Chapter **II**

INTERGRANULAR STRESS CORROSION CRACKING IN AUSTENITIC STAINLESS STEELS

2.1 Introduction

AISI 304 austenitic stainless steels containing 18Cr-8Ni has been extensively used in applications where high temperature and high corrosion resistance is required. It is widely used as the engineering material mainly because of its high corrosion resistance and its formability. The addition of chromium to stainless steels improved their corrosion resistance. The chromium in iron is required to make the iron surface passive to corrosion by forming a surface oxide film, known as the "passive film", which protects the underlying metal from corrosion [8]. However, numerous failures of type 304 austenitic stainless steels have occurred because of intergranular stress corrosion cracking (IGSCC).

This chapter will begin with an overview of definition and observations of IGSCC in austenitic stainless steels. Chromium depletion grain boundary is discussed, in which altered metallurgical structures have serious effects on IGSCC susceptibility. An aggressive environmentally induced IGSCC, effect of applied stress and a critical strain rate to produce IGSCC of sensitized austenitic stainless steels are also discussed in this chapter. Finally, brief descriptions of some techniques commonly used for evaluating the susceptibility of austenitic stainless steels to IGSCC will be provided.

2.2 *Intergranular Stress Corrosion Cracking of AISI 304 Austenitic Stainless Steels*

AISI 304 austenitic stainless steels have been extensively used in nuclear power plants as parts of the recirculation system, steam generators and core spray system mainly because of their excellent corrosion resistance. However, numerous failures of 304 austenitic stainless steels have occurred because of intergranular stress corrosion cracking (IGSCC). An example of IGSCC in sensitized, austenitic stainless steels is shown in figure 2.1.

Figure 2.1 Illustration of an example of IGSCC in sensitized, austenitic stainless steel.

The term IGSCC describing stressed alloy failure that occurs by the propagation of cracks preferentially along grain boundaries in specific environments. It has been well recognized that three conditions are necessary to be presented

simultaneously to produce IGSCC: a critical level of stress, an aggressive environment and IGSCC susceptible microstructure, figure 1.2. Generally, a critical stress that produced IGSCC needs not to be externally applied; it may be a residual one that results from rapid temperature changes and uneven contraction, or two-phase alloys in which each phase has a different coefficiency of expansion. The major cause of IGSCC susceptible microstructure in stainless steels is the precipitation of chromium carbides (mainly $Cr_{23}C_6$) at grain boundaries within heat affected zone (HAZ) resulting from welding and this process is called sensitization. The term sensitization refers to the breakdown in corrosion resistance which may occur if unstabilized austenitic stainless steels are slowly cooled from the solution anneal temperature (~1100°C) [9] or are improper heated to temperature between 500° and 800°C (950° and 1450°F) [10] for sufficiently long time periods. The amount of time required to form chromium carbides along the grain boundaries depends on the environmental temperature and/or the alloying elements.

The chromium depletion theory is generally accepted as providing the principal explanation for sensitization [9]. Several investigators have shown the correlation of the onset of sensitization with the presence of carbides at grain boundary [11]. It is believed that in the temperature indicated, the chromium is thereby removed from the solid solution, subsequently the chromium carbides are precipitated at the grain boundaries leading to depleted grain boundaries and nearby structure of chromium. An example of the chromium concentration profile across a chromium depleted grain boundary in a type 304 stainless steel heat treated for 10 hours at 700° C is shown in figure 2.2 [12]. Stawstrom and Hillert [13] proposed that the austenitic stainless steels are susceptible to IGSCC only when the chromium content falls below 13%. As a result, the grain boundary vicinities or the adjacent area, known as chromium depleted zone, are less resistance and are corroded preferentially. The chromium carbides particles that have precipitate along grain boundaries in stainless steels, and the attendant zones of chromium depletion are illustrated in figure 2.3. Consequently, the chromium depleted zone is much less corrosion resistance and now highly susceptible to corrosion.

Chromium, wt. %

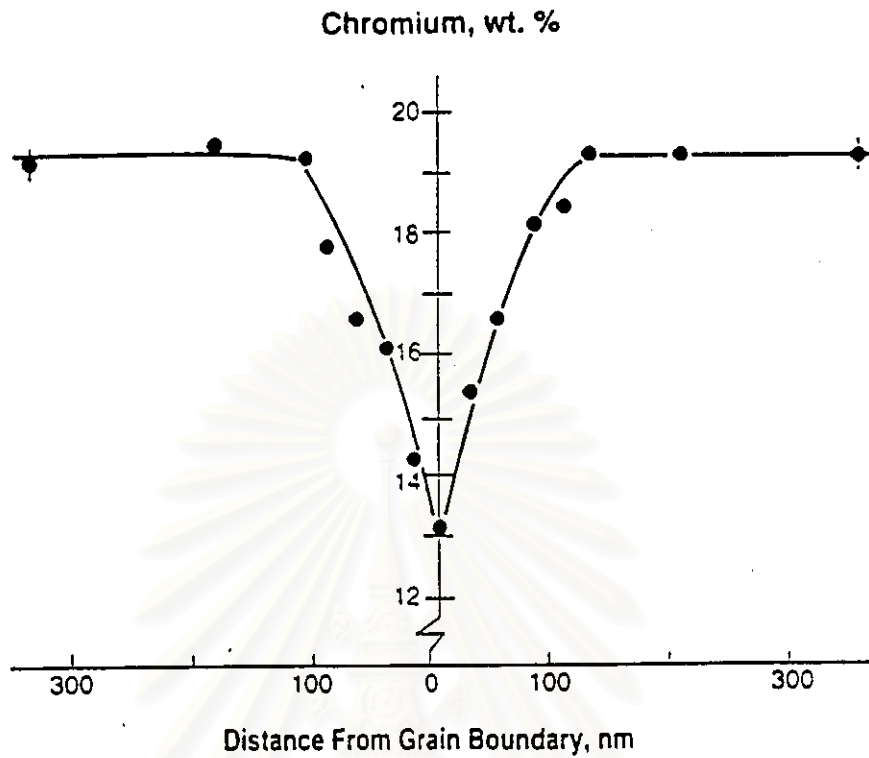

Distance From Grain Boundary, nm

Figure 2.2 An example of the chromium concentration profile across a chromium depleted grain boundary in type 304 stainless steel heat treated for 10 hours at 700° C [12].
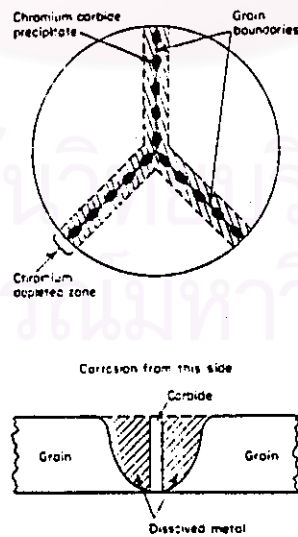

Figure 2.3 Schematic illustrates chromium carbide particles that have precipitated along grain boundaries in stainless steel, and the attendant zone of chromium depletion.

