

Electrochemical impedance spectroscopy of alloys in a simulated space shuttle launch environment

L.M Calle^{a,*}, M.R. Kolody^b, R.D. Vinje^b

^a NASA, YA-C2-T, Kennedy Space Center, FL 32899

^b ASRC Aerospace Corp., ASRC-15, Kennedy Space Center, FL 32899

Abstract

Type 304L stainless steel (304L SS) tubing is currently used in various supply lines that service the Orbiter at NASA's John F. Kennedy Space Center Launch Pads in Florida (USA). The atmosphere at the Space Shuttle launch site is very corrosive due to a combination of factors, such as the proximity of the Atlantic Ocean and the concentrated hydrochloric acid produced by the fuel combustion reaction in the solid rocket boosters. The acidic chloride environment is aggressive to most metals and causes severe pitting in many of the common stainless steel alloys such as 304L SS. Stainless steel tubing is susceptible to pitting corrosion that can cause cracking and rupture of both high-pressure gas and fluid systems. Outages in the systems where failures occur can impact the normal operation of the shuttle and launch schedules. The use of a more corrosion resistant tubing alloy for launch pad applications would greatly reduce the probability of failure, improve safety, lessen maintenance costs, and reduce downtime. A study which included ten alloys was undertaken to find a more corrosion resistant material to replace the existing 304L SS tubing. The study included atmospheric exposure at NASA's John F. Kennedy Space Center outdoor corrosion test site near the launch pads and electrochemical measurements in the laboratory which included DC techniques and electrochemical impedance spectroscopy (EIS). This paper presents the results from EIS measurements on three of the alloys: AL6XN (UNS N08367), 254SMO (UNS S32154), and 304L SS (UNS S30403). Type 304L SS was included in the study as a control. The alloys were tested in three electrolyte solutions which consisted of neutral 3.55% NaCl, 3.55% NaCl in 0.1N HCl, and 3.55% NaCl in 1.0N HCl. The solutions were chosen to simulate environments that were expected to be less, similar, and more aggressive, respectively, than those present at the Space Shuttle launch pads. The results from the EIS measurements were analyzed to evaluate the corrosion susceptibility of the alloys and to predict the long-term corrosion performance of the subject materials. The results from the EIS measurements for the three alloys indicated that the higher-alloyed 254SMO and AL6XN exhibited a significantly improved resistance to corrosion than the 304L SS as the concentration of hydrochloric acid in the 3.55% NaCl solution was increased. The polarization resistance values obtained from the EIS measurements were consistent with those from linear polarization measurements, and were indicative of the actual long-term corrosion performance of the alloys during a two-year atmospheric exposure study.

Keywords: EIS; 304L SS; 254SMO; AL6XN; Acidified chloride environment

1. Introduction

Type 304L Stainless Steel (304L SS) tubing is used in various supply lines that service the Orbiter at the Kennedy Space Center (KSC) launch pads. The atmosphere at the launch site has a very high chloride content caused by the proximity of the Atlantic Ocean. In addition, during a launch, concentrated hydrochloric acid is produced by the fuel combination reaction in the solid rocket boosters. The acidic chloride environment is aggressive to most metals and causes severe pitting in many of the common stainless steel alloys. 304L SS tubing is susceptible to pitting corrosion that can cause cracking and rupture of both high-pressure gas and fluid systems. The failures can be life threatening to launch pad personnel in the immediate vicinity. Outages in the systems where the failure occurs can also affect shuttle launch schedules. The use of a new tubing alloy for launch pad applications would greatly reduce the probability of failure, improve safety, lessen maintenance costs, and reduce downtime losses.

A previous investigation was undertaken in order to find a suitable replacement for the 304L SS in vacuum jacketed cryogenic supply lines at the Space Shuttle launch sites. Of the nineteen alloys that were included in the investigation, several nickel-based alloys were found to have a very high resistance to corrosion in the highly corrosive environment at the launch pads.¹²³⁴

In the present investigation, Electrochemical Impedance Spectroscopy (EIS) was used to study the corrosion performance of 254SMO, AL6XN, and 304L SS. Alloy 304L SS was included as a control. The EIS measurements were carried out under three different electrolyte conditions: neutral 3.55% NaCl, 3.55% NaCl in 0.1N HCl, and 3.55% NaCl in 1.0N HCl. These conditions were expected to be less severe, similar, and more severe respectively than the conditions at the launch pad. A parallel study was carried out in which tubes fabricated with the alloys were exposed to the atmosphere at the KSC corrosion test site near the Space Shuttle launch pads.⁵

2. Experimental

2.1 Alloys

Table 1 shows the chemical composition of the alloys chosen for this investigation. The test specimens were polished to 600-grit, ultrasonically degreased in a detergent solution and dried before immersion in the electrolyte.

Table 1
Chemical composition

Alloy	Fe	Ni	Cr	Mo	Mn	C	N	Si	P	S	Cu
304L	71.567	8.200	18.33	0.500	1.470	0.023	0.030	0.380	0.030	0.0002	0.460
AL6XN	48.11	23.88	20.470	6.260	0.300	0.020	0.330	0.40	0.021	0.0003	0.200
254SMO	55.162	17.900	20.000	6.050	0.490	0.012	0.196	0.350	0.019	0.001	0.680

2.2 Experimental Procedures

A Model 378 Electrochemical Impedance system manufactured by EG&G Princeton Applied Research Corporation was used for all EIS measurements. The system includes: (1) the Model 273 Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Power Sine[®] Electrochemical Impedance Software. Data were gathered in the frequency range from 100 kHz to 0.01 Hz. A 10 mV AC amplitude was used for the experiments.

The electrochemical cell (flat cell) included a saturated calomel reference electrode (SCE), a platinum-on-niobium counter electrode, the metal specimen working electrode, and a bubbler/vent tube. The specimen holder in the cell is designed such that the exposed metal surface area is 1 cm².

