INVESTIGATION OF CHLORIDE STRESS CORROSION CRACKING IN AUSTENITIC STAINLESS STEEL

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ABSTRACT

Chloride stress corrosion cracking (CSCC) of AISI 304 austenitic stainless steel are the most important corrosion processes that affect the performance of this stainless steel. SCC occurs when susceptible material under the stress is exposed to a specific environment such as corrosive environment. Since austenitic stainless steel are widely used in power boiler, nuclear power, chemical plant and marine industry, SCC can cause a major losses to these industry. The purpose of this project is to study the effect of chloride stress corrosion cracking in austenitic stainless steel based on the sensitization treatment of the specimens and different concentration mixtures of sulphuric acid and sodium chloride. Method use in this study was weight loss method. From the measurement and experiment result, it shows that mass loss for specimens with sensitization treatments is higher than mass loss for specimens without sensitization treatment. The experimental result also indicates that SCC occurs only at certain concentration mixtures of sulphuric acid and sodium chloride. This was confirmed by using scanning electron microscope and digital weighing balance.

ABSTRAK

Klorida tekanan retak kakisan (CSCC) daripada AISI 304 austenit keluli tahan karat adalah proses hakisan penting yang memberi kesan kepada prestasi keluli tahan karat ini. SCC berlaku apabila bahan mudah berkarat di bawah tekanan yang terdedah kepada persekitaran yang khusus seperti alam sekitar yang menghakis. Disebabkan austenit keluli tahan karat ini digunakan secara meluas di dalam dandang kuasa, kuasa nuklear, loji kimia dan industri marin, SCC boleh menyebabkan kerugian besar kepada industri ini. Tujuan projek ini adalah untuk mengkaji kesan hakisan tegasan klorida keretakan dalam austenit keluli tahan karat berdasarkan rawatan haba terhadap spesimen dan campuran berbeza kepekatan asid sulfurik dan natrium klorida. Kaedah yang digunakan dalam kajian ini adalah kaedah kehilangan jisim spesimen. Dari pengiraan dan keputusan experimen, ia menunjukkan bahawa kehilangan jisim bagi spesimen dengan rawatan haba adalah lebih tinggi daripada kehilangan jisim bagi spesimen tanpa rawatan haba. Hasil eksperimen juga menunjukkan bahawa SCC berlaku hanya pada kepekatan tertentu campuran asid sulfurik dan natrium klorida. Ini dapat ditentukan dengan menggunakan mikroskop pengimbas elektron dan penimbang berat digital.

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LIST OF SYMBOLS

δ	Delta
ε	Strain
ε_p	Plastic strain
K	Constant in corrosion rate equation
T	Time of exposure in hours
A	Area in cm^2
W	Mass loss in grams
D	Density in g/cm3

LIST OF ABBREVIATIONS

SCC	Stress Corrosion Cracking
Cl^-	Chloride ions
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
NaCl	Sodium chloride
SEM	Scanning electron microscope
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
$NaNO_2$	Sodium nitrite
Na_2SO_4	Sodium sulfate
$Ca(OH)_2$	Sodium hydroxide
$Cr_{23}C_6$	Chromium carbide
IGSCC	Intergranular stress corrosion cracking
N_2	Nitrogen gas
Pt	Platinum
AgCl	Silver chloride
Ag	Silver
CCD	Charge-coupled devices
VTR	Video tape recording
Cr	Chromium

HCl	Hydrochloric acid
Y_s	Yield strength
UTS	Ultimate tensile strength
t_{ss}	Transition time
t_f	Time to failure
SSRT	Slow strain rate test
PTFE	Polytetrafluoroethylene
$NaHSO_4$	Sodium hydrogen sulfate
$SO^{2-}{}_4$	Sulphide ion
TGSCC	Transgranular stress corrosion cracking

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This chapter explains about the background of study, problem statement, objectives and the scopes of this study. The main purpose for this study can be identified by referring at the problem statement of this study. Furthermore, the details of this study and outcome can be achieved on the objectives and its scopes.

1.2 BACKGROUND OF STUDY

One of the major problems in the petroleum refining and the petrochemical operations is corrosion. Process of corrosion is said to happen when essential properties within a given material begin to deteriorate, after exposure to elements that recur within the environment and corrosion of most metals (and many materials for that matter) is inevitable. All material types are susceptible to degradation. The corrosion of metals will also occur when the metals exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. The best known case of corrosion is that of the rusting of steel**.** Corrosion processes are usually electrochemical in nature, having the essential features of a battery.

Billions of dollars are lost each year because of corrosion and a huge amount of money is spent on prevention of corrosion and tarnishing of metals. Corrosion causes damage to car bodies, buildings, bridges, iron railings, underground water and sewage pipes, ships and all objects made of metals. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well.

