partially” recrystallized and “non-fully” homogenized weld seams, corrosion attack is very likely to initiate and propagate along the weld.²

The challenge for tubing producers is that high Mo nickel-based alloys are more difficult to cold work than stainless tubes. For high Mo nickel-based alloy welded tubes, the issue of inter-dendritic segregation at the weld seam must be minimized by carefully selecting heat treatment cycle time and temperature to achieve the desired homogenization of the weld seam. Additionally, the pilgering process of producing seamless tube may cause oil contamination if not properly degreased. When tubes were annealed at high temperature after cold work, excess carbon from grease decomposition diffuses into the alloy. Extra carbon could sensitize the metal and severely degrade the material corrosion performance.²

With these facts in mind, the objective of this study is to compare the corrosion performance of different types of tubular materials. Ni-Mo and Ni-Cr-Mo seamless and welded tubes were selected. Seamless tubing was produced by pilgering and/or drawing followed by solution annealing. The welded tubes available were as follows: as-welded, welded-planished, welded bead-worked, and welded fully cold-reduced. Welded-planished tube is a type made by first forming the sheet or plate into a near pipe shape, then welding along the length to produce the pipe form. It is subsequently processed through a set of dies and a mandrel that compresses or planishes the weld. Bead-worked tubing is similar to welded-planished except that it is produced from coil and the bead is reduced utilizing either a hammering or rolling process to flatten the bead or reduce the height of the bead. The cold work reduction is applied on the weld seam only, reducing the weld seam generally by 2-10%, followed by solution annealing. Welded and fully cold-reduced tubing is produced by cold working on both the weld seam and base metal with the minimum reduction around 20% of the total area. This process achieves optimum metallurgical conditions after solution annealing. General corrosion was evaluated in key acidic environments. The sensitization behavior of Ni-Cr-Mo C-type alloys was evaluated in ASTM G28A and G28B solutions.

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

1. UNS N10675 alloy
2. UNS N10276 alloy
3. UNS N06200 alloy
4. UNS N06022 alloy
5. 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*	-
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	-
N06022	Balance	22	13	3	3	0.5*	0.08*	0.01*	-	0.5*	V: 0.35*
N10362	Balance	15	22	-	2*	0.25	0.08*	0.01*	0.5*	-	Co: 1*

*Maximum

Within this group of nickel-based alloys, the most influential elemental additions are chromium and molybdenum. Chromium enables the formation of passive (protective) films in so-called oxidizing, aqueous solutions. Molybdenum greatly enhances nickel based alloys' resistance to 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. N10675 alloy excels in pure reducing hydrochloric and sulfuric acid. The C-type alloys offer outstanding resistance of hydrochloric and sulfuric acids containing oxidizers such as ferric/cupric ions and dissolved oxygen as a result of their balanced chromium/molybdenum ratios. The N10632 alloy exhibits exceptional resistance to chloride-induced pitting, crevice attack and stress corrosion cracking.⁴

EXPERIMENTAL PROCEDURE

Tubular coupons with lengths of about 2cm were directly cut from the as-produced tubes. The cut surface was ground using 600 grit paper. The coupons were then de-greased with acetone prior to weighing, followed by immersion testing. A total test duration time of 96h was selected, with interruptions every 24h for weighing the samples. The solutions used were different concentrations of reagent grade HCl and H₂SO₄ acids, specified in Table 2. Test temperature ranged from 52°C to the solution's boiling points. ASTM G28 standard is specifically designed to detect the susceptibility to intergranular corrosion in wrought nickel-based alloys.⁵ In this study, C-type alloy tubes were tested in G28A and G28B solutions. Due to chloride ions existing in G28B solution, susceptibility to pitting corrosion can also be evaluated. Post-test optical microscopy was performed with a Leica⁽⁵⁾ DM15000 M² inverted research microscope, and images were taken with a DFC425 digital microscope camera ⁽⁵⁾.

RESULTS AND DISCUSSIONS

Immersion corrosion results in various concentrations of reagent grade HCl and H₂SO₄ acids and temperatures are shown in Table 2 below. The corrosion rate (mm/y) of each tube exposed to specific acid concentrations and temperatures is given in Table 2.

As shown in Table 2, all four types of N10675 tubes in various concentration reagent grade HCl and H₂SO₄ acids at different temperatures have low corrosion rates, less than 0.4mm/y. The seamless and welded tubes have similar corrosion performance and the weld seam has similar low general corrosion attack as the base metal after cross sectional posttest. This is to be expected since N10675 has extremely high resistance in reducing acids.