Three different aerated electrolyte solutions were used: (1) 3.55% NaCl, (2) 3.55% NaCl in 0.1N HCl and (3) 3.55% NaCl in 1.0N HCl. The solutions were aerated by bubbling air into the cell for the duration of the data collection. Prior to the collection of EIS measurements, the open circuit potential (ocp) was monitored until the sample reached a potential that was stable within ± 5 mV for a period of 10 minutes. Multiple tests had essentially the same outcome. The reported results are the averages of two or more runs.

An atmospheric exposure site near the launch pads was used to evaluate the performance of the six alloys included in this study for their resistance to corrosion under conditions similar to those at the launch pad. Triplicate samples of tubes of each alloy were exposed. An acid slurry was prepared by mixing 500 ml of a 10 percent (v/v) solution of HCl and 28.5 grams of alumina powder to simulate solid rocket booster deposition. One set of tubes was sprayed every two weeks with the acid slurry to accelerate the corrosion effect. The other set was left exposed to the natural marine seacoast environment.

3. Results and Discussion

3.1. Open Circuit Potential

The open circuit potential (ocp) gives an indication of how noble a metal is in a given environment. In general, a more positive ocp means that the metal can be expected to be more resistant to corrosion in that particular electrolyte than one with a more negative corrosion potential. Thus, most metals can be ranked according to resistance to corrosion based on ocp. However, stainless steels, as passive materials, can fluctuate from an active to a passive state depending on the environment to which they are exposed, the velocity of the solution, and passivation treatments applied during manufacturing.

Figs. 1-3 show the variation of the ocp with immersion time for the alloys in the three different electrolytes. The data shown on Fig. 1 indicates that there is no significant difference between the ocp for the three alloys in neutral 3.55% NaCl. Fig. 2 shows that the presence of HCl in the electrolyte at a concentration of 0.1N results in ocp values that are lower for the 304L SS than for 254SMO and AL6XN. Fig. 3 shows that the difference between the ocp values for 304L SS and the other two alloys became more pronounced when the concentration of HCl in the 3.55%

NaCl solution was increased to 1.0N. Data were collected for a period of 408 hours except for the 304L SS in 3.55%-1.0N HCl for which data collection was terminated when a color change in the electrolyte, indicative of the loss of integrity of the sample, was observed.