The carbon content in the stainless steels plays significant roles in intergranular chromium carbides precipitation and is generally kept quite low to increase sensitization resistance because of when the lower carbon content the longer time periods required for sensitization. Figure 2.4 illustrates the sensitization diagram of AISI 304 austenitic stainless steels type for various carbon contents [14].
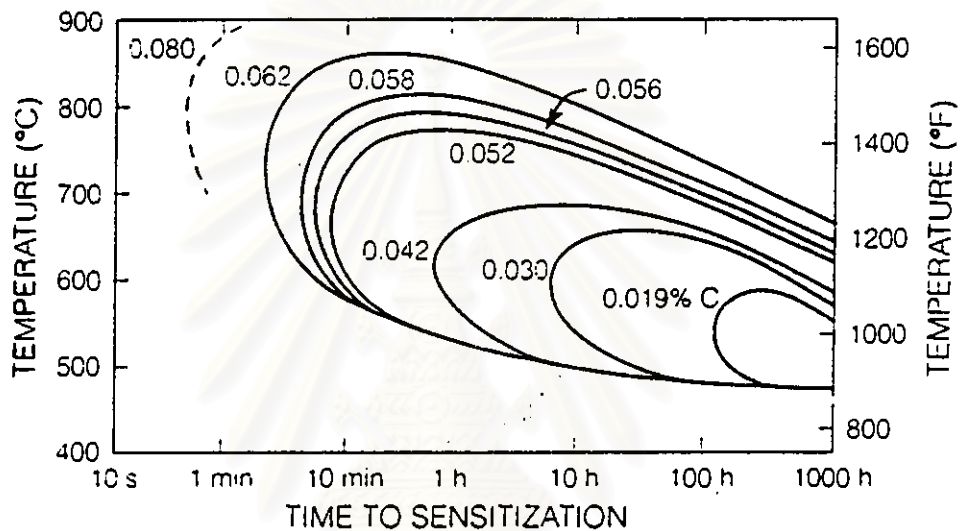

Figure 2.4 Illustrations of the sensitization diagram of type AISI 304 stainless steel for various carbon concentrations [14].

Generally, improper heating of austenitic stainless steels during welding can result in sensitization, known as weld decay, causing grain boundaries to become susceptible to IGSCC leading to catastrophic reduction in mechanical strength. Welding is a physical process that melts the adjoining zones of metal parts to bond them together. The weldment is defined as the melted and solidified weld metal and adjoining zones of the base metal alloy affected metallurgically by heating and cooling cycle as shown in figure 2.5. The weldment often has substantially lower corrosion resistance than the base metal parts. Thus, the metallurgical effects of welding are detrimental to corrosion resistance. Non-equilibrium cooling of the weld metal may produce grain boundaries segregation. It is important to note that the tensile

components of residual stress in weldment are important because they may cause IGSCC in austenitic stainless steels.
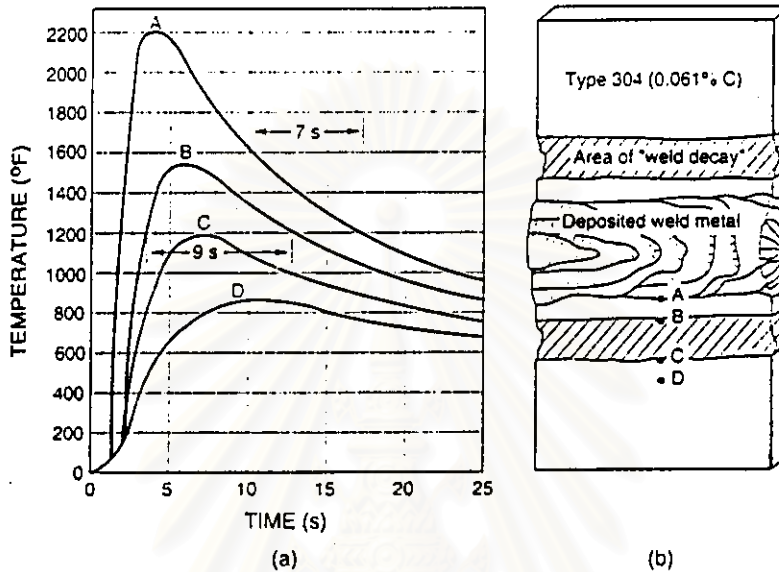

Figure 2.5 Thermal transient producing weld decay during welding of austenitic stainless steels. (a) Temperature-time relationship (b) location of thermocouples

Other sensitization studies related to the nuclear power industry suggest that at boiling water reactor (BWR) operating temperatures of 288°C, the combined effects of the elevated temperature and radiation can cause chromium depletion at the grain boundaries in type 304 austenitic stainless steels [14]. In this radiation assisted process there is no precipitation of chromium carbide, and chromium depletion is thought to occur by a process known as radiation induced segregation. Cracking associated with this process has been shown to be dependent on the temperature and radiation fluence. Sensitization of solutionized austenitic stainless steels is reported not to occur in service at neutron fluences below 0.3×10^{21} n/cm^2 or at temperature below 150°C. Maximum radiation induced segregation is reported to occur in the temperature range of 400-500°C [15].

