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EVALUATION of a SUPERAUSTENITIC ALLOY in STERILE 3.5% SALINE SOLUTION

by

Paul K. Whitcraft
Director, Application Engineering/QA
Rolled Alloys
Temperance, MI 48182

ABSTRACT

Water for injection (WFI) process systems and other sterile water process or transfer systems, with or without sodium chloride, have the potential to cause corrosion in standard Type 316L stainless components. AL-6XN® Alloy, UNS N08367, is a 25% nickel, 21% chromium, 6% molybdenum superaustenitic stainless steel alloyed with nitrogen that offers excellent resistance to corrosion from halogen ions. The AL-6XN Alloy is evaluated using established corrosion testing techniques in a 3.5% sterile saline solution. Type 316L stainless was also tested for comparison purposes. The data suggest that AL-6XN Alloy is highly resistant to corrosion attack even at temperatures as high as 149° C. Visual examination of the test coupons suggests that the alloy is also resistant to the phenomenon of "rouging".

INTRODUCTION

Stainless steels offer increased corrosion resistance relative to low alloy steels due to the formation of a protective oxide layer on the steel's surface. Chromium is the primary alloying element, with chromium oxides providing a protective film resistant to breakdown from many oxidizing media. Molybdenum is also very beneficial in enhancing the resistance of this protective film from breakdown due to halogen ions. Studies have shown that the sum of an alloy's chromium content plus 3.3 times the molybdenum plus 30 times the nitrogen (Cr + 3.3 * Mo + 30 * N) is proportional to increasing resistance to localized corrosion in ferric chloride. It is for this reason that the pitting resistance of 316L is greater than that of 304L. Increasing nickel content in stainless alloys is also beneficial in enhancing the overall resistance of the protective layer to corrosive attack.

While surface finish (i.e. polishing) and the quality of the protective film (passivation) do have an impact on the overall level of corrosion resistance of a component, the gains possible through these techniques are significantly overshadowed by the effects of alloy content. In fact, as steel making technology has evolved, the level of molybdenum present in 316L has dropped from roughly 2.4% to approximately 2.1%. This small gradual change may have more of an impact on corrosion resistance than the effects of passivation.

AL-6XN is a registered trademark of Allegheny Ludlum Corporation.

Although water is not considered to be particularly corrosive relative to inorganic acids, high purity water can cause localized attack in basic stainless alloys such as 304L and 316L. Electrochemical measurement techniques have been developed which can quantify an alloy's resistance to localized attack in various media. In addition, sample coupons were exposed to a saline solution at temperatures above boiling atmospheric pressure. These techniques were employed to illustrate the levels of resistance in the materials examined.

EXPERIMENTAL TECHNIQUE

U-Bends

To more closely simulate an actual WFI system, sections of 2″ O.D. x 0.065″ Wall tubing were orbitally welded to form joints identical to those expected in an actual installation. The nominal chemistries of the materials tested are shown in Table 1. Five different alloy/joint combinations were used as shown in Table 2. Because of the tendency for segregation of alloying elements in the welds of high alloys, AL-6XN Alloy is normally welded in the field by using an even higher alloy filler metal. To evaluate the importance of this effect, joints involving AL-6XN Alloy were welded with both the 625 Alloy filler and autogenously. The 625 Alloy filler took the form of production insert rings which fit snugly into the circumferential butt joint. Orbital welding was done using the programmable Dimetrics Centaur III. For the 316L/316L tube joints, a standard set up developed by Tri-Clover was used. For other joint combinations the only changes made in settings were to adjust torch amperage as shown in Table 2.

TABLE 1
NOMINAL COMPOSITIONS

Element	316L	AL-6XN Alloy	Alloy 625
Chromium	16.2	20.5	21.0
Nickel	10.2	25.0	61.0
Molybdenum	2.1	6.1	9.0
Nitrogen	0.05	0.22	0.03
Columbium	--	--	3.75

The welded tube joints were sectioned and flattened to produce 1″ wide U-Bends with the circumferential weld running across the 1″ width. The U-Bends were formed so as to have the original inside diameter (I.D.) surface of the circumferential weld located at the outside apex of the bend. The U-Bends were maintained in the stressed condition by using Alloy C-276 bolts and PTFE washers. Individual samples were separated by using PTFE sheet and immersed in the sterile 3.5% NaCl solution inside an Alloy C-276 autoclave. The solution temperature was maintained at 300° F (149° C). The samples were weighed to the nearest 0.1 mg prior to testing. The coupons were visually removed and examined after approximately 250 hour intervals until the test was ended at 990 hours. At the end of the test the coupons were carefully cleaned and weighed to determine a final weight loss.