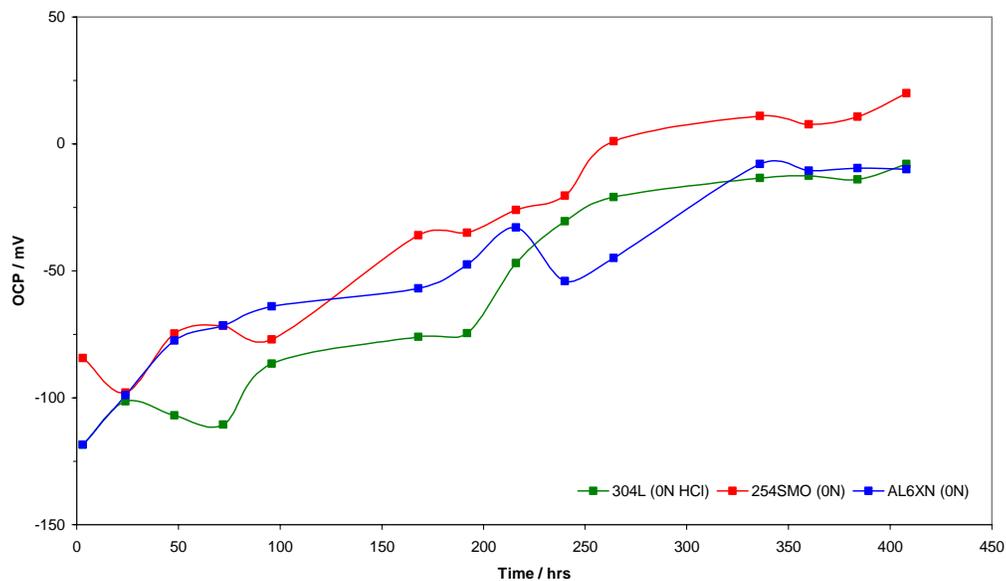


Fig. 1. Corrosion potential of alloys in neutral 3.55% NaCl

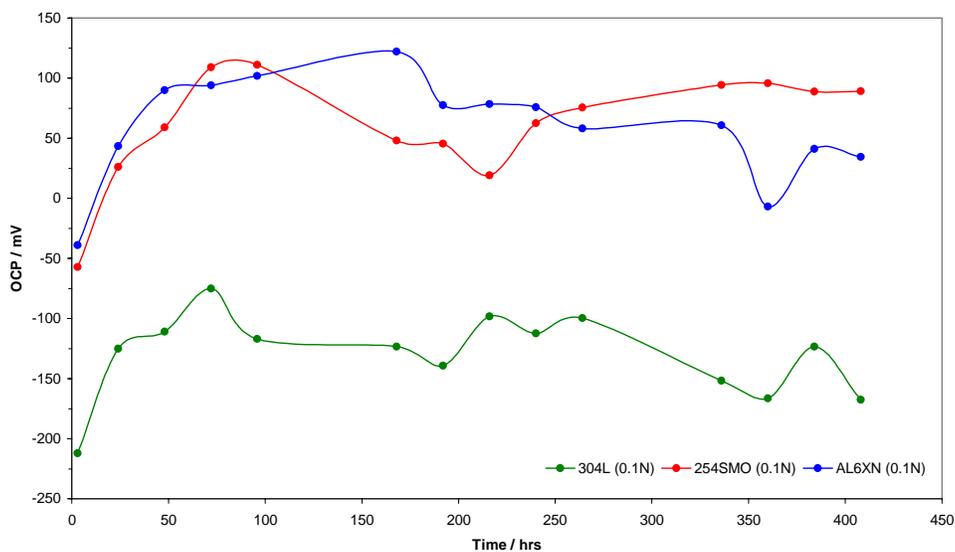


Fig. 2. Corrosion potential of alloys in 3.55% NaCl in 0.1N HCl

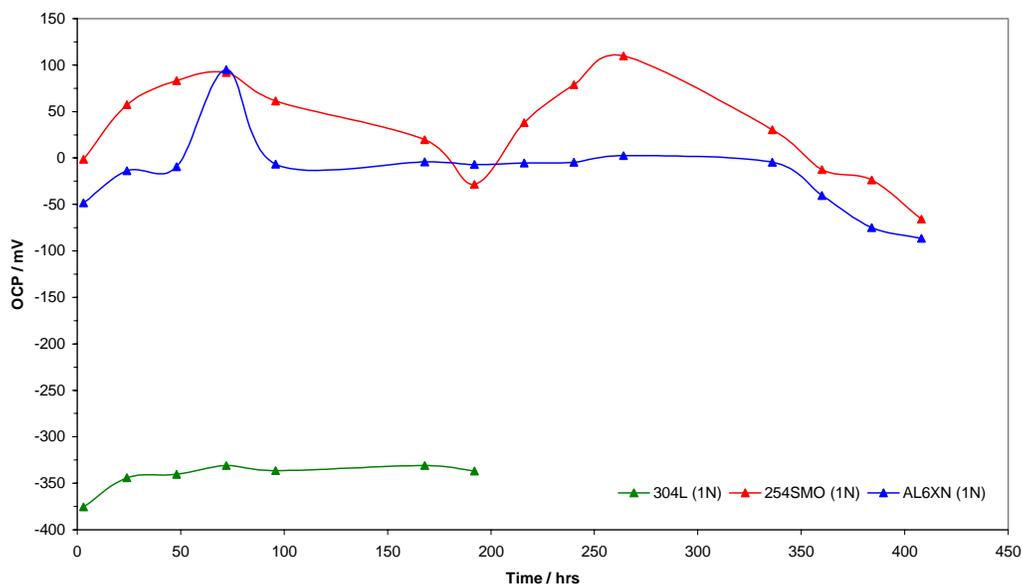


Fig. 3. Corrosion potential of alloys in 3.55% NaCl in 1.0N HCl.

3.2. Impedance Spectroscopy

The impedance data for the alloys in the three different electrolyte solutions were gathered after the ocp had stabilized. Nyquist as well as Bode plots of the data were obtained. It was determined that the response of the alloys with immersion time was more evident in the Nyquist plots. The Nyquist plots for the alloys in the three different electrolyte solutions are shown in Figs. 4-12. The three alloys showed a similar behavior in the neutral 3.55% NaCl solution. As seen in Figs. 4-6, the Nyquist plots show an increase in corrosion resistance during the first 24 hours of immersion that remains fairly unchanged thereafter. Figs. 7-11 show that when HCl is present in the electrolyte solution, the initial increase in the corrosion resistance of the material is followed by a gradual decrease except for 304L SS. This alloy exhibited a significant decrease of its corrosion resistance. Fig. 12 shows that the behavior of 304L SS when the concentration of the acid in the electrolyte is increased to 1.0N is significantly different from the other alloys. There is a significant decrease in its corrosion resistance starting at the initial immersion time.

The Nyquist plots exhibited only one capacitive contribution represented by a semicircle. An equivalent circuit consisting of a parallel RC arrangement in series with the solution resistance, R_s , was used to simulate the data. In the simulation, a constant phase element, Q, was used instead of the capacitance, C. The impedance of the equivalent circuit is given by:

$$Z = R_s + \frac{R_p}{1 + (j\omega CR_p)^n}$$

where R_p is the polarization resistance, C is the capacitance and n is the fit exponent. The polarization resistance is a direct measure of the corrosion resistance in the solution at open

circuit condition since the rate of corrosion is inversely proportional to the polarization resistance.

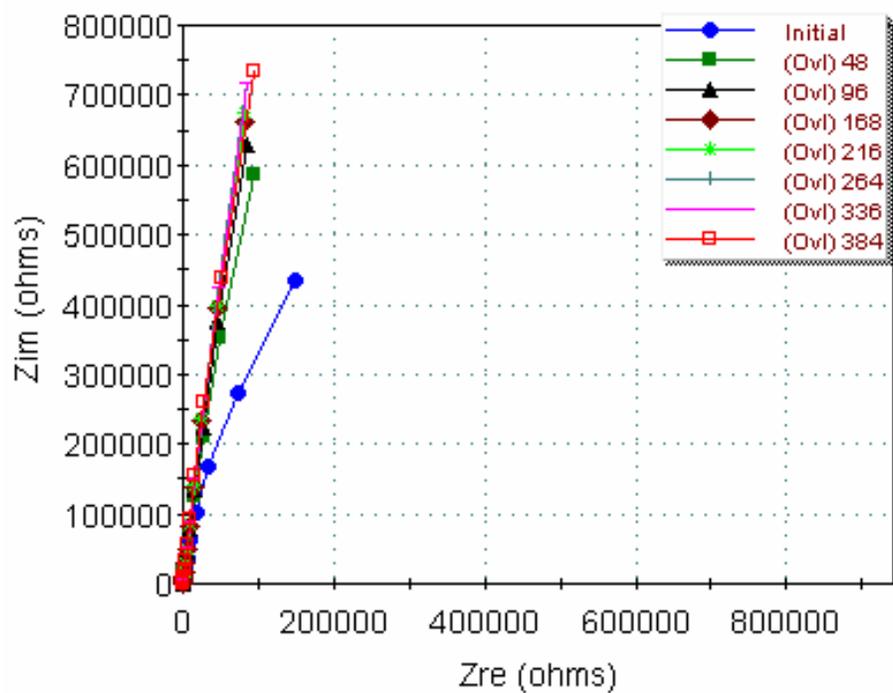


Fig. 4. 254SMO in neutral 3.55% NaCl at different immersion times (hrs)

