Chapter IV

EXPERIMENTAL PROCEDURE AND APPARATUS

4.1 Introduction

This chapter provides the applications of slow strain rate tensile (SSRT) testing and doppler broadened positron annihilation (DBPA) spectroscopy as a tool for detecting the degree of sensitization which related to the susceptibility to intergranular stress corrosion cracking (IGSCC) of AISI 304 austenitic stainless steels. The SSRT testing has been widely used to evaluate the degree of sensitization of type 304 stainless steels. However, this technique is time-consuming and destructive. The DBPA spectroscopy was proposed to use as a quantitative, non-destructive testing (NDT) and rapid method for determining degree of sensitization in type 304 austenitic stainless steels. The main theme of this thesis is to establish the correlation between DBPA signals, degree of sensitization and IGSCC susceptibility of 304 austenitic stainless steels.

This chapter begins with the experimental apparatus used in this thesis. The manners by the microstructures of AISI 304 austenitic stainless steels leading to different degree of sensitization will be provided. An etching technique to confirm microstructures of the sensitized specimens will also be presented. The application of SSRT testing for evaluating the IGSCC susceptibility with varying degree of sensitization of samples in dilute thiosulfate solutions at ambient temperature is discussed. A brief description of DBPA spectroscopy used for evaluating the degree of sensitization of samples with varying microstructures will be also described.

4.2. Experimental Program

The experimental program was accomplished by integration of the 3 major sections. The approach to the first section will be accomplished by varying microstructures leading to different degrees of sensitization in AISI 304 austenitic stainless steels. In general, the susceptible to IGSCC of sensitized stainless steels occurs because of the precipitation of chromium rich carbides in the vicinity of grain boundaries. The width and depth of the chromium depleted zone and the morphology of precipitates depend on the aging time and temperature. Thus, the degree of sensitization can be altered by aging specimens at different times and temperatures. The second part will be accomplished by macroscopically testing specimen of various degree of sensitization obtained in diluted thiosulfate under SSRT testing. The final task is set to quantitatively establish the correlation between DBPA signals, degree of sensitization and severity of IGSCC. Hence, the DBPA signal together with the results from SSRT tests can be directly compared to the degree of IGSCC. This correlation could lead to the insight of microstructures controlling IGSCC susceptibility without disturbing materials integrity.

4.3 Material Preparation

Commercial grade type AISI 304 austenitic stainless steels were used in this study. Chemical composition (% wt) was given in the table 4.1. The material donated by Thainox Steel Limited was in the form of 1.2-mm thick sheet. Tensile specimens with 35-mm in length, 6-mm in width, and 1.2-mm thick were machined from the sheets using Engraving Plotter ME-300 machine. Equipped with special high speed TiN-carbides coarse and fine cutting tools, the machine can prepare fine finish tensile specimen leaving no tool marks deep enough to act as stress concentrating notches. Figure 4.1 shows the milling machine -Mimaki 300.

Table 4.1 Chemical composition of type 304 stainless steel used in this thesis (weight percent).

Element	weight percent	Element	weight percent
Fe	Balance	Cu	0.08
Cr	18.2	S	0.005
Ni	8.99	Al	0.01
Mo	0.17	Co	0.04
Si	0.46	Nb	0.02
Mn	1.67	Ti	0.01
P	0.03	V	0.01
C	0.04	B	0.002
N	0.02	Sn	0.003