Crevice Tests

Crevice corrosion coupons were also tested in accordance with Standard Practice ASTM G48B, except that the 3.5% NaCl solution was utilized. These tests were conducted on sheet stock coupons which did not contain circumferential welds. The test temperatures were 50° C, 60° C and 70° C. Modified G48 crevice tests were then performed on flattened samples of the welded tube sections. The tests were modified to provide multiple crevice sites using Delrin washers. These tests were conducted at 70° C for 72 hours also using the 3.5% saline solution.

TABLE 2
ORBITAL WELDING

Alloys	Weld Metal	Amperage	% from Base
316L / 316L	Autogenous	76.7	0
AL-6XN / AL-6XN	Autogenous	71.3	-7
AL-6XN / AL-6XN	Alloy 625	79.8	+4
316L / AL-6XN	Autogenous	71.3	-7
316L / AL-6XN	Alloy 625	90.6	+18

I.D. purged with 99.8% Argon. Orbital welding head used 99.8% Argon and a 2% Thoriated tungsten, 3/32" diameter electrode.

Potentiodynamic Scans

Since corrosion processes are electrochemical in nature, measurement of relative electrical potentials versus current flow in a corrosive media can help predict a material's performance in that environment. Potentiodynamic scans were conducted on AL-6XN Alloy and 316L at 30° C in the 3.5% NaCl solution. A second scan was performed on AL-6XN Alloy at 50° C. These tests were conducted in accordance with Standard Practice ASTM G61.

RESULTS

U-Bend Tests in Autoclaves

Duplicate U-Bend test samples were run simultaneously in separate autoclaves. A summary of the test results is shown in Table 3. Visual examinations of the samples were consistent from one autoclave to another. The 316L sections began to show evidence of crevice attack at the PTFE washers after the first 258 hour period in nearly every instance. By the end of the 990 hour total test time, it was obvious that crevice attack had occurred on all eight 316L crevice locations.

On one of the AL-6XN Alloy coupons, welded with Alloy 625, a small crack became apparent after the first 258 hour period. Further examination revealed this to be a minor weld imperfection. No other evidence of degradation was noted on the AL-6XN Alloy sections until the tests were completed and the U-Bends unbolted. Once the PTFE washers were removed, a very light etching of the surface under the washer could be noted.

It was also observed that nearly all of the 316L coupons, whether attached to 316L or AL-6XN, also exhibited a slight rust like discoloration. In general, this condition appeared to be corrosion product and was very reminiscent of "rouging" that has been previously noted in high purity water systems. These "deposits" were tightly adherent and difficult to remove. There was no visual evidence of corrosion beneath the stains. The AL-6XN Alloy coupons appeared to be free of this condition. Further investigation between the correlation of this condition and the service condition is planned.

TABLE 3
U-BEND TEST RESULTS

		Autoclave A		Autoclave B	
Alloy	Filler	Weight Loss, mg	Comment	Weight Loss, mg	Comment
316L/316L	None	1.5	CC	23.9	CC, SC
AL-6XN/AL-6XN	None	0.9	E	1.4	E
AL-6XN/AL-6XN	625	1.1	E	6.5	WCR
316L/AL-6XN	None	1.0	E	30.6	CC, SC
316L/AL-6XN	625	1.5	CC	24.8	CC, SC

Key: CC - Crevice Corrosion under PTFE washer on 316L.
SC - Stress Cracking at hole on 316L.
E - Slight etching of surface under PTFE washer.
WCR - Crack at minor weld defect in 625 weld.

Finally, it should be noted that while the conditions in the two autoclaves were intended to be identical, the coupons in Autoclave B suffered more attack. Weight losses on the 316L samples were significantly higher. Evidence of stress cracking was noted on the 316L samples in the second autoclave, while none was noted from the other unit. This variability in results also underscores the difficulty in trying to reproduce actual service results in a laboratory test setting. The extent of the cracking present in Autoclave B was still less than that anticipated for 316L stainless. Since these were closed systems, the oxygen within the system was probably depleted by the crevice attack before more extensive stress corrosion could occur. The potential for SCC in 316L stainless in an actual installation is probably greater, since the presence of adequate amounts of oxygen is more likely.

Crevice Corrosion

Test results from standard G48B type crevice tests are shown in Table 4. These tests were performed on standard flat coupons to establish a suitable test temperature for crevice testing the tubing samples in the saline solution. For the standard G48B test solution consisting of 6% $FeCl_3$, Type 316L will begin to show crevice attack at temperatures as low as -3° C. In this same test, AL-6XN Alloy is resistant up to about 43° C. Since the saline solution is not as aggressive, higher temperatures are needed to initiate attack.