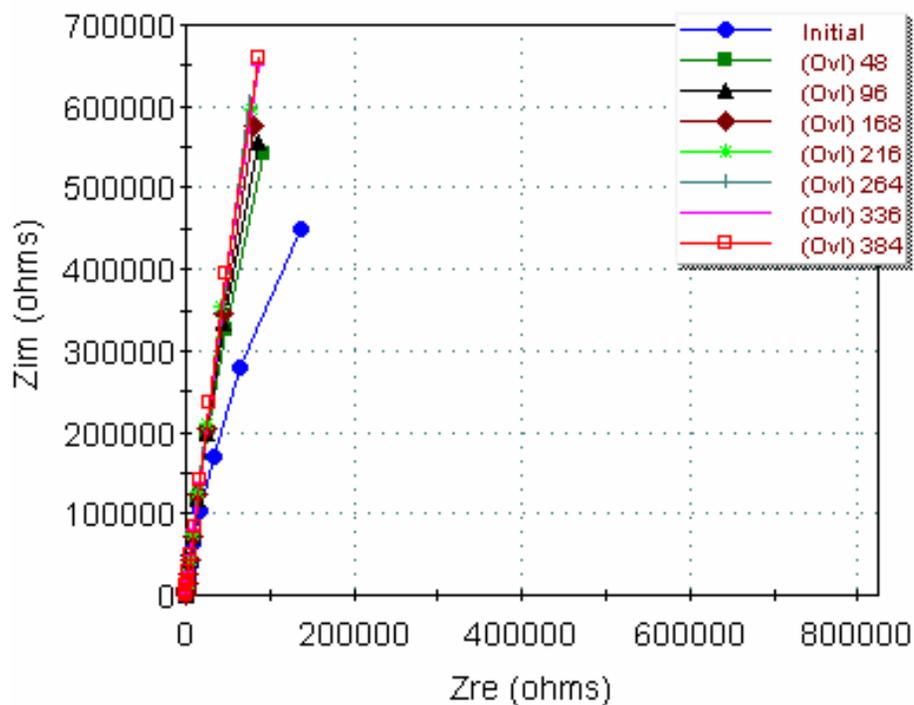


Fig. 5. AL6XN in neutral 3.55% NaCl at different immersion times (hrs)

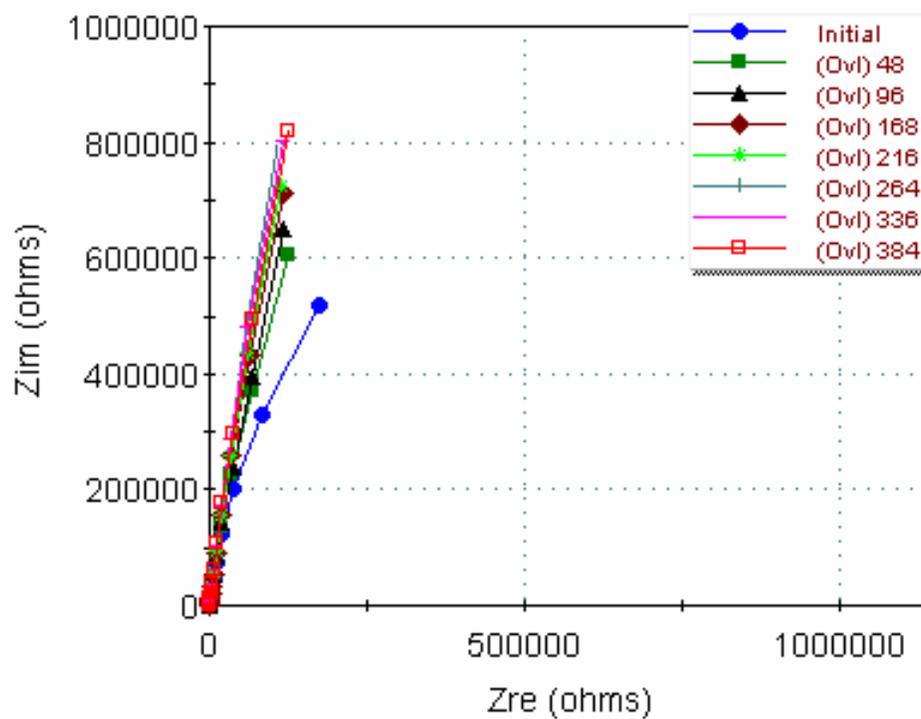


Fig. 6. 304L in neutral 3.55% NaCl at different immersion times (hrs)

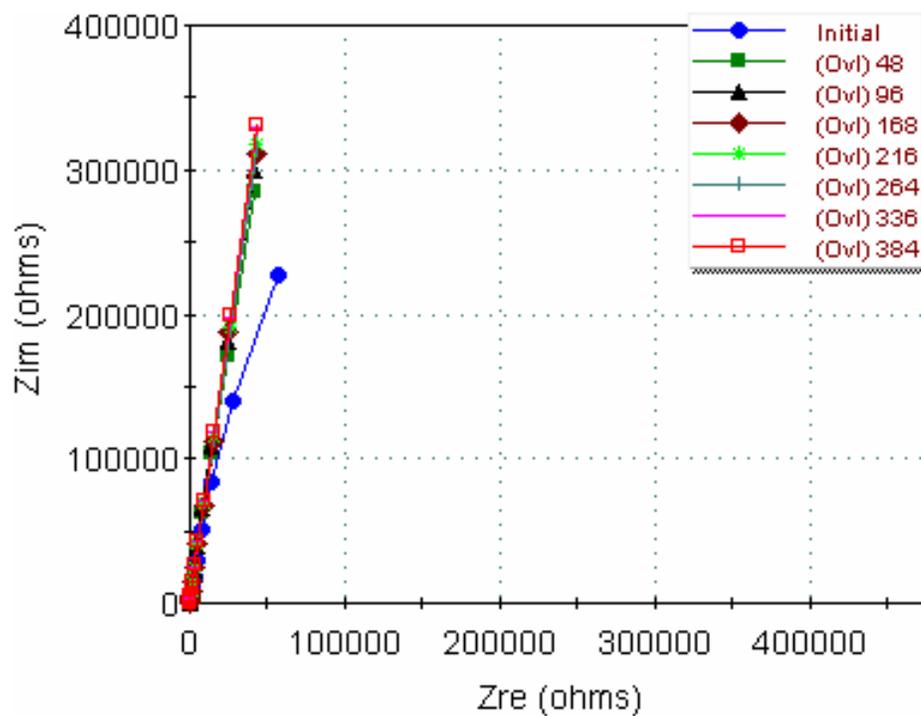


Fig. 7. 254SMO in 3.55% NaCl-0.1N HCl at different immersion times (hrs)

