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Honors Scholar

Passivity Analysis using Anodic Potentiostatic Method for Various Stainless Steels

Honors Thesis
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Abstract

The formation of anodic polarization curves for 430 ferritic stainless steel was conducted. Repeatable results were obtained through the creation of an updated procedure based on ASTM Method G5-94: Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements. The discrete zones of active, passive, and transpassive zones were stable through each test run. This stability prompted an examination into the polarization differences of various stainless steels. Three types were studied, 304L, 316L, and 430 stainless steel. Each type was subjected to identical conditions, a 1N solution of sulfuric acid. The various metal types showed a large difference between i_{crit} values and the range of the passive zone. A multiple linear regression plot was performed to determine what factors attributed to these two important corrosion values. Nickel content was determined to be significant with respect to the i_{crit} values, and the combination of chromium and nickel contents was determined to be significant to the range of the passive zone.

Introduction

This senior thesis has focused on the evaluation of corrosion rates of 304L, 316L, and 430 stainless steels in a solution of 1N sulfuric acid. The steel sample is subjected to the application of an electric potential that gradually increases via a potentiostat. The potentiostat instrument measures the current density between a metal electrode and counter electrode when voltage is increased stepwise. A working electrode measures and records the associated current density. This test yields an anodic polarization curve complete with active, passive, and transpassive zones. Analysis of the anodic polarization curve will give a range of electric potentials in which the passive zone exists. The minimum corrosion rate will be found in the passive zone at a current density known as i_{pass}. The location of this passive zone is vital when applying anodic protection to a metal that is servicing a corrosive environment. Anodic protection intentionally produces a passive film on the surface of the metal by increasing the potential for E_{corr} to a value near the mid-point in the passive zone. Figure 1 shows a typical anodic polarization curve.

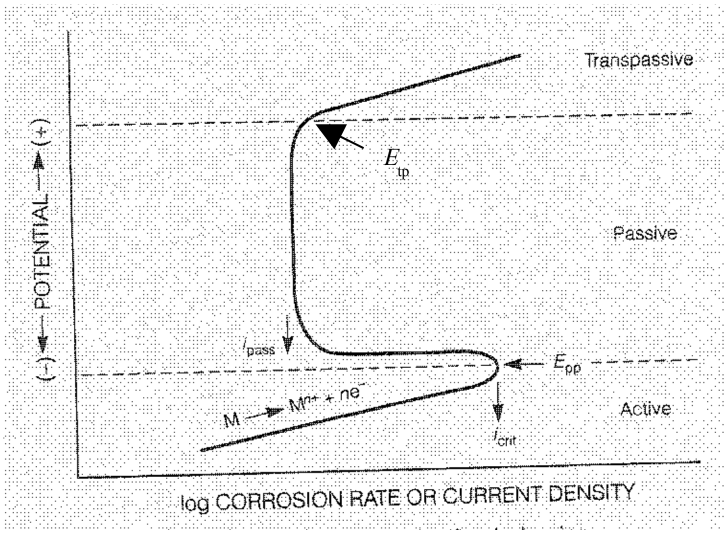

Figure 1. Regionalized breakdown of generic anodic polarization curve

This study will focus on the formation of the passive film from which this zone is aptly named. A definition of passive film describes it as a thin, hydrated, oxidized, passive surface in which corrosion rates are significantly diminished. The success of anodic protection relies on the ability to create a sustainable passive film on the surface of the metal. An understanding of passivity must first be addressed to understand its effects. Passivity is defined as a condition of corrosion resistance due to formation of a thin and "impermeable" film of metal oxide on the surface. Corrosion rates will be low because the reagents such as H^+ OH^- and $O_{2(aq)}$ cannot penetrate the film easily. A passive film is formed by an electrochemical reaction with iron, as shown in reaction 1.