When the material under stress is exposed to an environment specific to the material, stress corrosion cracking (SCC) takes place with the formation of the local cracking (Satoshi Sunada et al., 2006). The criteria for the stresses are simply that they have tensile stress and sufficient magnitude. The source of these stresses may be due to the applied stress, residual stress, and thermal or from the welding. Austenitic stainless steel type 304 and 316 are the common materials used in a wide range of industries because of the ability to withstand very many corrosive conditions and high temperature without the need for protective measures. The presence of the stress element is needed since stress is one of the requirements in SCC mechanism. As stated by Cottis and Newman (1993), austenitic stainless steel will not undergoes cracking process or fails mechanically unless the stress applied is not high enough. Whereas Fathia et al. (2009) prove that temperature also give an effect to stress corrosion cracking since by increasing the temperature, the stress corrosion life is decrease as well.

Other than that, other factors that contribute to SCC in stainless steel is sensitization treatment since sensitization occurs because of the chromium depletion within or near regions of the grain boundaries in austenitic stainless steels in which chromium rich carbides precipitate. Sensitization represents both a microchemical and microstructural condition at an interface. Both heat treatment and thermomechanical processing appear to have an important influence on sensitization or the degree of sensitization reached, as well as intergranular stress corrosion cracking (Murr et al., 1990). The understanding of the factors that contributes to SCC will help in avoiding losses and damaged in the industry especially in the marine industry.

1.3 PROBLEM STATEMENT

Stress Corrosion Cracking (SCC) is one of the major problem that controls and determines the suitability of materials as they are very expensive modes of failures, of particular relevance to desalination and power plants. Stress corrosion cracking, SCC is one of the most significant corrosion issues concerned. Chloride stress corrosion cracking can be defined as the cracking that caused by the presence of tensile stress, a susceptible material and a specific corrosive medium such as the presence of chloride ions in the environment. This type of corrosion usually difficult to be detected since it occurs at a certain condition especially when the structure undergoes sensitization treatment. Stainless steel with sufficient carbon content will exposed to the grain boundaries attack when heated in the range of 415-850^{0}C as the microstructure becomes susceptible to the precipitation of chromium rich carbide along the grain boundaries. This will lead to occurrence of stress corrosion cracking. SCC occurs resulting from the sensitization treatment, a corrosive environment, a susceptible materials and the presence of stress. Sensitization treatment will accelerate intergranular stress corrosion cracking (IGSCC) susceptibility by shortening failure time and accelerating crack initiation and propagation rates. Different types of environment will also result in different types of corrosion in austenitic stainless steel. The study of the effect of sensitization treatment and effect of concentration mixtures of sulphuric acid and sodium chloride on the austenitic stainless steel is important in order to reduce and prolong the formation of SCC in austenitic stainless steel and predict types of corrosion that might occur at a certain environment with the information obtained in this study.

1.4 OBJECTIVES

The objectives of this study are as follows:

i. To study the sensitization effect to the chloride stress corrosion cracking of stainless steel.
ii. To investigate the influence of different concentrations mixtures of sulphuric acid (H_2SO_4) and sodium chloride (NaCl) on the chloride stress corrosion cracking of stainless steel.

1.5 SCOPES

Scopes of this study are outline as follows :

i. Material used in this study is AISI 304 stainless steel.
ii. Sensitization treatment of the specimens is done at 800^0C for 2 hours in a furnace.
iii. Specimens used are U-bend specimens according to ASTM G30 standard.
iv. Different concentrations mixtures of H_2SO_4 (0 kmol.m^{-3} to 3.0 kmol.m^{-3}) and NaCl (0.5 kmol.m^{-3} to 2.0 kmol.m^{-3}) are used for immersion test at room temperature.
v. Corrosion rate measurement is determined by using weight loss method.
vi. Microstructure analysis of the specimens is done by using scanning electron microscope (SEM).

1.6 THESIS OUTLINE

This thesis consists of 5 chapters which illustrate the flow work of this project from introduction until conclusion. There are different contents present in each chapter.

The reader will understand more on the detail and the outcome of the project after they read the entire chapters in the thesis.

Chapter 1 discusses about the background of the study, problem statement, objectives and the scope of this study.

Chapter 2 contains all the literature reviews and some progress of earlier work. This chapter also discusses some detail of material that used in this study (austenitic stainless steel 304). The concepts which are related to stress corrosion cracking also discuss in Chapter 2. Some explanation of microstructure analysis also will be explained in this chapter.

Chapter 3 discusses about summary of research methodology of this project. The progress of flow work of this project which includes the steps of this project conducted.