2.3 Environmentally Induced IGSCC

Generally, an aggressive environment is necessary to produce IGSCC in austenitic stainless steels, however, a corrosive environment species are often specific to the alloy systems and may not have an effect on the other alloys of different type. The recent studies have been suggested that sensitized, austenitic stainless steels are highly susceptible to IGSCC in a variety environment such as: an aqueous solution that containing chloride ion, high purity waters, and polythionic acid and reduced sulfur species. The effects of some environment that induced IGSCC are discussed below:

Effects of chloride solution: IGSCC of austenitic stainless steels in hot acid chloride solutions (60°- 200°C) [16] is perhaps the most widely know and intensely studied example of IGSCC. Chlorides ion are ubiquitous in seawater and industrial process stream. Although the hazard is lessened in lower concentrations of chloride, boiling at the heat-transfer surfaces of heat exchangers and condenses or evaporation to ambient atmosphere can concentrate solutions at the surface sufficiently to initiate IGSCC. A few investigators suggested that this type of failure be also occurred frequently in apparently environments containing only a few ppm chlorides or less. Susceptibility to IGSCC of austenitic stainless steels increases with temperature. It should be noted that chloride IGSCC does not occur in nonsensitized austenitic stainless steels at temperature below 60°C in near neutral chloride. However, it has been shown that under the severe conditions encountered in a SSRT test, this minimum temperature can be lowered to 50°C for annealed type 304 and to temperature approaching ambient for sensitizes type 304 [17]. Times to failure of type 304 stainless steel in various magnesium chloride solution shows in figure 2.6 [18].
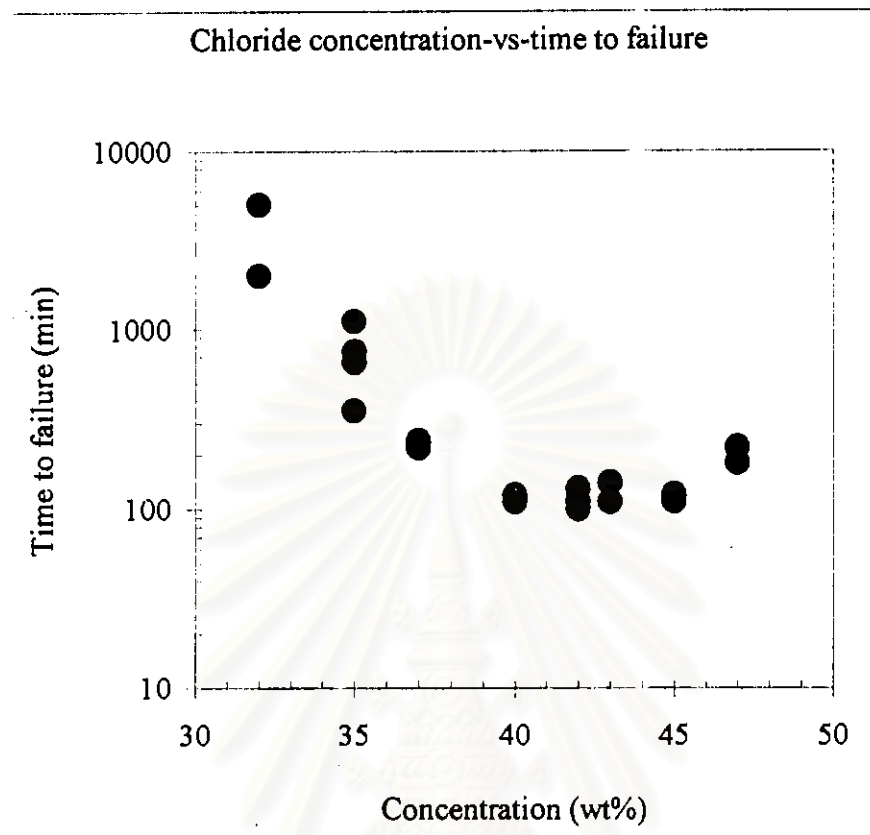
Figure 2.6 Times to failure of type 304 stainless steels in various magnesium chloride concentrations [18].

Effect of high temperature water: Austenitic stainless steels are frequent selected for use in boiler and heat transfer exchangers of fossil and nuclear fuel power plants. Although they are generally resistances in such environments, careful control must be exercised over dissolved oxygen. Figure 2.7 shows stress-vs-strain curve for sensitized 304 stainless steel in water with different dissolved oxygen concentration. IGSCC of sensitized austenitic stainless steels has been a recurring and expensive problem in the cooling-water pipe of boiling water nuclear power plants [19]. In general, hydrogen water chemistry is very effective in reducing the dissolved oxygen concentration during steady-state operation [20] and if used during start-up operation, it will probably be more effective than the oxygen control methods.
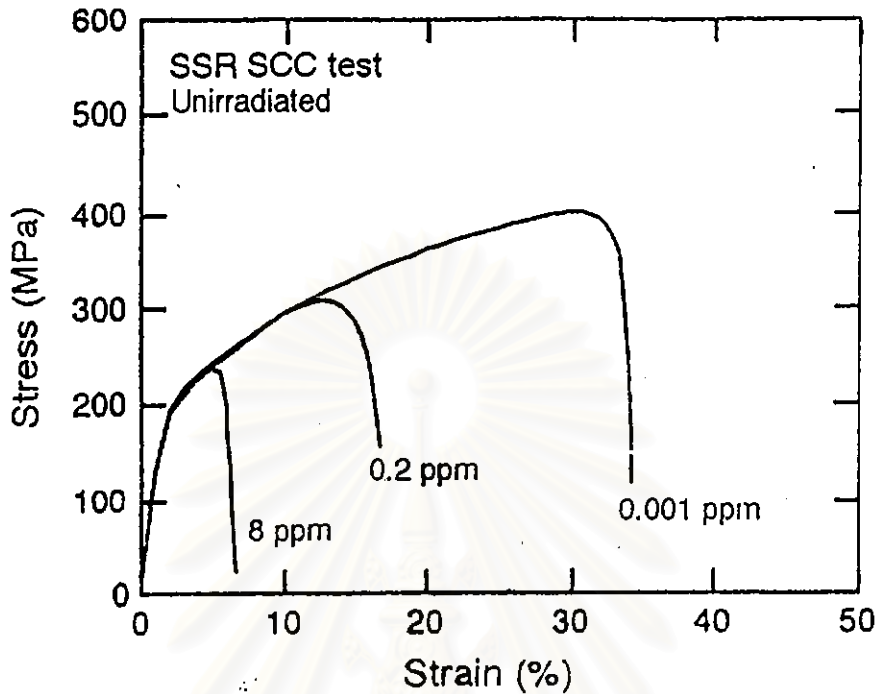
Figure 2.7 Stress-vs-strain curve for sensitized type 304 stainless steel with different dissolved oxygen concentrations [19].

P.L. Andresen [20] studied the effect of transient in water chemistry on IGSCC of AISI 304 stainless steels by conducting the tests in pure water which oxygen and hydrogen peroxide were injected to provide a concentration versus time that is simulated a boiling water reactor (BWR) start up cycle. It was found that under severe conditions where the material would be cracked quickly, reducing the oxygen retards cracking by about an order of magnitude. The conclusion of these tests is that the high-oxygen transient exposure to passive film exerts a powerful influence on the resistance to crack initiation at the high temperatures. An IGSCC characteristic of failure in impure water environments shows in figure 2.8.