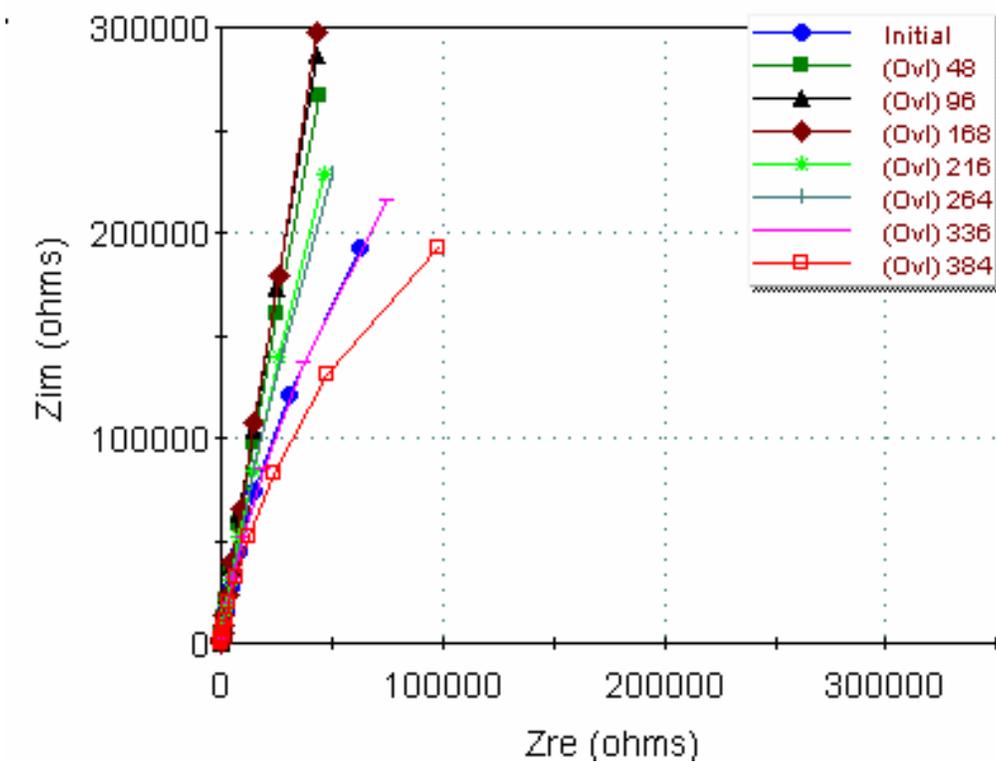


Fig. 8. AL6XN in 3.55% NaCl-0.1 N HCl at different immersion times (hrs)

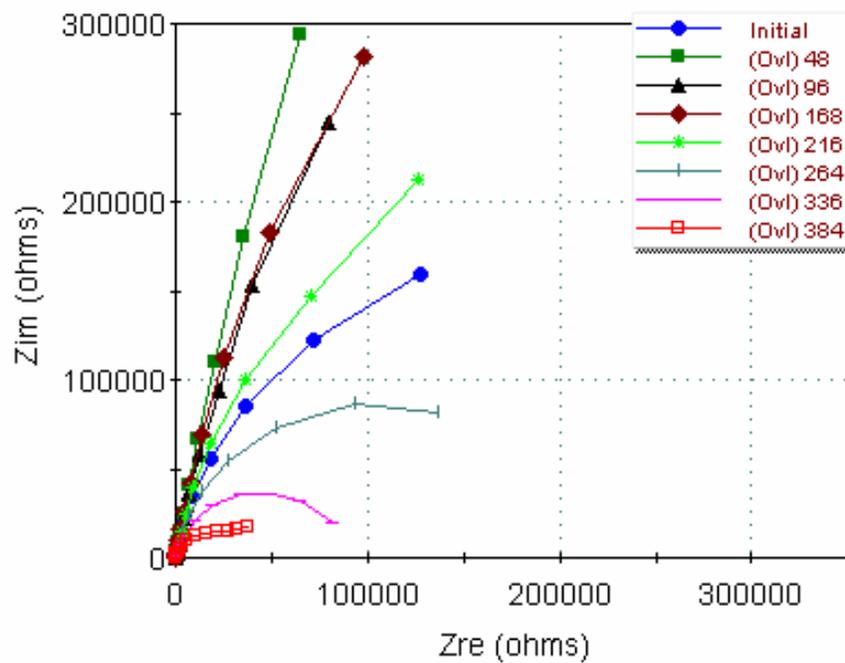


Fig. 9. 304L in 3.55% NaCl-0.1N HCl at different immersion times (hrs)

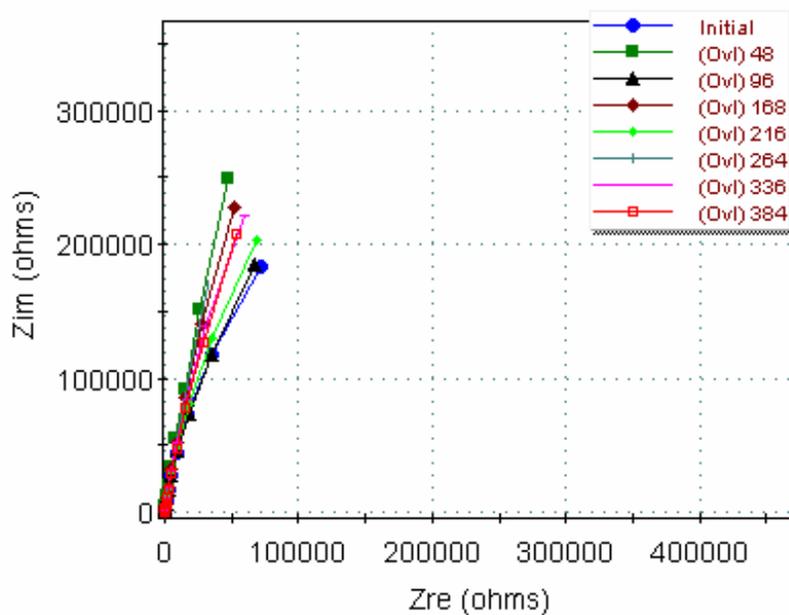


Fig. 10. 254SMO in 3.55% NaCl-1.0N HCl at different immersion times (hrs)

