Chapter I

INTRODUCTION

1.1 Background

Stainless steels (SS) are iron-carbon alloys with high percentage of chromium at least of 11%[1] and many other elements are added to provide specific properties or ease of fabrication. The main reason for the existence of the stainless steels is its corrosion resistance which is imparted by the formation of chromium oxide on the surface. However, numerous failures of the stainless steels have occurred because of intergranular stress corrosion cracking (IGSCC) particularly within the heat affected zone (HAZ) resulting from welding. Figure 1.1 illustrates the IGSCC in AISI 304 stainless steels pipe resulting from welding. It has been well recognized that three conditions need to be presented simultaneously to produce IGSCC: a critical environment, some component of tensile stress and susceptible microstructure to IGSCC, figure 1.2. Metallurgically, the main cause of IGSCC susceptibility is the precipitation of chromium carbides leading to chromium depletion at grain boundaries and the process is called "sensitization".

Generally, the chemical testing and/or slow strain rate tensile (SSRT) testing are the routine techniques for evaluating IGSCC susceptibility in stainless steels. These techniques have become necessary to qualify heat treatment for acceptance in construction. The sulfuric acid-copper sulfate (ASTM A708-86) or Strauss test [2] was first proposed to detecting sensitized grain boundaries in stainless steels. This test consists of exposure to boiling 16% H_2SO_4 + 6% $CuSO_4$ solution for one 72 hour period. Dissolved Cu^{2+} acts as an oxidizer in sulfuric acid to passivate the grain and attack the chromium depleted grain boundaries. However, the rate of attack is relatively low, and this technique now is recommended only for highly sensitized specimen.

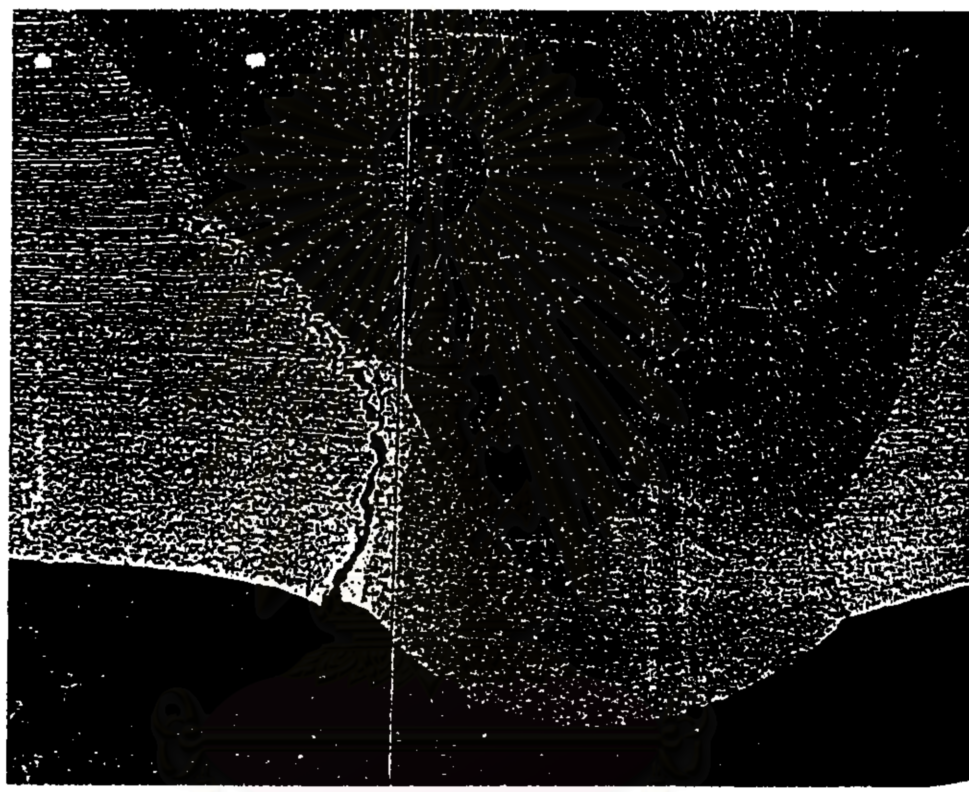

Figure 1.1 Illustration of IGSCC in 304 stainless steel pipe resulting from welding.