Effects of sulfur-bearing solutions: Sulfur can exist in oxidation states from –2 to +6 in aqueous electrolytes. Therefore, many chemical forms of sulfur are very important

in corrosion. Furthermore, sulfur is a frequent product of biological decay and is often found in waters from domestic and industrial wells, geothermal energy recovery systems, and petroleum production and refining plants. Reduced sulfur is metastable in oxidation states but is the cause of some unique and very damaging corrosive effect. It is well known that sensitized austenitic stainless steels fail by IGSCC when exposed to polythionic acid, dilute thiosulfate, hydrogen sulfides and some reduced sulfur species. Corrosivity of some dissolved sulfur in reduced states of oxidation is discussed below.
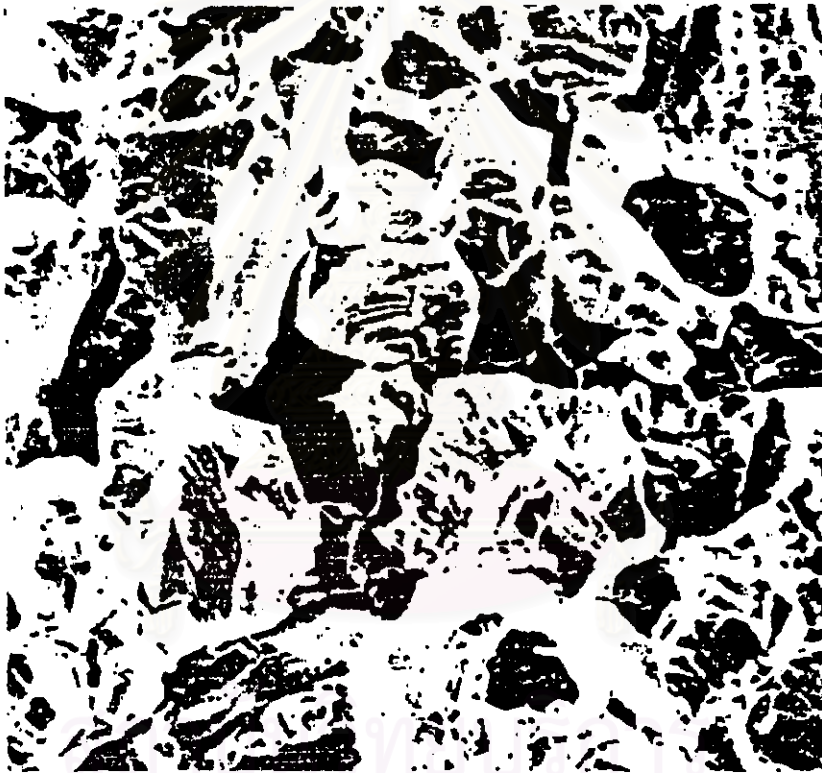

Figure 2.8 IGSCC characteristics of failure in impure water environments [20].

In petrochemical refinery equipment, Polythionic acids ($H_2S_nO_6$; n = 2 to 5) are formed by reaction of sulfide surface scales with moisture and oxygen [22]. The sulfide form on stainless steels surfaces of furnace, heat exchangers, and vessels exposed to high temperature sulfide gases in petroleum refinery [23]. The surface sulfides react with oxygen and water or water vapor, forming polythionic acids, which

cause rapid IGSCC near weld, where a microstructure sensitized to IGSCC is present. However, the exact forms and oxidation state of dissolved sulfur responsible for polythionic acids IGSCC are uncertain. Figure 2.9 Shows IGSCC due to polythionic acids in type 304 stainless steels furnace tube near a weld to carbon-steel tube.
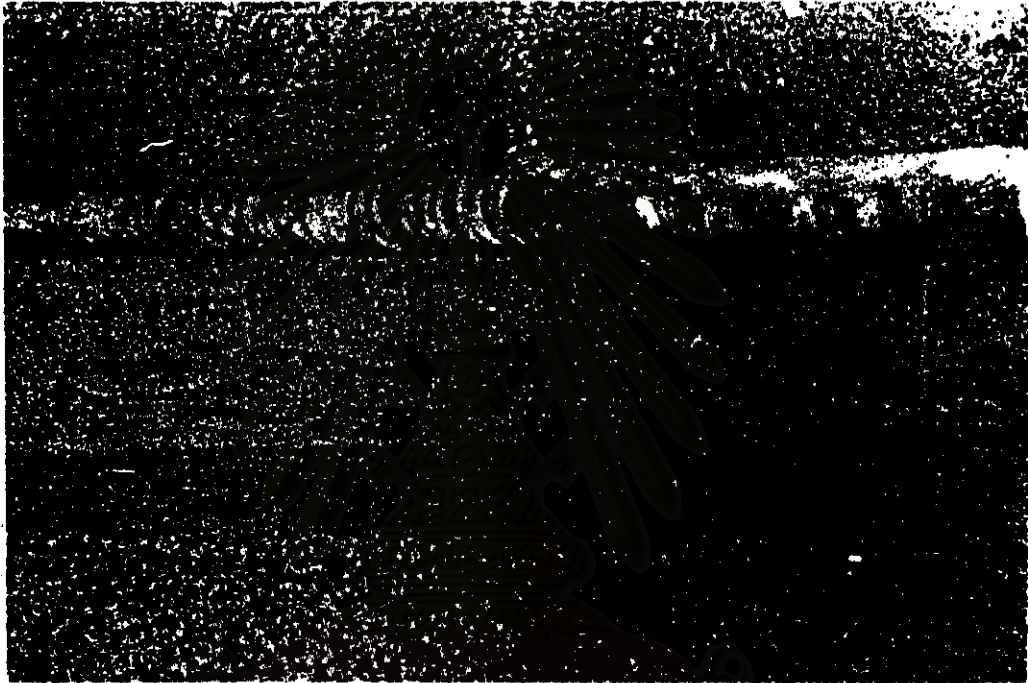

Figure 2.9 Illustration of IGSCC due to polythionic acids in type 304 stainless steel furnace tube near a weld to carbon-steel tube.