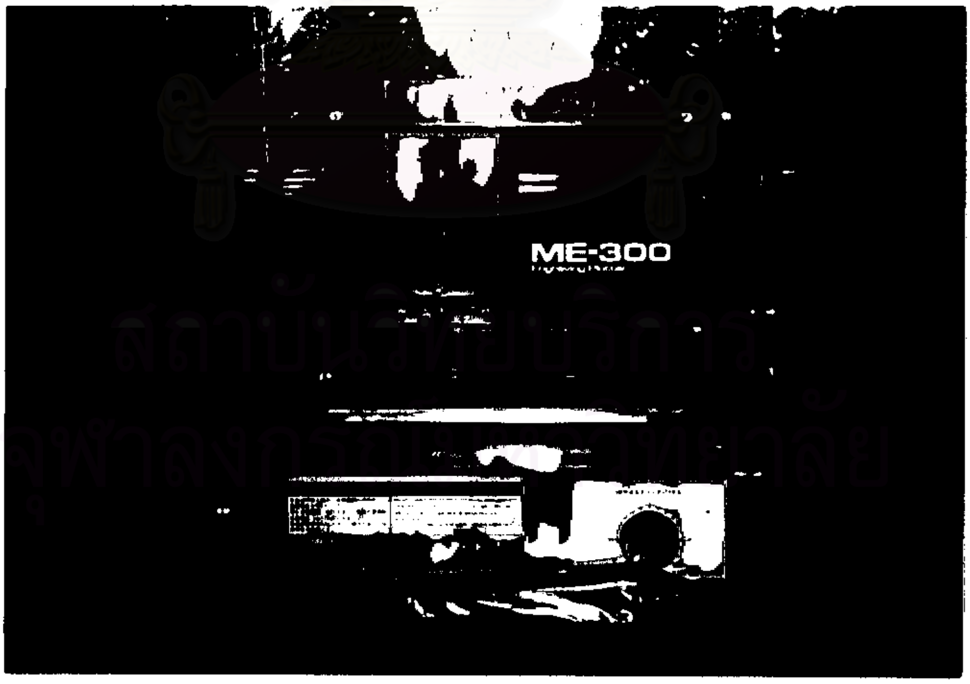

Figure 4.1 Illustration of the mini-computerized milling machine-Mimaki 300 used for preparing the tensile specimens.

The specimens were solution annealed at 1070°C for 30 minute under flowing argon and then water quenched using the developed high temperature vertical furnace, figure 4.2.

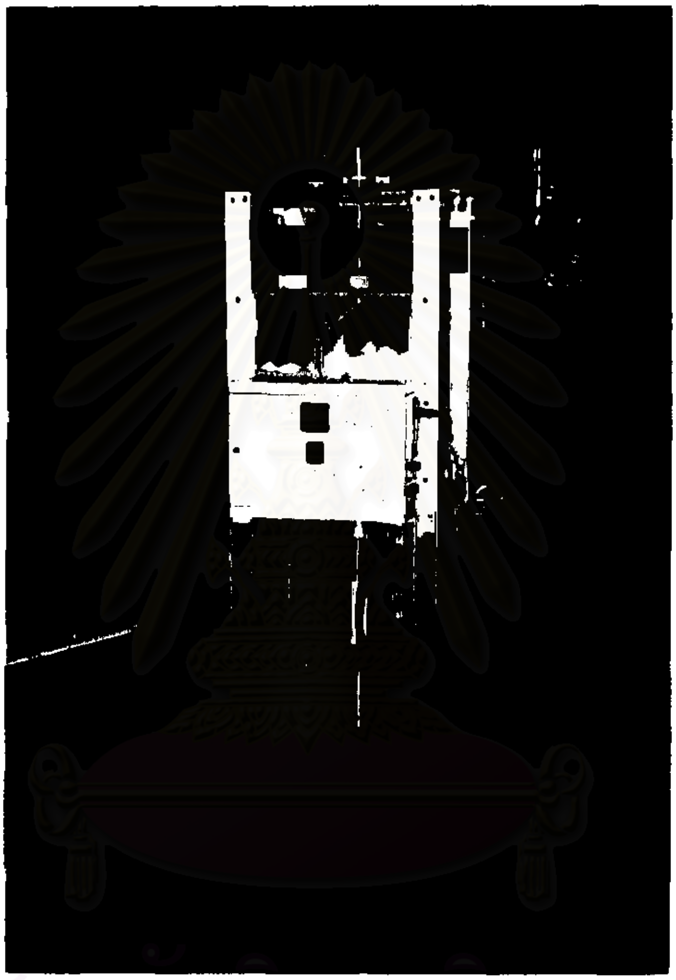

Figure 4.2 Illustration of the high temperature vertical furnace for heat treatment all specimens.

This furnace was constructed with the purposed to better controlling heat treating conditions of subjected materials. The furnace tube was made of impervious ceramics containing 60% Al_2O_3-pythagoras-with maximum working temperature of 1400° C. The temperature within furnace tube was measured by a K-type OMEGA thermocouple. The furnace was powered by resistive heating of a 6 silicon carbide heating elements providing at least 2 kW of power. The heating elements were controlled by OMEGA Miniature Temperature Controller model CN9000A series. The high temperature vertical furnace was used to prepare the varying microstructure in thc specimens by solution annealing and sensitization under argon gas (99.99% purified), and then water quenched. The quenching technique is needed to control the microstructure of the specimens. Moreover, the specimens were wrapped in the stainless steel foils to reduce the oxide formed on the metal surface during solution annealed and sensitization. To vary the microstructures of the specimens, the solution annealed specimens were given isothermal heat treatment at 650° C for a different duration time from 2 to 16 hour followed by water quenching to room temperature.