$$Fe + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+ + 2e^- \qquad (1)$$

The generation of electrons during passive film formation is an issue that requires attention. It is seen from reaction 1 that, if electrons are removed from the system after generation, the reaction will be ensured to proceed in the forward direction and the iron oxide film is maintained. The electrons are removed by the cathodic reaction above E_{corr} in a potentiostat. If the potential is conducted in a deaerated solution the cathodic reaction may be given as reaction 2.

$$2H^+ + 2e \leftrightarrow H_{2(g)} \qquad (2)$$

i_{crit}, shown in Figure 1 is the maximum corrosion rate of the metal dissolution (reaction 1) before the metal surface starts to become passivated with the $Fe(OH)_2$ film. i_{crit} may be interpreted as a measure of how difficult it is to passivate the metal surface. In other words, the higher i_{crit}, the more difficult it is to passivate the metal surface.

Iron-based alloys containing at least 10.5% chromium are classified as stainless steels. They are classified as ferritic, austenitic, duplex, martensitic, and precipitation hardening. Each has special compositions of alloying elements and characteristics that perform well in certain situations. The scope of this paper will cover ferritic and austenitic stainless steels, as they encompass the metal types this study evaluated.

The ferritic stainless steels are favored wherever stress corrosion cracking is a concern. Type 430 has been used in architectural and automotive trim for mild to moderate atmospheric exposure. Austenitic stainless steels have a higher nickel content than ferritic, which stabilizes the face centered cubic austenitic phase and improves corrosion resistance synergistically with chromium. The corrosion resistance of this metal type is derived from the thin, hydrated, oxidized, chromium-rich, passive surface layer. Type 304 has been used for valve parts, pump shafts, fasteners, and screens in fresh water low in chloride. An addition of 2% molybdenum in 316 stainless steel improves resistance to chloride pitting and stress corrosion cracking.

It is generally known that the chromium content in stainless steels renders a wide range of passivity in terms of potential and solution pH. The inclusions of nickel and molybdenum reinforce the stability of passivity in the metal. The objective of this study is to quantify i_{crit} with various amounts of chromium, nickel, and molybdenum in three types of stainless steels; 430, 304L, and 316L.

Experimental Procedures

The beginning of this research focused on the test methods and procedures used to track the formation of the anodic polarization curve. The goal was to form a set of procedures that could yield a reproducible, repeatable polarization curve for various samples of stainless steels. Only when this procedure was satisfactory, could exploration into a new test sequence be conducted. The basis of these procedures was the ASTM method G5-94: Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.

Before experimentation could proceed, a set of ground rules for testing a metal specimen were specified. Outside contaminants could have a negative effect on the study, therefore cleanliness was vital. Therefore, before each experiment, the test cell and all its parts were thoroughly cleaned with deionized water and air dried.

Ensuring the potentiostat was transmitting accurate electric potentials was proven first. This was done through calibration of the potentiostat/galvanostat. The potentiostat instrument used in these experiments was the Princeton Applied Research Model 283 Potentiostat/Galvanostat with the test cell provided by the same company. This calibration was completed after assistance from the manufacturer. Once the equipment was ready, a 900mL 1N sulfuric acid solution was added to the test cell and the carbon counter electrodes and reference electrode (reference electrode is in the saturated KCl solution) were put into place. Then the solution in the test cell, with a rubber stopper in place of the working electrode was purged with ultra high-grade nitrogen through the gas sparger for 30 minutes to remove oxygen content. At the same time, the potentiostat was turned on at least 30 minutes before testing. The nitrogen purge was continued for the duration of the experiment.

Metal specimens were of three types of stainless steels; 304L, 316L, and 430. Each had dimensions of 0.953cm diameter and 1.44cm long. The metal specimen was polished to the same degree before each test run. Films of corrosive material coat the specimen after every test, and must be removed before the next test can be run. A lathe was used to rotate the specimen while wet grinding with 600-grit sandpaper. The wet grinding was conducted using acetone, which varied from the ASTM method which used deionized water. The use of acetone ensured that any oils were removed from the specimen. It is important to note that testing must take place within two hours of polishing, to ensure no corrosive films have begun to form, thereby disrupting the test results. A polishing procedure was created to ensure uniform polishing was completed before every test. This procedure has resulted in excellent repeatability for the test. The polishing step ensured that any corrosion products generated from previous tests or environment reactions were removed.