Thiosulfate at ppm levels has been known to causes IGSCC of sensitized austenitic stainless steels [24] in water at ambient and slightly elevated temperature. H.S. Isaac et al. [25] studied the IGSCC of sensitized austenitic stainless steels in thiosulfate solutions and found that sensitized austenitic stainless steels are extremely susceptible to IGSCC in the presence of thiosulfate. Only 0.1 ppm $Na_2S_2O_3$ was found to give rise to material fail by IGSCC, which is equivalent to about 40-ppb sulfur [26]. Figure 2.10 illustrates the micrograph of a fracture surface in 0.9% $Na_2S_2O_3$ test. In a similar manner, both thiosulfate and tetrathionate have produced IGSCC of sensitized

Alloy 600 [27]. IGSCC occurs in a narrow range of potential, where active dissolution of Ni and stability of elemental sulfur coincide. Therefore, dissolved metastable reduced sulfur species apparently are cathodically converted to adsorbed sulfur on the surface during IGSCC.
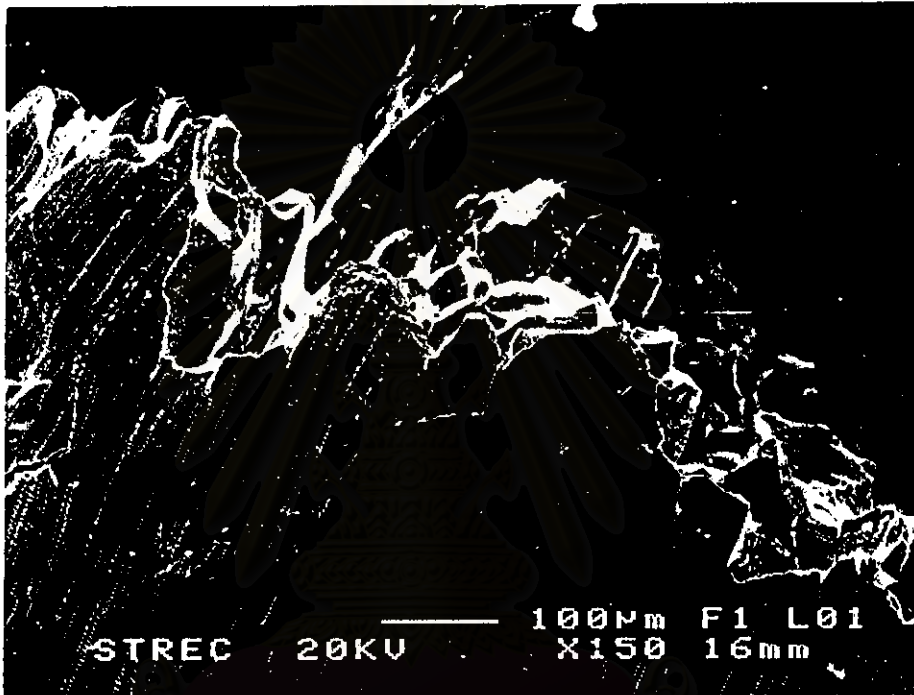

Figure 2.10 A micrograph showing a fracture surfaces in 0.9% sodium thiosulfate test.

IGSCC by polythionic acids, thiosulfate solution or reduced sulfur species can occur in unexpected circumstance. An example is the well-known 1981 nuclear reactor failure at Three Mile Island pressurized water nuclear reactor (PWR) in Pennsylvania. Intergranular cracking was also found extensively in the stream generator after lay up during the downtime following the nuclear accident in 1983. The generator tubes are made of Inconel, since the corrosion is occurring on the insides of the tubes, through which the primary coolant flow [28]. Extensive leaking from the primary (reactor) side to the secondary (stream) side of the generators aborted the start up. During hot functional testing of the unit in August 1981 by

General Public Utilities Corporation (GPU), there were no indications of leak. However, in lower pressure testing in November it was found that 134 tubes leaked and about 8000 to 10000 of the 31000 tubes were affected in 3 months later. Most of the degradation occurred at approximately the same level in each of the two generators. The cracks are intergranular and penetrated either completely or about 80 to 90% through the tube walls. Subsequent to this, the unit was maintained at a cold shut down temperature of around 40°C. It is therefore believed that the cracking occurred at low temperature and propagated very rapidly. Extensive subsequent investigation revealed intergranular cracking in the alloy 600 heat exchanger tubing, which had been sensitized by stress-relief annealing during manufacture. Sulfur was found on the crack surfaces and on the primary side tube surfaces. Levels of 0.7-ppm thiosulfate were measured in the primary water, probably due to accidental leakage of water containing thiosulfate from an auxiliary safety cooling system. Thus, it was conclude that the failure was due to sulfur induced intergranular cracking.

It should be noted that many chemical form of sulfur is very important in stress corrosion cracking of sensitized austenitic stainless steel. Furthermore, sulfur is a frequent product of biological decay and is often found in waters from domestic and industrial wells, geothermal energy recovery system, steam generator in pressurized water nuclear reactor (PWR), and petroleum production and refining plants. Reduced sulfur is metastable in oxidation states but is the cause of very damaging corrosive effect. Effect of thiosulfate concentration on time to failure shown in figure 2.11. The following reaction takes place on the acidification of a thiosulfate solution [29].

$$2S_2O_3^{2-} + 3H^+ \quad \rightarrow \quad 2S + SO_2 + HSO_3^- + H_2O \qquad (2.1)$$
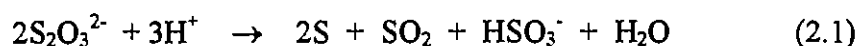
Apparently, all three-sulfur species generated from the above reaction are aggressive to sensitized stainless steel [30]. It is also known that wet elemental sulfur significantly increases the corrosion rate of iron and mild steel. The specimens cracked rapidly when the pH of thiosulfate solution was reduce. Interestingly, if the pH of the thiosulfate solution is lowered too much, the cracking dose not occurs. This is