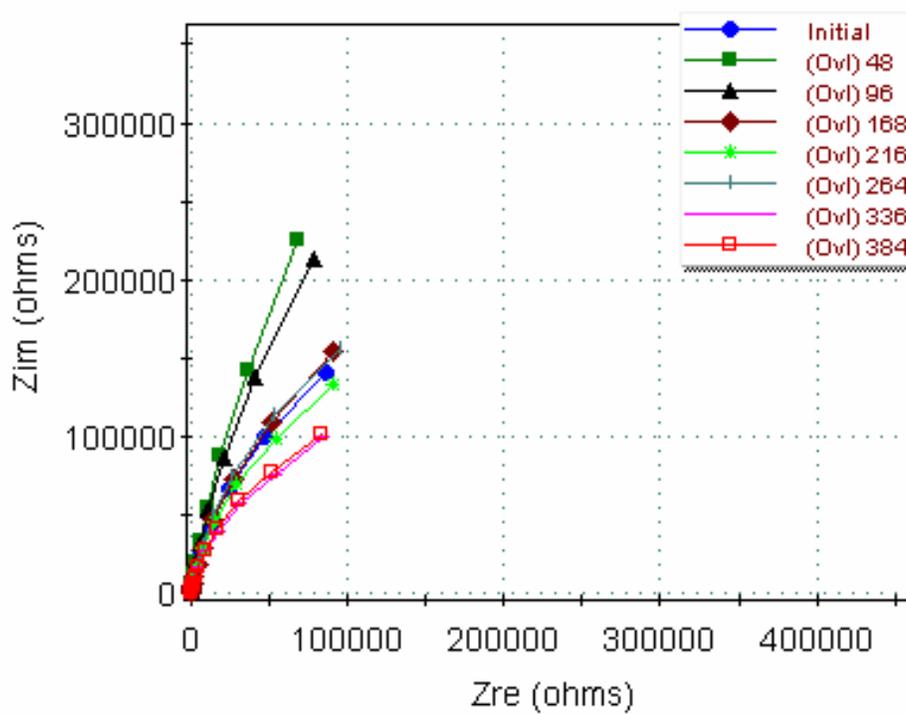


Fig. 11. AL6XN in 3.55% NaCl-1.0N HCl at different immersion times (hrs)

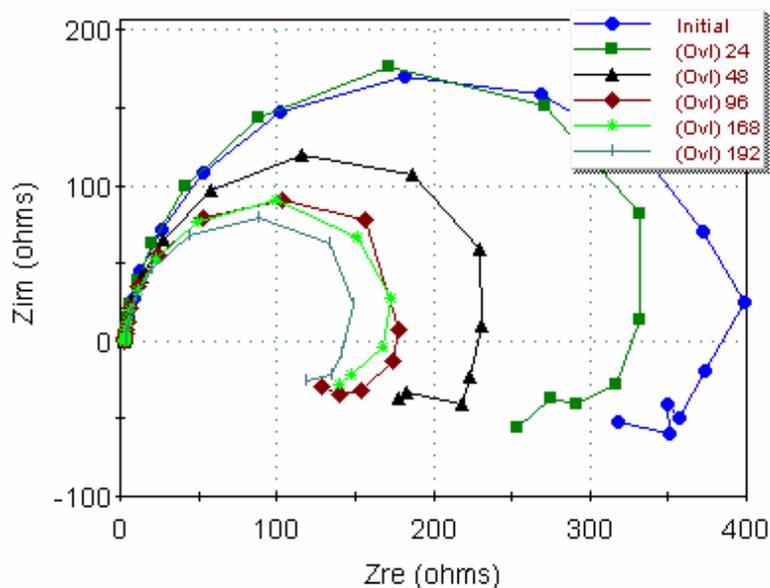


Fig. 12. 304L in 3.55% NaCl-1.0N HCl at different immersion times (hrs)

Fig 13 shows the variation of R_p with immersion time for the three alloys in the three electrolyte solutions. Fig. 13 shows that there is no significant difference in the R_p values for the alloys in neutral 3.55% NaCl. Fig. 14 shows that when the concentration of HCl in the solution is increased to 0.1N, the R_p values for the alloys are not significantly different during the first 72 hours of immersion. It was observed that the R_p values of 304L SS start to decrease thereafter. Fig 15 shows that when the concentration of the acid in the electrolyte is further increased to 1.0N, there is a significant difference between the R_p values of 304L SS and those for 254SMO and AL6XN at all immersion times. Data collection for the 304L SS samples was terminated when a color change in the electrolyte solution was observed and the data became very noisy. The changes in the R_p values with immersion time were consistent with those obtained previously from linear polarization data.⁶ It was noticed that when the concentration of the acid in the 3.55% NaCl solution was 0.1N, the ocp values for 304L SS were different from those of AL6XN and 254SMO from the beginning of immersion while the R_p values for the three alloys were not significantly different until the immersion time reached 72 hours.