The copper-sulfuric acid-copper sulfate or copper accelerated Strauss test increases the rate in the same solution by making the stainless steel an anode in a galvanic couple with copper metal. Both the Strauss tests are evaluated by bending the plate specimen over a mandrel. Because of its difficulty to evaluate the chromium depleted area by inspection of bent specimens, M.A. Streicher [3] of the Du Pont Co. has developed the Streicher test or the sulfuric acid-ferric sulfate for detecting chromium depleted area in stainless steels. Striecher test uses one 120 hour period boiling 50% H_2SO_4 + 2.5% $Fe_2(SO_4)_3$; is accelerated by increasing the acid concentration to 50% and substituting Fe^{3+}, a strong oxidizer, for the Cu^{2+} in Strauss test. Attacked on sensitization austenitic stainless steels is evaluated by weight loss, which is more quantitative than visual inspection of bent specimens in the Strauss test. The copper accelerated Strauss and Streicher tests are the most popular for evaluation of sensitization by chromium depletion.

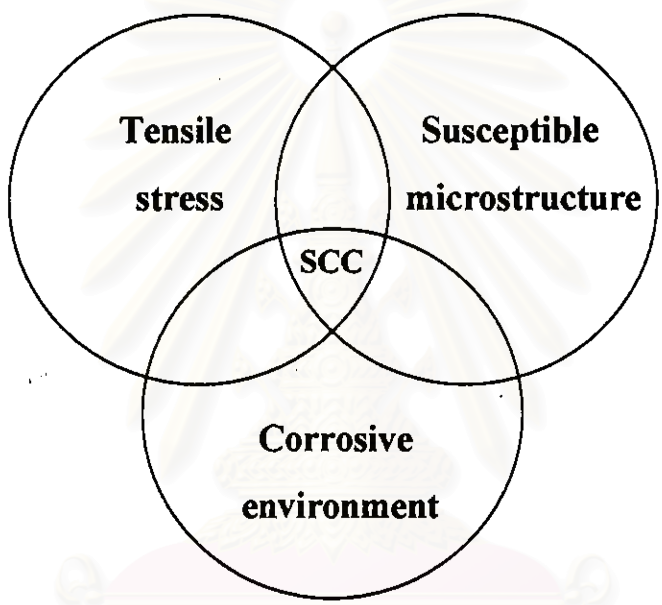

Figure 1.2 Schematic diagram showing the 3 main conditions need to be presented simultaneously to produce IGSCC.

The other chemical techniques are also available but they are not effective in detecting sensitization by chromium depletion. Table 1.1 shows the major testing procedures that have been used to detect the IGSCC susceptibility for stainless steels. Most of the techniques in table 1.1 were originally developed to simulate specific plant conditions [4]. Thus they have reduced their used in service environment to detection of stainless steels metallurgical structure.

Table 1.1 Shown the standard procedures used in chemical testing for evaluates IGSCC susceptibility in stainless steels.

ASTM Standard (common name)	Environment	Exposure	Evaluation	Species Attacked
A 708-86 (Strauss)	16% H_2SO_4 + 6% $CuSO_4$ Boiling	One 72 - Hour period	Macroscopic appearance after bending	Chromium Depleted area
A 262-86 Practice A (Oxalic Etch)	10% $H_2C_2O_4$	1.5 min. Anodic at one A/cm^2. Ambient temp.	Microscopic type of attacked	Various Carbides
A 262-86 Practice B (Striecher)	50% H_2SO_4 + 2.5% $Fe_2(SO_4)_3$ Boiling	One 120 Hour period	Weight loss per unit area	Chromium Depleted area
A 262-86 Practice C (Huey)	65% HNO_3 Boiling	Five 48 hour periods	Average Weight loss per unit area. Fresh solution each period	Chromium Depleted Area, σ phase and Carbides
A 262-86 Practide D (Warren)	10% HNO_3 + 3% HF 70^0 C	Two 2-hour periods	Weight loss per unit	Chromium Depleted area in Mo. Bending steels
A 262-86 Practice E (Copper Accelerated Strauss)	16% H_2SO_4 + 6% $CuSO_4$ Boiling. Specimen in contact with copper metal	One 24 - hour period	Macroscopic appearance	Chromium Depleted area after bending