To prepare the specimens for SSRT test, the heat treated specimens were mechanically polished to a 1-μm diamond finish. These specimens were electropolished in perchloric acid ($HClO_4$) + ethanol (C_2H_5OH) solution for 45 second at 20 volts and electroetched to reveal carbide precipitation along grain boundaries in oxalic acid solution for 10 second at 6 volts. Figure 4.3 shows the tensile specimens during SSRT test.

4.4 Slow Strain Rate Tensile Testing

The stress corrosion cracking test were performed using the slow strain rate tensile (SSRT) testing in the 0.5-M $Na_2S_2O_3.5H_2O$ solution at a constant extension rate of 6×10^{-5} mm per second. The details of the SSRT were described in chapter III. To accelerate the test, thiosulfate solution was used. The analytical grade sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$) chemical and distilled water was used to make the solution. The SSRT was performed at room temperature while the specimen was situated in an acrylic container with the thiosulfate concentration of 0.5-M $Na_2S_2O_3.5H_2O$ adjusted to a pH of 4 using 3 drops of hydrochloric acid from 2 ml pipette.

All specimens were tested in thiosulfate solution at ambient temperature using an initial strain rate of 1.73×10^{-6} per second. Specimens were tested to failure and the stress-vs-strain curves and load-vs-time curves were recorded. After the test, fracture surfaces were examined in a scanning electron microscope (SEM) to reveal the nature of cracking. Low magnification SEM photographs of full fracture surfaces were taken to show the extent of SCC failure on the fracture surfaces.

Figure 4.3 Illustration of the tensile specimens during SSRT test.

4.5 Doppler Broadened Positron Annihilation Spectroscopy

The doppler broadened positron annihilation (DBPA) spectroscopy used to determining the degree of sensitization in type 304 austenitic stainless steels has been described in details by P. Swatewacharkul [40]. The technique has been adapted to provide a quantitative, non destructive testing (NDT) and rapid method for determining degree of sensitization. The recent studies suggest that positron tend to annihilate in low density regions around the lattice defects [41]. As positron entered and trapped at lattice defects, they combine with electron and annihilate yielding gamma rays an exhibiting a doppler broadening around its mean value of 511 keV. The signals of DBPA measurement are different in perfect and imperfect lattice. Because of the shape of DBPA spectrum must be quantifiably described and the resolution of the line-shape of DBPA spectrum is generally insufficient for evaluating the shape profile of annihilation line reflecting the state of microstructures inherent in materials, thus the S parameter was introduced for estimated electron momentum density.

The S parameter, introduced by Mackenzie [42], is widely used to evaluate the shape profile of an annihilation spectrum reflecting the state of microstructure inherent in solid. The S parameter is defined as a ratio of the centroid area (n) to the total peak area (N), can be expressed as follow;

$$S = \frac{n}{N} \tag{4.1}$$

Currently, there is no established criterion to define the centroid of the spectra [43], therefore it is impossible to compare the absolute values of S parameter obtained by different investigator. Generally, the centroid area is fixed as the area between 511± $\Delta\varepsilon$ keV where $\Delta\varepsilon$ is the energy shift depending on the materials being investigated. It should be noted that the selected value of $\Delta\varepsilon$ has never been clarified in most of the literature and the value of 1 keV was cited in a few occasion [40]. The choice of $\Delta\varepsilon$ can greatly affect the value of S parameter and thus, was found to lack of its clear physical and/or statistical meaning. Furthermore, S values are affected by many variables such as: counting rate, temperature, humidity, geometry, instrumental instability, liquid nitrogen level etc., resulting in stability of the line-shape affecting the accuracy of S parameter. Thus, several correction and/or compensation techniques was proposed in order to keep the S parameter errors low providing better statistical confidence. The statistic of S parameter is concerned because the change of S value is only in the order of a few percent as defects change by almost 1-2 order magnitudes. P. Swatewacharkul [40] satisfactorily employed a new compensation technique for analyzing the S parameter to reduce errors associated with the S parameter. A computer program was developed by the author to obtain and analyze the S parameter as proposed by Swatewacharkul [40] with high degree of credibility and described in details in Appendix II.

The solution annealed and sensitized specimens were all examined by DBPA spectroscopy to established the correlation between ultimate tensile stress (UTS) strain to failure, and sensitization time establishing the stress corrosion cracking susceptibility of stainless steel with varying microstructural conditions and DBPA spectroscopy. The information obtained from SSRT testing together with DBPA spectrum will provide us with an insight into structure and property relationship without disturbing materials integrity.