Based on these results which indicated some significant crevice attack on the Type 316 at 70° C, Modified G48B tests, using Multiple Crevice test fixtures, were performed on flattened sections of the tube samples. The Multiple Crevice Assembly (MCA) uses Delrin washers which actually provide 20 small crevice sites for each washers, or 40 per test coupon. This approach greatly improves the statistical significance of the test results. For the sample consisting of two alloys, the washers were positioned to have half of the crevice sites on each material. The results of these tests are presented in Table 5. No crevice corrosion was observed on any of the superaustenitic stainless alloy coupons, while each sample of 316L tubing was slightly attacked.

TABLE 4
ASTM G48B CREVICE CORROSION TESTS

3.5% Saline Solution - 72 Hours

Alloy	° C	Wt. Loss (mg/cm^2)	Deepest Crevice (mils)
316	50	0.0, 0.0	2, 1
AL-6XN	50	0.0, 0.0	No Attack
316	60	0.1, 0.1	10, 9
AL-6XN	60	0.0, 0.0	No Attack
316	70	0.1, 0.2	11, 10
AL-6XN	70	0.0, 0.0	No Attack

TABLE 5
MULTIPLE CREVICE ASSEMBLY

70° C - 3.5% Saline Solution - 72 Hours

Alloy	Filler	Weight Loss, mg	Deepest Crevice (mils)	Comment
316L/316L	None	3.2	< 1	29 of 40 Sites
		1.9	< 1	13 of 40 Sites
AL-6XN/AL-6XN	None	0.4	No Attack	No Attack
		0.4	No Attack	No Attack
AL-6XN/AL-6XN	625	0.6	No Attack	No Attack
		0.5	No Attack	No Attack
316L/AL-6XN	None	2.1	< 1	13 of 20 on 316L
		2.7	< 1	17 of 20 on 316L

Potentiodynamic Scans

Potentiodynamic scans can be used to monitor the corrosion potential (E) and corrosion current (I) of a corrosion coupon while being exposed to a corrosive media. Increasing the potential simulates a more oxidizing environment, such as increasing chloride content. The higher the potential before breakdown of the passive film, the greater the pitting resistance of the material under test. The corrosion current itself is a measure of the rate of corrosion and is usually plotted on a logarithmic scale.

Anodic polarization curves for AL-6XN Alloy and type 316L in the saline solution at 30° C are shown in Appendix I. These plots substantiate the test results reported above. The corrosion current increases significantly for the 316L when polarized above a breakdown potential of about 0.2 V_{SCE}. There is a very low current (rate of corrosion) for the AL-6XN Alloy until the very high breakdown potential of about 1.0 V_{SCE} is reached. Additionally, the plot indicates that the AL-6XN Alloy readily repassivates as the potential is reduced, while the 316L must drop to a lower potential than its starting point for repassivation to take place. The polarization curve for AL-6XN Alloy at 50° C also illustrates a material operating in a passive region which repassivates at a higher potential than from where it started.

SUMMARY

The results of testing 316L and a superaustenitic alloy in a sterile 3.5% saline solution illustrate the superior localized corrosion resistance of the more highly alloyed material. These results parallel those of similar tests conducted in more severe environments. The difference in the temperature needed to initiate crevice corrosion in the 316L material between a standard 6% $FeCl_3$ test solution (-3° C) and the 3.5% sterile saline solution (≈ +55° C) helps explain why 316L has provided reasonably good service in this environment. As experience has demonstrated, however, 316L is not free of corrosion in this type of service.

AL-6XN Alloy does provide significantly higher resistance to chloride and aqueous corrosion. All of the Al-6XN Alloy samples tested in this study were virtually unaffected by exposure to the 3.5% saline solution. Additionally, the appearance of the type 316L coupons was very similar to equipment which has been described as suffering from rouging. This condition appears to be corrosion product resulting from the small weight losses observed on the coupons. The fact that the weight loss on the superaustenitic material was so small, suggests this material may be free of this phenomenon in service.

Finally, this work also helped to characterize issues relative to orbital butt welding of sanitary tube sections of the superaustenitic alloy. The preparation of the tube samples for this project demonstrated the ability to join this material using techniques already in use for 316L. The use a higher alloy filler in the form of an Alloy 625 ring insert was also shown to be viable. For this particular environment, autogenous joints of AL-6XN Alloy appeared to be as corrosion resistant as the base metal. In more severe environments, such as the 6% $FeCl_3$ crevice corrosion tests, the over alloyed weld filler is required to fully utilize the benefits of the alloy.