A more advanced in IGSCC testing technique is the SSRT testing. The particularly advantage of SSRT technique over chemical testing is the variable strain rate and it can be used in varying corrosive environment. Therefore, the SSRT technique can be applied to use in any service environment and has been used as a screen test for service materials. The tensile specimen is slowly pulled at an initial strain rate ($< 1 \times 10^{-5}$ s^{-1}) to failure, while exposed to a corrosive environment. The SSRT testing machine consists of a motor driven pulled rod with a load cell and/or linear variable differential transformer (LVDT) to measure the load and extension on the specimen continuously. Figure 1.3 shows the typical SSRT apparatus [5]. The result is a load versus time or stress versus strain curve. Figure 1.4 illustrates of a pair of stress-strain curves [6] for carbon-manganese steel, one conducted in sodium nitrate solution and the other in oil, both at 80° C and a strain rate of 10^{-6} s^{-1}. The specimen exhibiting stress corrosion cracking in the nitrate showed a much lower time or strain to failure. The ductility of the specimens can also be measured conventionally by percent reduction in area. There are several parameters, which can be used to evaluate IGSCC in SSRT test such as time to failure, elongation or strain at failure, percent reduction in area and ultimate tensile strength. To accelerate the test, the SSRT technique often requires elevated temperature or an increase in solution concentration.

Both chemical testing and SSRT techniques are destructive, so they can not be used in field measurement. Nevertheless, There are some non-destructive testing (NDT) techniques available to detect cracks and flaws in materials such as X-ray or gamma ray radiography, Eddy current technique, and ultrasonic testing. Although, these techniques provide valuable information on internal defects before catastrophic failure, most are not sensitive enough to evaluate IGSCC susceptibility. Because of the annihilation characteristic of positrons which are related to electron distribution in materials [7], attention has now been paid to develop the doppler broadened positron annihilation (DBPA) spectroscopy as a new NDT technique for evaluating material defect. The system for measuring DBPA spectroscopy consist of a positron source, Na^{22}, a semi-conductor detector, a gamma ray detection system and a computer unit for processing and collecting information.

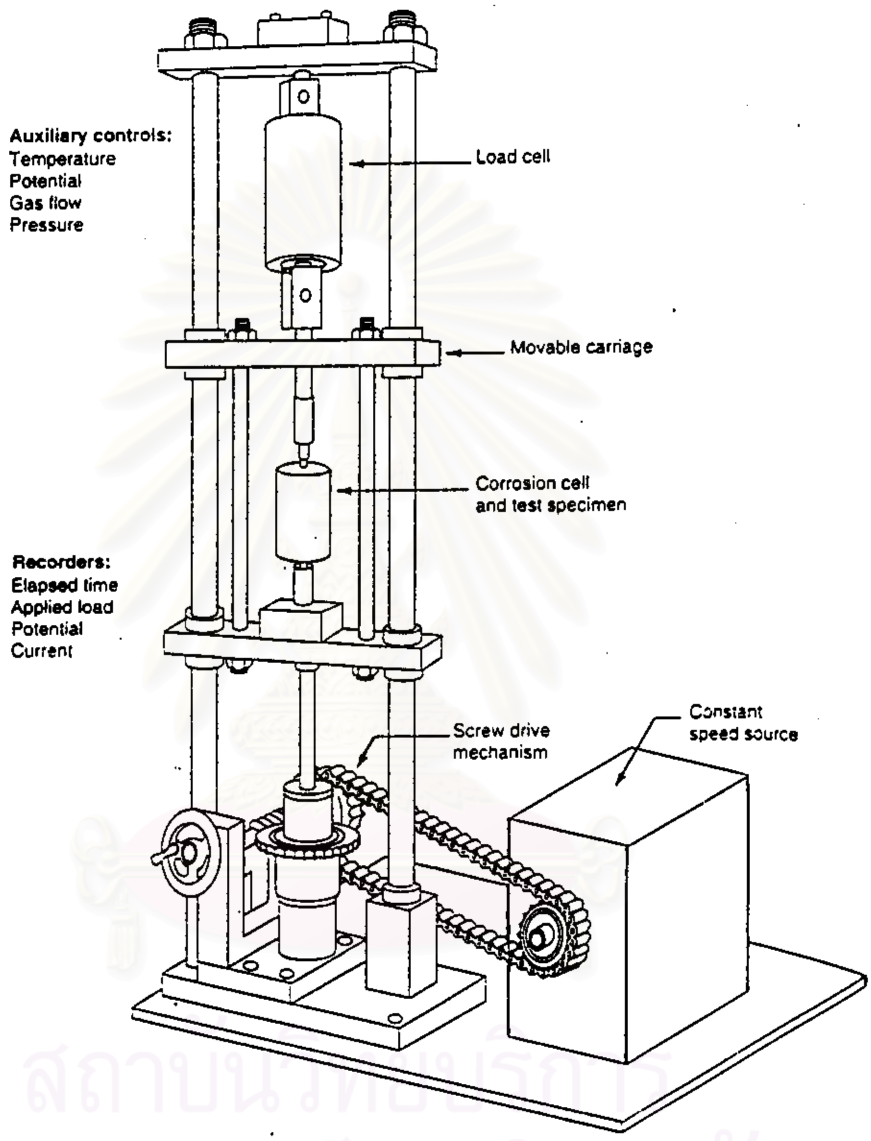

Figure 1.3 Illustration of a typical SSRT machine.