After the testing sequence was refined to deliver repeatable results, the next step was to ensure that each test would capture all key information needed for the study. This was achieved by examining several earlier tests for trends that could apply to all test sequences. It was found that the standard used to analyze electric potential ranged from -1.1 volts to 1.2 volts. Although this range captured all zones of interest on the anodic polarization curve, its magnitude often resulted in over-voltage errors with the potentiostat. These problems were alleviated by narrowing the potential range down to -0.6 volts to 1.1 volts. This change greatly reduced issues associated with over-voltage.

The procedures listed above were followed for each test run conducted. The potentiostat sent potential-current results to a computer operating Powersuite software v2.12.1. The software allowed the potential range to be set, and tracked the simple linear scan.

Results

Two identical potentiostat tests were conducted on the same stainless steel 430 sample. The tests were run 40 days apart to gauge the repeatability of the experimental data. The results of two test runs are shown in Figures 2 and 3.

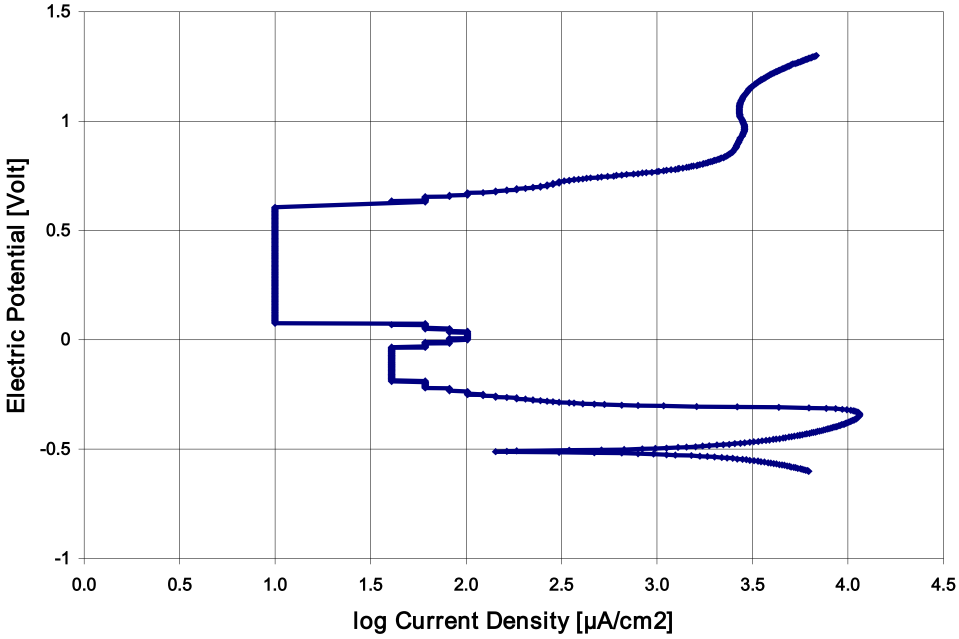

Figure 2: Anodic polarization curve 1

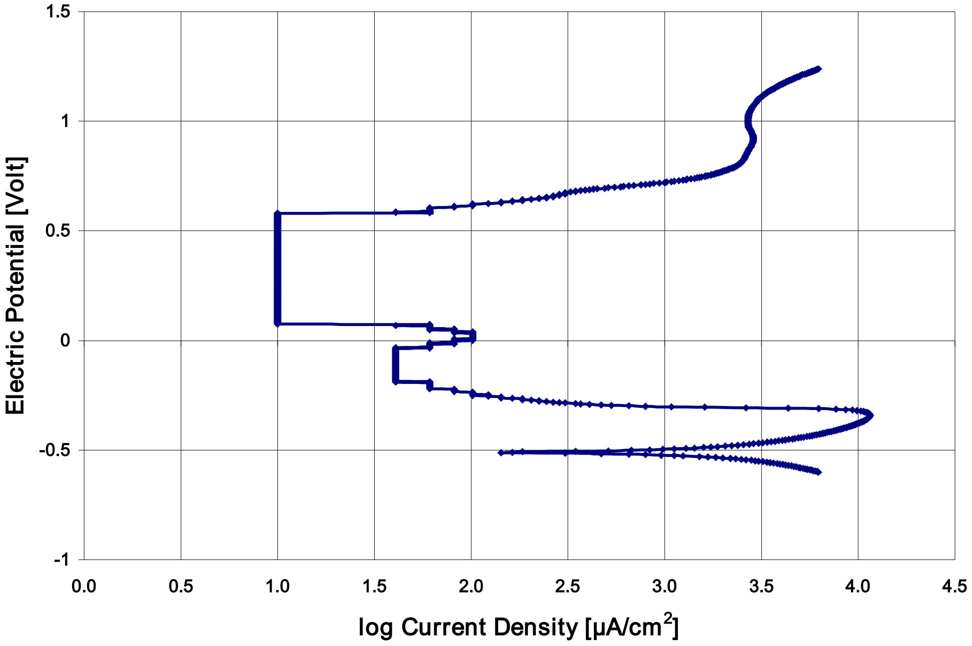

Figure 3: Anodic polarization curve 2

A comparison of these anodic polarization curves shows that repeatable results can be obtained using the lab setup and procedures created. At this point in the research, two additional test specimens were obtained, 304L and 316L stainless steel. These specimens were tested under identical conditions, and a comparison of their corrosion behaviors was conducted. A side by side comparison of each anodic polarization curve is given in Figure 4.