Chapter 4 contains the results that achieved during the experiment in this study. This chapter also explains the analysis and discussion of the results that obtained.

Chapter 5 discusses about the conclusions of the project. This chapter also contains some future recommendation of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter will discuss about the previous related study and researches on chloride stress corrosion cracking. The sources of the review are extracted from journals, articles, reference books and internet. The purpose of this section is to provide additional information and relevant facts based on past researches which related to this project. This chapter will cover the corresponding terms such as the stress corrosion cracking, medium for corrosion and type of specimen used which had been proved experimentally.

2.2 STRESS CORROSION CRACKING

Expensive modes of failures is one of the major problem which is essentially controls and determines the compatibility of materials from a wide range of materials, which is particular relevance to desalination and power plants is stress corrosion cracking (Prakash et al., 1999). Stress corrosion cracking (SCC) is one of the corrosion failure commonly encountered due to combined action of stress and corrosion medium. Stress corrosion cracking is only possible in selective environments where a passive film form at the metal surface. Under tensile stresses if the environment is too aggressive and the film formation rate is very slow then general corrosion occurs. If the rate of surface film formation is very fast, then the passive film on the metal surface will immediately repassivate upon the rupture. In SCC, the surface is able to passivate, but when the film ruptures the surface of the sample temporarily remains exposed to the environment and locally corrode. Stress corrosion cracks can initiate at abnormalities on the metal surface, including pits, grain or phase boundaries, inclusions, secondary phases, or physical defects such as scratches . Crack can propagate intergranularly or transgranularly through the microstructure once it initiates. Crack growth occurs when the reactions occur faster at the crack tip than on the metal surface or crack sides. When the critical crack length reaches, the crack continues to spread through the metal and causes the remainder surface to fail (Gary wu, 2011). Figure 2.1 shows SEM fractrograph when the sample undergoes intergranular stress corrosion cracking.

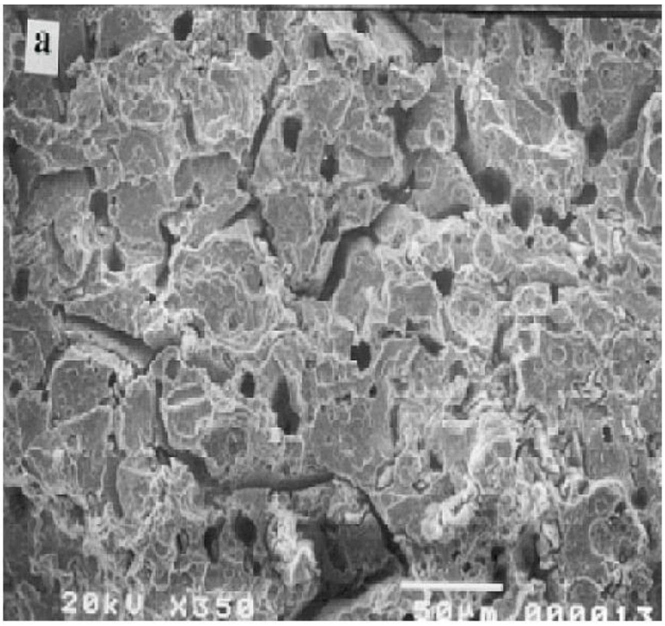

Figure 2.1: SEM fractrograph of SCC showing intergranular fracture modes

Source: Prakash et al. (1999)

The fracture surface is indicative of brittle failure and other fractographic features are dependent on the SCC mechanism. Stress corrosion cracking is an insidious form of corrosion and produces a drastic loss of mechanical strength without significant metal loss (Bhattacharya, 2008). Stress corrosion cracking causes a rapid, brittle failure of the steel without any prior indication and hence is considered catastrophic. Others major disasters have been attributed to stress corrosion cracking of steel equipment, including rupture of high-pressure gas transmission pipes, boiler explosions and severe damage in power stations and oil refineries (Bhattacharya, 2008). The steel is exposed more to stress corrosion cracking in carbonate, bicarbonate, acetates and phosphate environments and is identified as the main reason of cracking in natural gas transmission lines. In low alloy steels, oxygenated water at high temperature, $NaNO_2$–Na_2SO_4 solutions, alkaline chloride solutions such as NaCl-$Ca(OH)_2$ under pitting conditions, and anhydrous ammonia-methanol solution in the presence of chloride caused stress corrosion cracking to occurred (Prakash et al., 1999).