believed to occur because thiosulfate will react with the acid and the resulting sulfur quickly precipitates. It was also found that one has to add a much smaller amount of acid and the resulting sulfur remains in the form of a colloidal suspension for a long time, and may even attack the metal. Therefore, it might be conclude that the studies on sensitized type 304 austenitic stainless steel in reduced sulfur also show that pH significantly influences SCC at all concentrations tested [31].
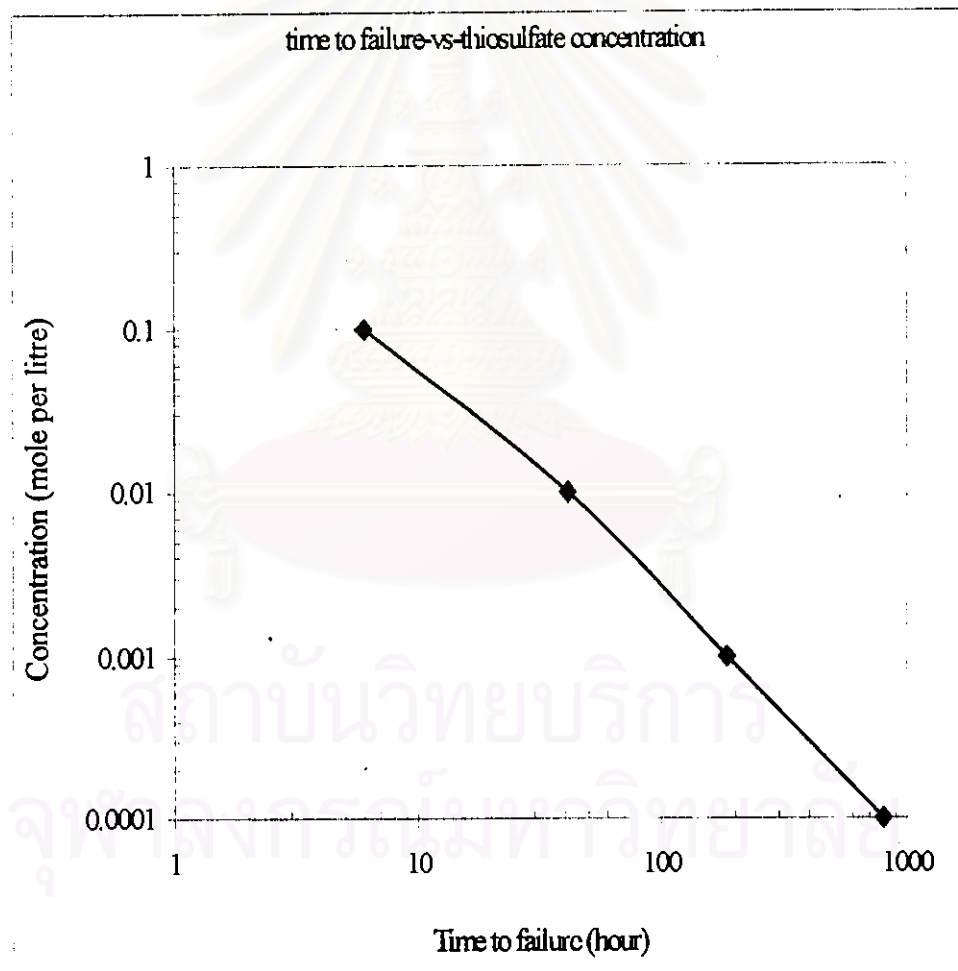

Figure 2.11 Illustration of the influence of thiosulfate concentration on time to failure.

According to, Equation (2.1), the susceptibility to cracking may be described as a function of the pH and aggressive decomposition products. Generally, tetrathionic acids have also been implicated in the SCC of sensitized stainless steel [32] and might have been produced in the presence of an oxygenated solution of sulfur dioxide in water [33]. Thus, sulfur dioxide (SO_2) was identified as a potent cracking agent for sensitized type 304 austenitic stainless steel [34] and cast Fe-Ni-Cr alloys of various compositions [35]. Based on the above- mentioned, increasing in the susceptibility to SCC of stainless steel in thiosulfate solution may be ascribed to a combination of thiosulfate decomposition products and tetrathionic ion, which occur later.

2.4 Effect of Stress and Strain Rate

An applied stress and strain during sensitization also accelerate sensitization presumably by accelerating the nucleation and growth process involved in carbide precipitation [36] that are linked to more rapid chromium diffusion. The time temperature sensitization curves for type 304 austenitic stainless steels sensitized at various applied stresses are shown in figure 2.12 [37].

Although an applied stress are required to produced IGSCC, it needs not externally applied; it may be a residual one that results from rapid temperature changes and uneven contraction, as occurred during welding, or two-phase alloys in which each phase has a different co-efficiency of expansion. It is well known that increasing stress decreases the time before cracking occurs, as shown in figure 2.13 [38].

There is some conjecture concerning the minimum stress required to present cracking. This minimum stress depends on temperature, alloy composition, and environment composition. In some case it has been observed to be as low as about 10% of yield stress. In other case, cracking does not occur below about 70% of the yield stress. For each environment there is probably threshold stress for each alloy.

This threshold value must be used with considerable caution since environmental conditions may change during operation.
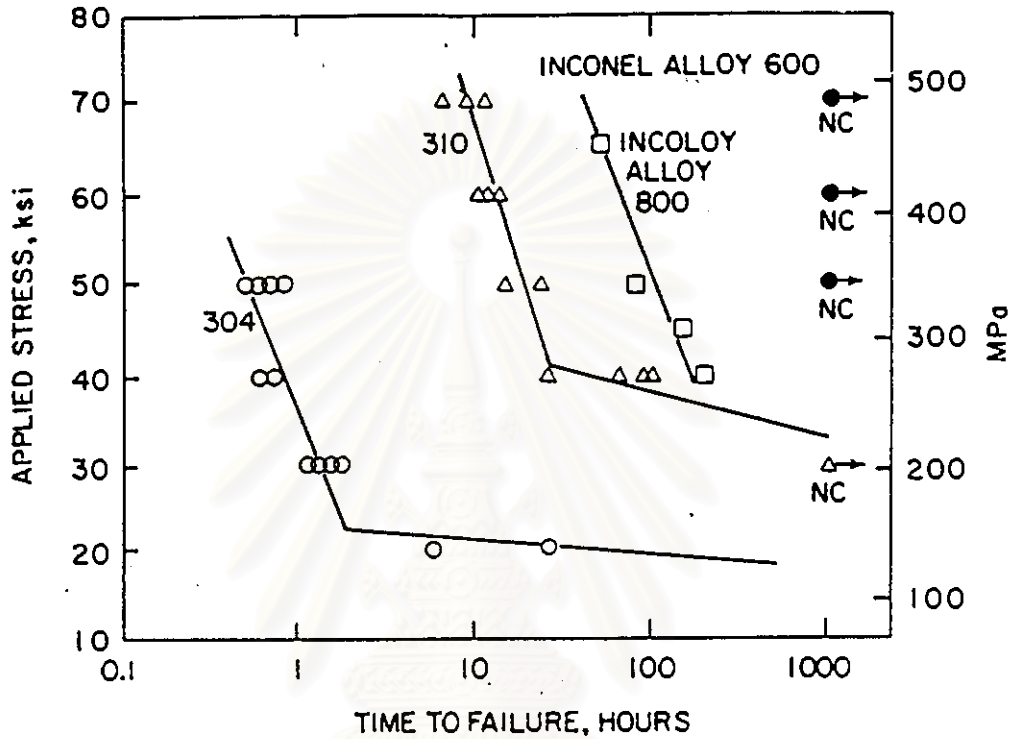

Figure 2.12 The time temperature sensitization curves for type 304 stainless steel at various applied stress [37].