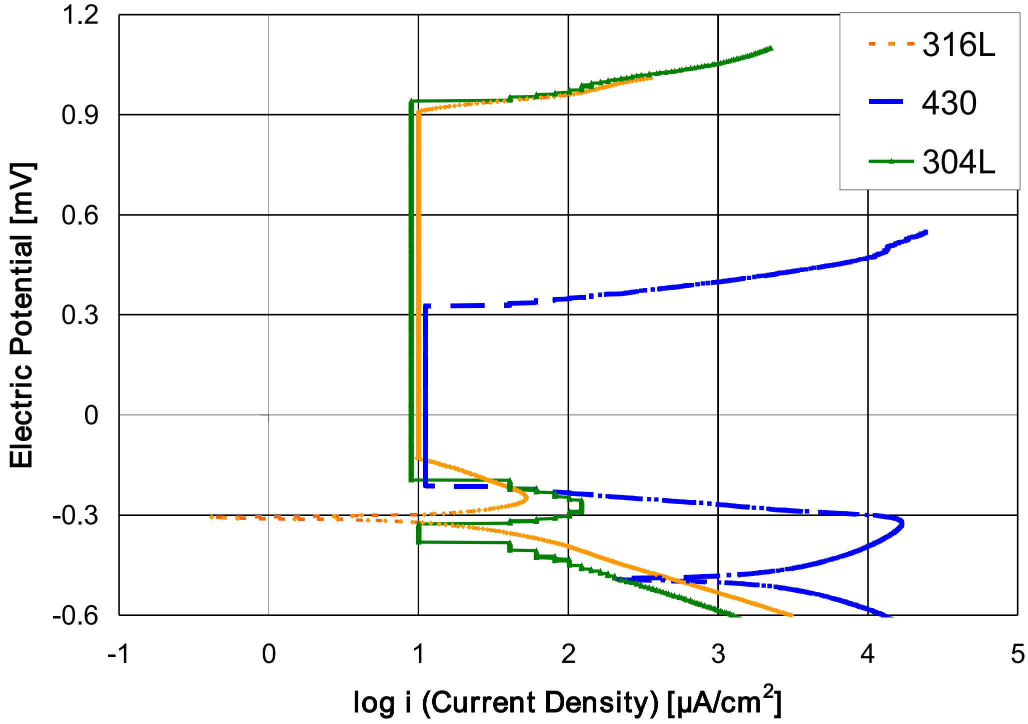

Figure 4. Anodic polarization curves of 304L, 316L and 430 stainless steels.

Analysis of Figure 4 shows a distinct difference between 430 stainless steel and the 300 series steels. Examination of the critical current, i_{crit} shows a large difference across metal types. i_{crit} is vital to anodic polarization since the metal must be polarized from the active state through E_{pp}, where current is a maximum at i_{crit}. This means that in order to reach the passive zone, a large enough current must be supplied to the specimen to overcome the critical hurdle. A summary of the i_{crit} values and passive zone data, together with a breakdown of each metal types composition are given in Table 1.

Table 1. Elemental breakdown by metal type.

	Metal Type	304L	316L	430
	I_{CRIT}	2.08796	1.7025	4.2124
Passive Zone	Start	-0.19	-0.11575	-0.17525
	End	0.9415	0.9135	0.32675