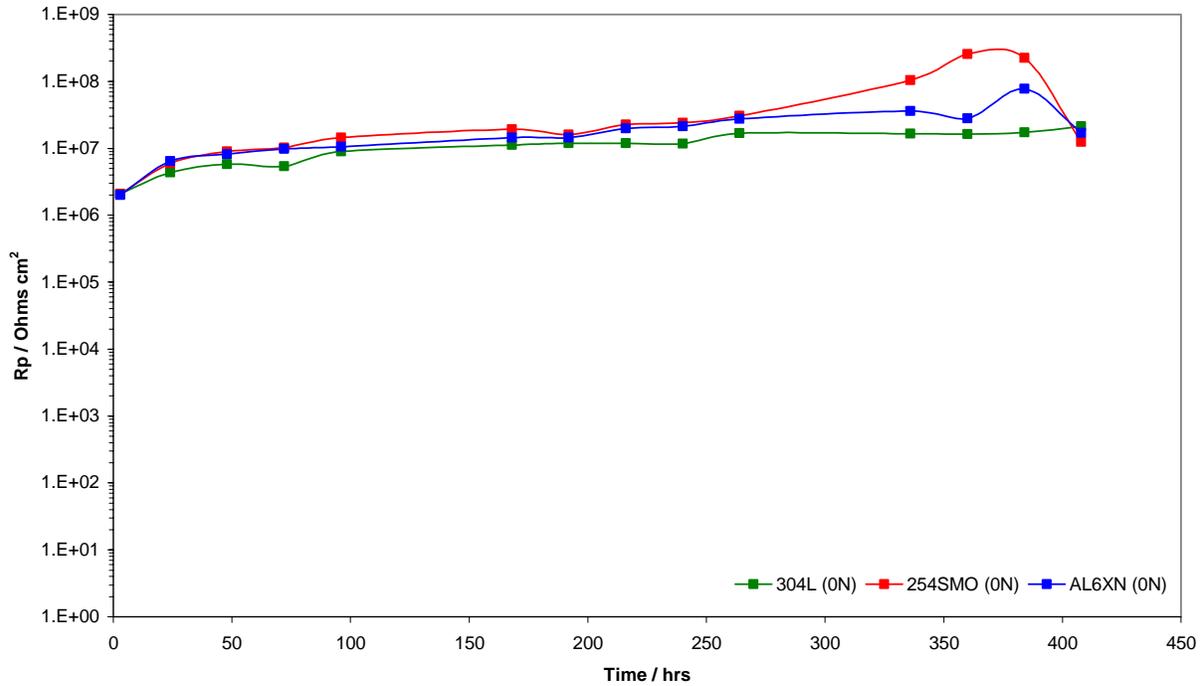


Fig. 13. Average R_p in neutral 3.55% NaCl at different immersion times

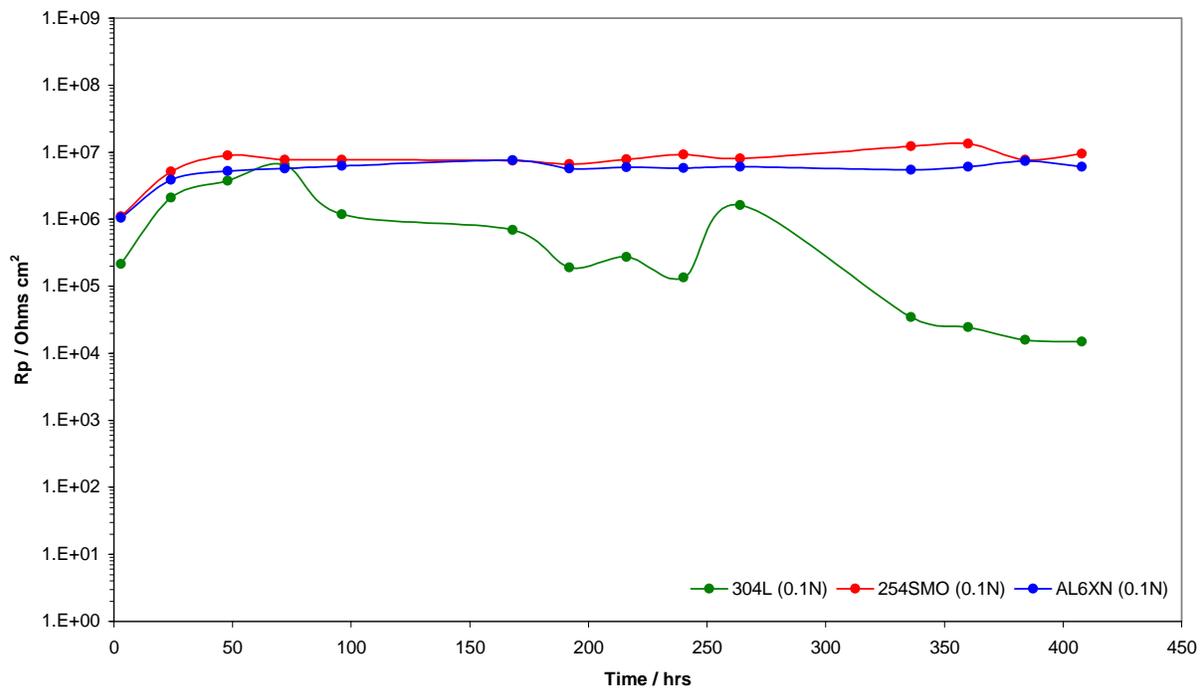


Fig. 14. Average R_p in 3.55% NaCl-0.1N HCl at different immersion times

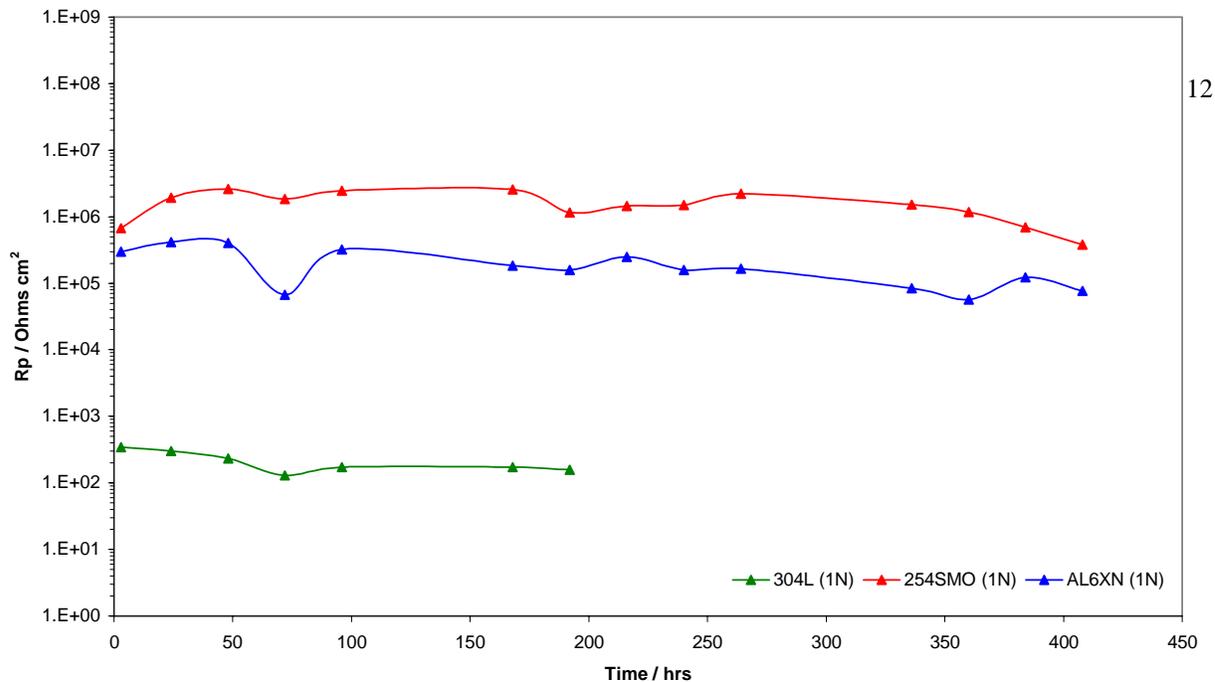


Fig. 15. Average R_p in 3.55% NaCl-1.0N HCl at different immersion times

Atmospheric Exposure

The most important criteria of any laboratory test for corrosion is that it must rank alloys consistently with their actual long-term service performance. The laboratory results were compared to those from a two-year atmospheric exposure study under conditions designed to simulate those present at KSC's Space Shuttle Launch Pads. Detailed results of the atmospheric exposure study have been reported elsewhere.⁵ Photographs of the tubes at the atmospheric exposure site near the launch pads are shown in Fig. 16. Fig. 17 shows close ups of the tubes (three for each alloy) after one year of natural atmospheric exposure. The photographs show corrosion on 304L SS and its absence in the other two alloys. This finding indicates that one year of natural marine atmospheric exposure at the test site is more aggressive than 408 hours of immersion in the neutral 3.55% NaCl electrolyte solution. A summary of the visual evaluation of the tubing test articles after two years of atmospheric exposure is presented in Table 2.



Fig. 16. Racks at the atmospheric exposure site

TABLE 2 Summary of visual observations of tube specimens after two years of atmospheric exposure

Visual observations after two years of atmospheric exposure		
Alloy	Natural	With acid-alumina slurry rinse
304L	Tubes in poor condition with pits and brown spots over entire surface	Tubes failed due to pitting. Pits went through the thickness of the tube
AL6XN	Light brown color over entire surface of the tube.	Tubes in good condition with slight discoloration
254SMO	Tubes in good condition. Some spots along the seam weld.	Tubes in good condition except for pits on the seam weld



304L



AL6XN

254SMO

Fig. 17 Tubing after one year of natural seacoast atmospheric exposure (no acid rinse)

4. Conclusions

The data showed that there is no significant difference between the ocp for the three alloys in neutral 3.55% NaCl. While the ocp values for 254SMO and AL6XN remained fairly unchanged with the increase in the concentration of HCl in the 3.55% NaCl solution, those for 304L SS dropped significantly. These findings are consistent with the long-term corrosion performance of the alloys in the atmospheric exposure study.