It should be noted that a nominal strain rate, which related to a critical stress, is important to produced IGSCC. ·Figure 2.14 [3] shows the influence of the strain rate on the value of the ultimate tensile stress (UTS) of a 316 alloy in a 153° C MgCl₂ solution. In high strain rate test the effect of environment, is not apparent. As a result, the specimens could have been failed in a ductile manner, but a brittle behavior is observed with a marked reduction of the UTS take place at lower strain rate. Thus, slow strain rate tensile test in an aggressive environment has become widely used technique for evaluating the IGSCC susceptibility in austenitic stainless steels with varying degree of sensitization.
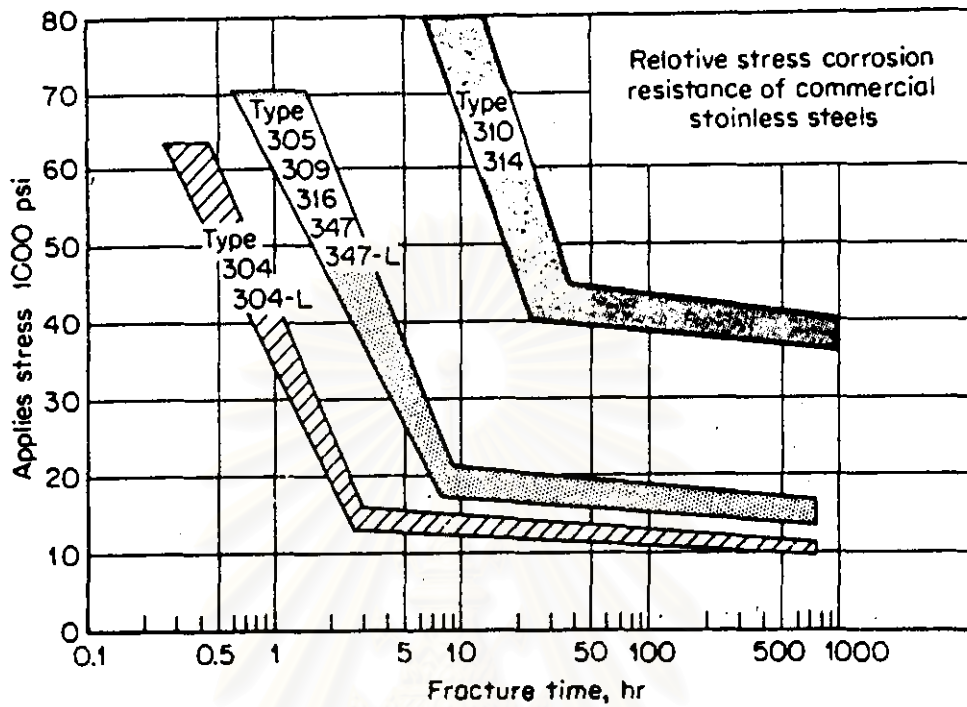
Figure 2.13 The relationship between applied stress and time required for SCC to occur [38].
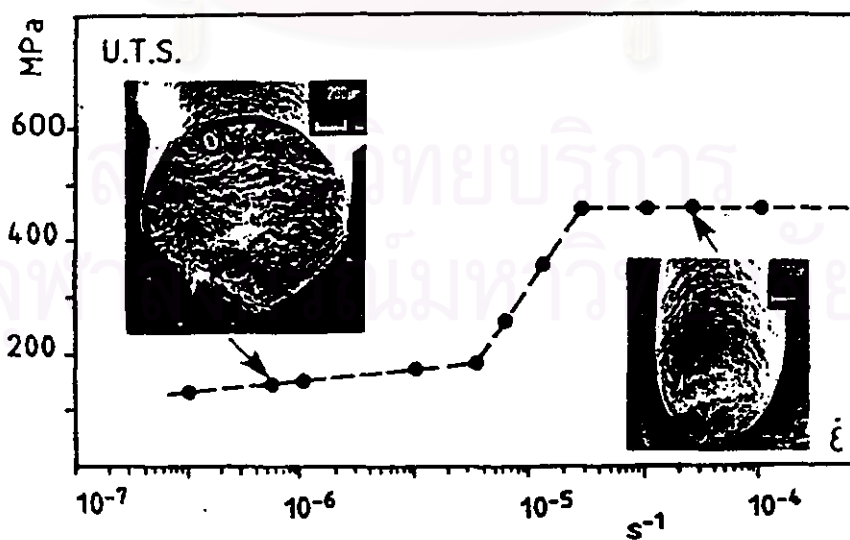

Figure 2.14 Illustration of the influence of the strain rate on the value of UTS of a 316 alloy in 153° C magnesium-chloride solution [3].

Although the three conditions necessary to produce IGSCC as presented in figure 1.2 are not usually present together, time and service conditions may conspire to produce the necessary combinations that result in surprising and expensive failures. Boiling and evaporation can concentrate the critical solutes in very dilute and otherwise non-aggressive solutions. Tensile stresses even below yield are sufficient to cause IGSCC and may result from bolting and fastening parts that fit together imperfectly. Uneven thermal expansion and contraction can produce residual tensile stress after welding and other heat treatment. IGSCC normally associated with static tensile stresses. However, only slight, long-term variations in loading are known to accelerate the onset of IGSCC.

2.5 A New Technique for Determining the IGSCC Susceptibility of 304 Stainless Steel

A major problem of IGSCC in sensitized, austenitic stainless steels have long been recognized in industries and much effort has been done to minimize and prevent it from occurring. The conventional techniques for detecting sensitization in austenitic stainless steels essentially are chemical testing or slow strain rate tensile (SSRT) testing. Moreover, the. quantification of the degree of sensitization using these techniques is difficult and they are destructive technique therefore are limited to be used in field measurement. Thus far, non-destructive testing (NDT) techniques such as gamma or X-ray radiography, eddy current and ultrasonic testing have been the important tools in detecting and locating these defects without affecting the service performance of the structure. Although, these techniques provide the mean to detect flaws and defects before catastrophic failure, most are not sensitive enough to reveal small defect until they are too far advance to be repaired. More importantly, none of the above-mentioned technique yields any information on the state of microstructures which are often responsible to material degradation and failure including the sensitization of stainless steels.