	Range	1.1315	1.02925	0.502
ELEMENTAL ANALYSIS	Carbon	0.018	0.020	0.046
	Manganese	1.381	1.750	0.410
	Chromium	18.259	16.770	16.280
	Copper	0.282	0.520	0.120
	Nitrogen	0.082	0.050	0.037
	Silicon	0.300	0.400	0.420
	Nickel	8.622	10.310	0.140
	Molybdenum	0.256	2.040	0.020

It is seen from Table 1 that the i_{crit} value is significantly higher for the 430 specimen than for any other metal types. A potential reason for this may be due to differences in composition.

Analysis of the compositions shows major variations in the chromium, nickel, and molybdenum content of each metal. A regression analysis was run to determine if these differences could be the cause of differences in the i_{crit} values and the range of the passive film. The results of the i_{crit} regression is shown in Figure 5.

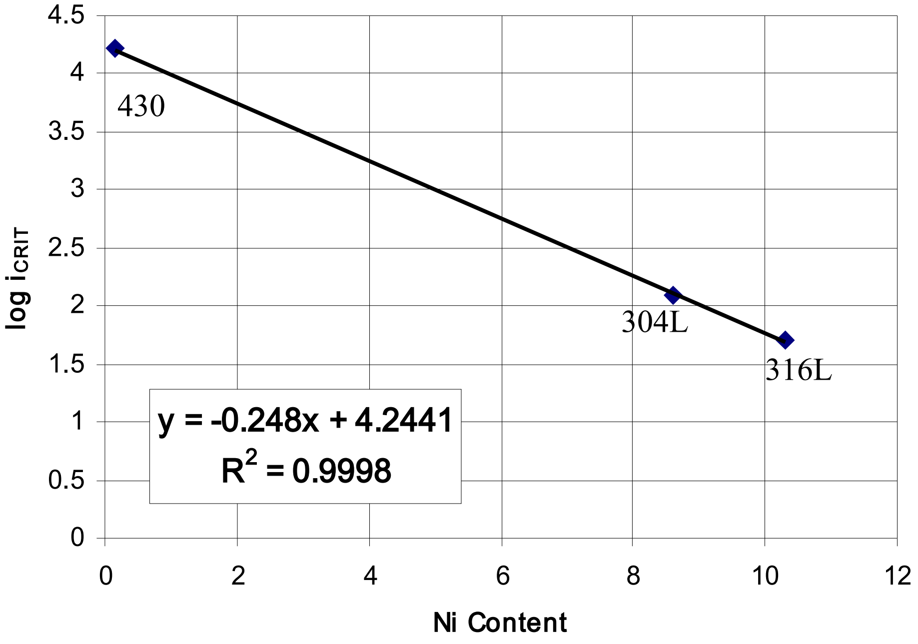

Figure 5. Factors of influence on i_{crit} results.