The Nyquist plots obtained from the EIS data exhibited only one capacitive contribution represented by a semicircle. An equivalent circuit consisting of a parallel RC arrangement in series with the solution resistance, R_s , simulated the data. The R_p values obtained from the equivalent circuit simulation at the early immersion times were consistent with those obtained by

dc electrochemical measurements, and were in agreement with the long-term corrosion performance of the alloys as determined in the atmospheric exposure study.

One year in the natural marine environment at the KSC outdoor exposure facility near the launch pads is more aggressive to 304L SS than immersion for up to 408 hours in the neutral 3.55% NaCl electrolyte solution.

It was concluded that 254SMO and AL6XN are suitable alloys to replace the 304L SS currently used at the launch pads.

Acknowledgements

The authors gratefully acknowledge the funding of this project by the Kennedy Space Center's Director Discretionary Fund (CDDF). The authors also wish to thank Ms. Nancy Zeitlin for her support with project management.

References

- ¹ L.M. Calle and L.G. MacDowell, "Application of Electrochemical Impedance Measurements to Corrosion Prediction in the Space Transportation System Launch Environment", *Corrosion/94*, Paper No. 320, The NACE Annual Conference and Corrosion Show, Houston, TX: National Association of Corrosion Engineers, 1994.
- ² L.M. Calle and L.G. MacDowell, "Electrochemical Impedance Spectroscopy of Metal Alloys", *NASA Tech Briefs* journal, Volume 17, p 66, January 1993.
- ³ C. Ontiveros and L. G. MacDowell, *Corrosion* 90, Paper No. 94, NACE (1990)
- ⁴ L.M. Calle and L.G. MacDowell, "Study of Metal Corrosion Using AC Impedance Techniques in the Space Transportation System (Space Shuttle) Launch Environment," *ADVMAT/91, First International Symposium on Environmental Effects on Advanced Materials*, Houston, TX: National Association of Corrosion Engineers, 1991.
- ⁵ R.G. Barile, L.G. MacDowell, J. Curran, L.M. Calle, and T. Hodge, "Corrosion of Stainless Steel Tubing in a Spacecraft Launch Environment," *Corrosion/2002*, Paper No. 02152, The NACE Annual Conference and Corrosion Show, Houston, TX: National Association of Corrosion Engineers, 2002.
- ⁶ L.M. Calle, R.D. Vinje, and L.G. MacDowell, "Electrochemical Evaluation of Stainless Steels in Acidified Sodium Chloride Solutions," *CORROSION/2004*, Paper No. 04303 (Houston, TX: NACE 2004).