The nickel-chromium-molybdenum C-type alloys are very versatile. They contain high levels of both chromium and molybdenum. The Ni-Cr-Mo alloys are very resistant to pitting, crevice attack and stress corrosion cracking caused by chlorides.⁴ N10276 is widely used in many industries. In the past, "bead-worked" N10276 tubes were reported to have failed prematurely at the weld seam in various corrosive services. Replacement by "cold drawn" seamless or "welded and fully cold-reduced" tubing within the same ASTM specification was reported in literature.² The "bead-worked" N10276 tubes had "non-optimum" microstructures at weld seams with "partially" recrystallized and "non-fully" homogenized microstructure, corrosion attack is very likely to initiate and propagate along the weld.² In this work, a welded and fully cold-reduced N10276 tube was evaluated in various key acids listed in Table 2. The corrosion rate of the fully cold-reduced N10276 tube is very similar to those of mill-annealed wrought alloy sheet product forms reported in literature.⁶

⁽⁵⁾ Trade Name

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Table 2: Corrosion rate (mm/y) in HCl and H₂SO₄

Alloy	Test Media	5% HCl	20% HCl	37% HCl	5% H ₂ SO ₄	50% H ₂ SO ₄	70% H ₂ SO ₄	96% H ₂ SO ₄
	T, Corrosion Rate	79°C, mm/y	66°C, mm/y	52°C, mm/y	66°C, mm/y	107°C, mm/y	107°C, mm/y	107°C, mm/y
N10675	seamless	0.37	0.18	0.09	0.26	0.20	0.29	0.21
	as-welded	0.32	0.18	0.10	0.22	0.19	0.17	0.20
	welded & fully cold-reduced	0.32	0.19	0.06	0.14	0.07	0.04	0.07
	welded bead-worked	0.25	0.20	0.08	0.18	0.12	0.10	0.13
N10276	welded & fully cold-reduced	0.78	0.50	0.11	0.03	1.11	1.07	1.37
N06200	seamless	0.99	0.64	0.18	0.04	0.64	7.22	0.82
	welded & fully cold-reduced	0.93	0.69	0.20	0.03	0.80	4.10	0.84
	welded bead-worked	0.99	1.01	0.20	0.02	0.87	5.09	0.75
N06022	seamless	1.6	1.0	0.17	0.02	2.78	3.95	3.11
	as-welded	1.97	0.87	0.22	0.01	3.31	4.72	3.97
	welded & fully cold-reduced	1.80	1.02	0.18	0.03	2.72	3.59	4.01
	welded bead-worked	1.58	0.96	0.20	0.02	1.80	2.96	3.29
N10362	welded & fully cold-reduced	0.26	0.30	0.08	0.02	0.17	0.12	0.14

Recent developments of wrought Ni-Cr-Mo alloys include higher chromium contents (e.g. N06022 alloy) to help coping with industrial environments containing oxidizing impurities, and the addition of copper (e.g. N06200) for improved resistance to sulfuric and hydrofluoric acids.⁴ Three types of N06200 tubes and four types of N06022 tubes have been evaluated in this work. The corrosion rates in Table 2 are plotted in Figure 1. As shown in Figure 1(a), the corrosion rate of N06200 seamless tube and two welded tubes (welded & fully cold-reduced and welded bead-worked) are similar to each other in these key acids. The N06200 tubes showed a much lower corrosion rate than N10276 and N06022 in 50% H₂SO₄ and 96% H₂SO₄, respectively. It is noted that the corrosion rate of all three N06200 tubes in 70% H₂SO₄ was particularly high. The high corrosion rate in 70% H₂SO₄ is not related to tubular types but related to acid concentration, test temperature and alloy materials. It was reported that significant changes in the electrochemical behavior of H₂SO₄ acid were observed if the acid concentration exceeded ~70%.⁷ Many hypotheses have been forwarded concerning the redox reactions in these acids at high temperatures. The cathodic process was believed to be an unspecified reduction of SO₄²⁻ to S, SO₂, H₂S or HS⁻ etc.^{7,8} There were high S-containing black/brown spots deposited on C-type alloys N10276, N06022 and N06200 tubular samples with high material corrosion loss.⁹ One photo example of N06200 seamless tube after 70% H₂SO₄ immersion test at 107°C is shown in Figure 2(a). EDS analysis result is shown in Figure 2(b).

Figure 1(b) shows the corrosion rates of all four types of N06022 tubes in various acid concentrations at different temperatures. There is no significant corrosion performance difference between these tubes in