As observation of the composition suggested, nickel appears to be the only element of primary influence on the value of i_{crit}. Although the differences in the i_{crit} values are a result of the several factors and their interactions with each other, the high composition of nickel in 316L stainless steel allows its i_{crit} value to be lowest. Nickel has intrinsically low corrosion rates in acid solutions in the active state. Alloying additions of chromium lower the active rate even further, but no evidence of its affect on the i_{crit} value was found.

An analysis on the range of the passive zone was conducted. The results are shown in Figure 6.

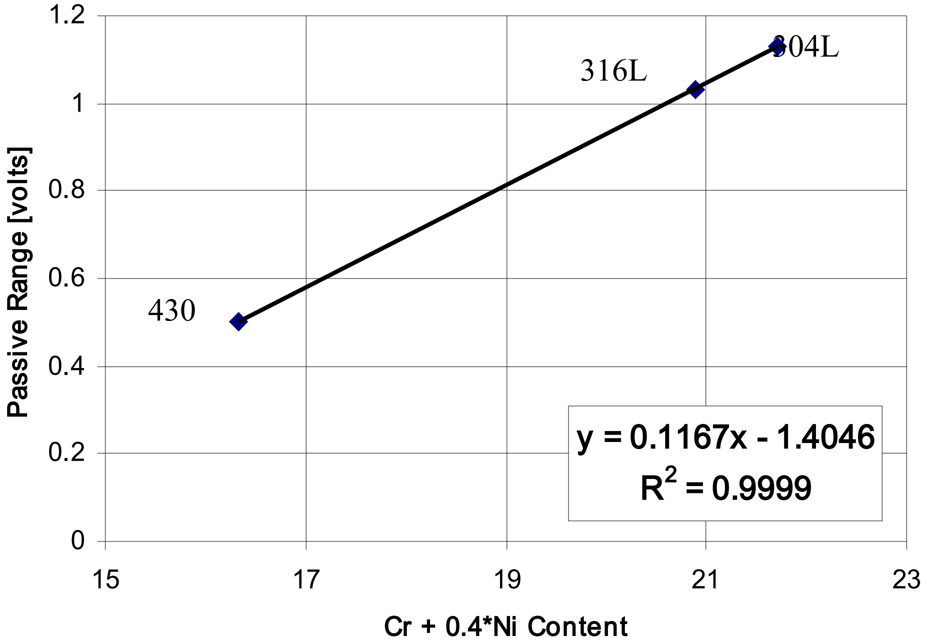

Figure 6. Factors of influence on the passive range.

The passive range appears to be dictated by the elemental presence of chromium and nickel, as illustrated by Figure 6. A weighted elemental analysis summing the total chromium content and 40% of the total nickel content yielded the results in Figure 6. Chromium is a vital element in the formation of a chromium-rich, passive oxidized film that is highly resistant to acid attack. More testing into the anodic polarization behavior of these three metals would perhaps find that molybdenum is a key element in evaluation of the passive zone.

Conclusions

Three test runs using 430 ferritic stainless steels were conducted. Repeatable results were obtained for these runs. The discrete zones of active, passive, and transpassive zones were stable through each test run. This stability prompted further examination into new variations on the formation of anodic polarization curves. Stainless steel types 304L, 316L, and 430 were tested under identical conditions and major differences in i_{crit} and the range of the passive zone were identified. A multiple regression analysis of the data showed that the difference in i_{crit} was due to variations in the nickel contents of the steels. The range of the passive zone was due to variations in the chromium and nickel contents of the steels.

References:

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