Despite much effort and improvement in NDT technology, none of commercially available NDT techniques can identify the susceptibility in austenitic stainless steels to IGSCC. The manner by which positrons interact and annihilate with electrons in metals yield distinctive doppler-broadening signals depending upon defect characters and distribution which leads to a possibility of using it as a tool to reveal atomic defects. For example, N. Maeda et al.[39] studied the application of positron annihilation line-shapes analysis to fatigue damage of nuclear plant materials. It was found that positron annihilation line-shape is sufficiently sensitive to detect microstructural defects such as fatigue damage of type 316 stainless steel and SA508 ferritic steel as shown in Figure 2.15. The typical set up of the system for evaluating the shape of doppler broadened positron annihilation (DBPA) spectrum is shown in figure 2.16.
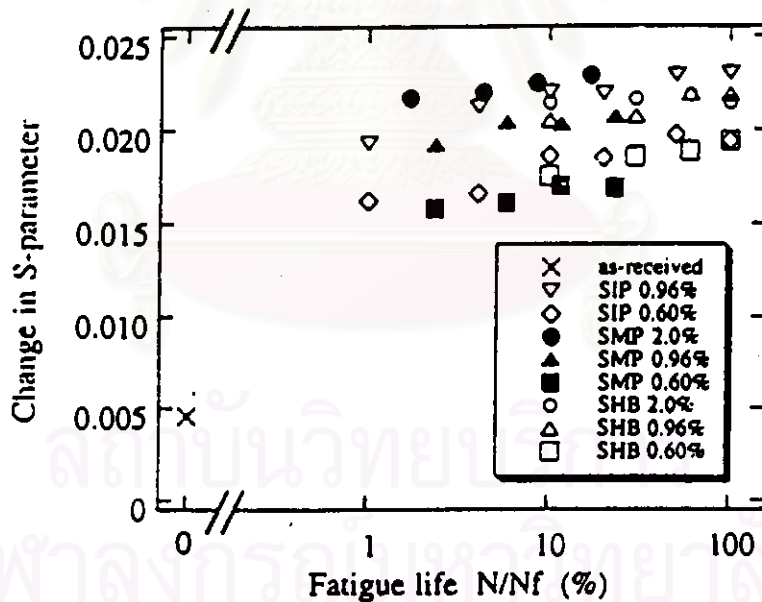

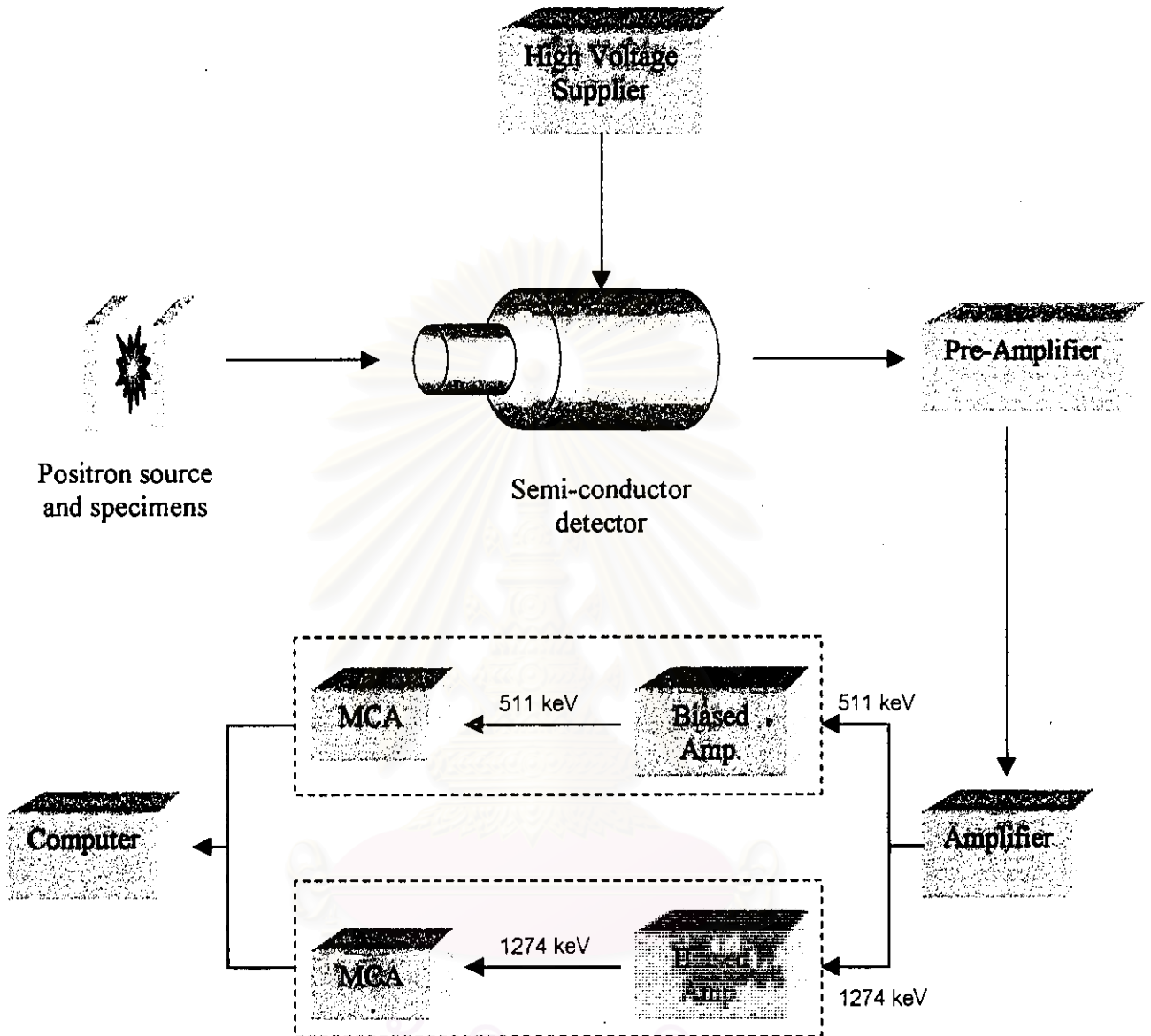Figure 2.15 Change in S parameter in type 316 stainless steel as a function of the fatigue life [39].

Figure 2.16 Schematic illustrates the typical DBPA spectroscopy system [40].

This thesis will attempt to use positron annihilation spectroscopy as a possible NDT technique to evaluate the IGSCC susceptibility in austenitic stainless steels. Since IGSCC susceptibility in austenitic stainless steels is defined by its microstructures, the manner by which positron annihilates with these microstructural features can provide valuable signals in relation to the microstructural states yielding microstructure/property relationship without disturbing materials integrity.