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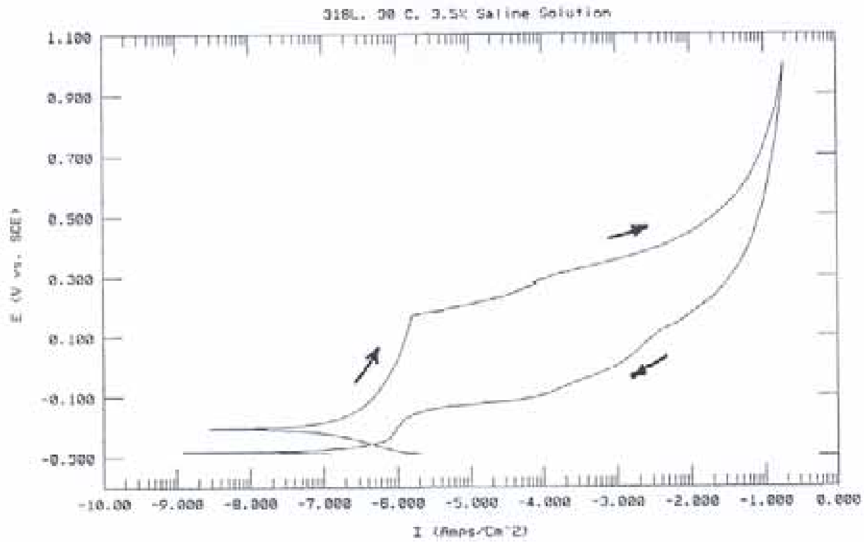
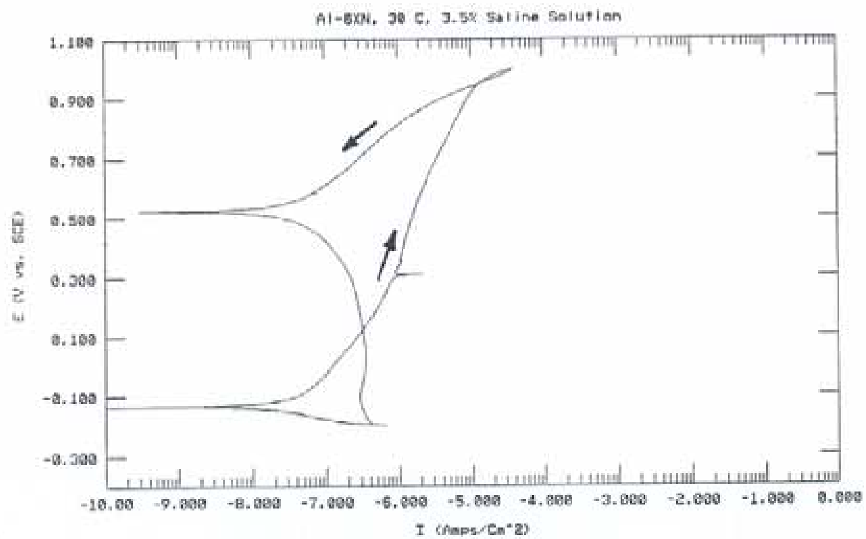
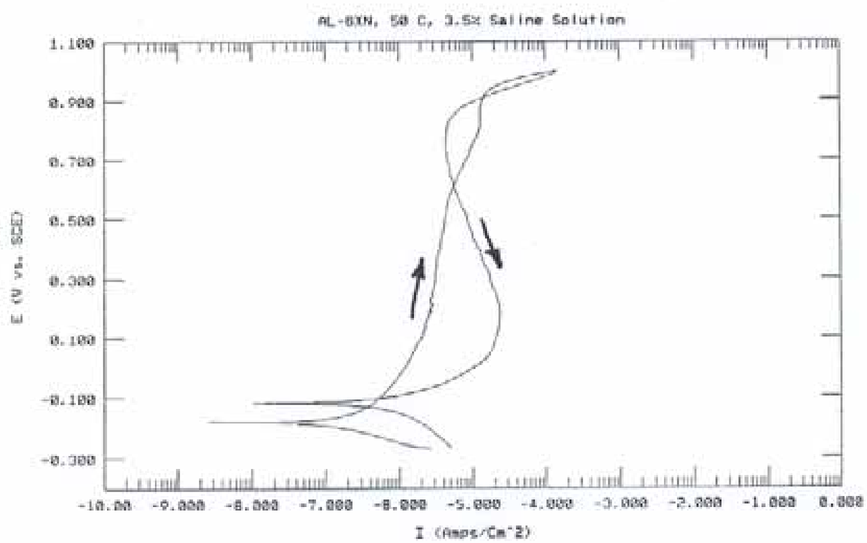

316L, 30 C, 3.5% Saline Solution
E (V vs. SCE)
I (Amps/Cm^2)


Al-6XN, 30 C, 3.5% Saline Solution
E (V vs. SCE)
I (Amps/Cm^2)


AL-6XN, 50 C, 3.5% Saline Solution
E (V vs. SCE)
I (Amps/Cm^2)

APPENDIX I