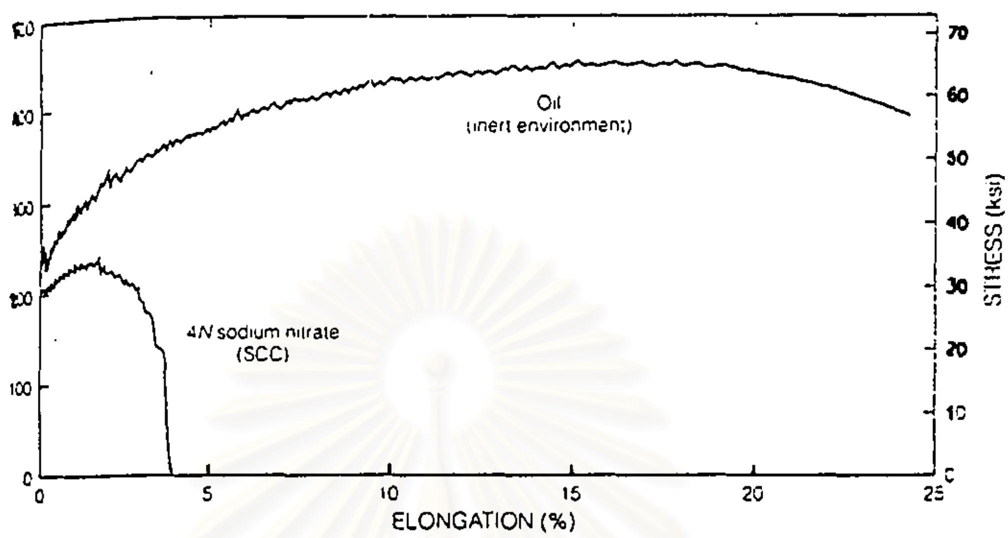

Figure 1.4 Illustration of the stress-vs-strain curve of carbon manganese steel conduct in sodium nitrate and in oil.

The main theme of this thesis is to apply the DBPA spectroscopy technique as a new NDT technique for evaluating IGSCC susceptibility in stainless steels. This thesis focuses on developing software to analyze DBPA spectrum and using SSRT testing machine to establish the correlation between IGSCC susceptibility of stainless steels with varying microstructural conditions and DBPA spectroscopy. Information obtained from SSRT test on IGSCC susceptibility of stainless steels together with DBPA spectrum will provide an insight into microstructure and property relationship without disturbing materials integrity.

1.2 Objective

1. To establish the correlation between intergranular stress corrosion cracking and varying microstructures in type 304 austenitic stainless steels.
2. To develop the system and technique for slow strain rate tensile testing.
3. To apply doppler broadened positron annihilation spectroscopy for evaluating the intergranular stress corrosion cracking susceptibility in type 304 austenitic stainless steels.

1.3 Scope of thesis

1. Design and develop the slow strain rate tensile testing machine in dilute acid.
2. Vary the susceptible microstructures leading to different degrees of intergranular stress corrosion cracking susceptibility in stainless steels.
3. Apply the slow strain rate tensile testing and doppler broadened positron annihilation spectroscopy technique for evaluating intergranular stress corrosion cracking susceptibility in stainless steels with varying microstructures.

1.4 Methodology

1. To conduct literature search and review.
2. Design and develop the slow strain rate tensile testing machine in dilute thiosulfate acid.
3. Test the stability of developed slow strain rate tensile testing machine.
4. Heat treating stainless steels at various times and temperatures.

5. Apply the slow strain rate tensile testing and doppler brroadened positron annihilation spectroscopy technique for evaluating the microstructures in sample.
6. To establish the correlation between intergranular stress corrosion cracking and varying microstructures in stainless steels.
7. Conclude research results and write up the thesis.

1.5 Potential Application of the thesis

1. Establish the correlation between the varying microstructures and intergranular stress corrosion cracking in stainless steels.
2. Apply the doppler broadened positron annihilation spectroscopy technique as a new non-destructive testing technique for evaluating intergranular stress corrosion cracking susceptibility in stainless steels.