2.3 HEAT TREATMENT

Heat treatment is defined as the operation or combination of operations which is involving heating materials at a specific rate, soaking at a certain temperature for a period of time and cooling at some specified rate. The purpose of this heat treatment is to obtain a desired microstructure to achieve certain predetermined properties such as physical, mechanical, corrosion, magnetic or electrical (Baderestani et al., 2004). In general, heat treatment is the term for any process employed which changes the physical properties of a metal by either heating or cooling.

The purpose of heat treatment is to cause desired changes in the metallurgical structure and thus the properties of metal parts. Heat treatment is sometimes done due to manufacturing processes that either heat or cool the metal such as welding or forming. In addition, heat treatment also to increasing the strength of material, but it can also be used to alter certain manufacturability objectives such as improve machining, improve formability and restore ductility after a cold working operation. Annealing, normalizing, quench hardening, tempering, and austempering are five of the important heat treatments often used to modify the microstructure and properties of steels (Sanjib, 2008).

2.3.1 Sensitization

Sensitization is a major problem in stainless steels that affects the alloy's durability. Chromium additions in steel were the main contributor to sensitization. Sensitization is defined when a carbide precipitation induced by the welding process or heat treatment can cause chromium-depletion near the grain boundaries (Sourmail et al., 2003). Chromium is extremely reactive with oxygen and will form a very thin chromium oxide layer on the surface of stainless steel. The film that is created is on the order of nanometers in size and is what protects the underlying metal alloy from corrosion and further oxidation. Sensitization treatment significantly modifies the stress corrosion cracking behavior and the cause of this is the intergranular precipitation and the grain boundary chromium depletion. The depletion zone of chromium making the material vulnerable to corrosion particularly intergranular corrosion (Garcia et al., 2000). Figure 2.2 shows microstructure of austenitic stainless steel that undergoes sensitization treatment.

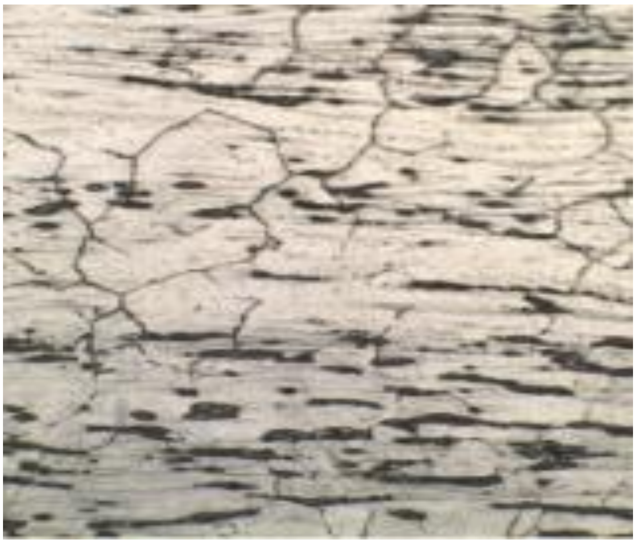

Figure 2.2: Microstructure of sensitized austenitic stainless steel

Source: Sarvesh Pal et al. (2011)

Sensitization is attributed due to the alloy element, degrees of temperature and time of heat exposure. The precipitation of $Cr_{23}C_6$ formed when austenitic stainless steels have been exposed for period of time of high temperature and slowly cooled in air. As stated by Garcia et al.(2000), chromium Cr rich carbide precipitation developed at intergranular and the precipitation of δ-ferrite formed at transgranular in the region of heat affected zone . These precipitations of δ-ferrite and chromium depleted zones were attacked in a medium that containing chloride anion. Therefore, it shows that heat input was one of the factors that affecting microstructure of materials.

2.3.2 Annealing

In general, annealing is the opposite of hardening, the metals were annealed to relieve internal stresses, soften them, make them more ductile, and refine their grain structures. Annealing consists of heating a metal to a specific temperature, holding it at that temperature for a set length of time, and then cooling the metal to room temperature (Fargas et al., 2009). The method of the cooling depends on the metal and the properties desired. Some of the metals are furnace-cooled, and others are cooled by burying in ashes, lime, or other insulating materials.

2.3.3 Quenching

Quenching of steel in heat treatment is a technological phase which has an important influence on microstructure changes and consequently on quality of a machine part (Janez et al., 2001). The cooling rate of an object depends on many things. The size, composition and initial temperature of the part and final properties are the deciding factors in selecting the quenching medium. A quenching medium must cool the metal at a rate rapid enough to produce the desired results.

2.4 AUSTENITIC STAINLESS STEEL

Stainless steels are mainly iron based with 12% to 30% chromium, up to 22% nickel and minor amounts of carbon, copper, molybdenum, selenium and titanium (Maricica, 2012). The AISI (American Iron and Steel Institute) designation of these materials is well known with the number series 300 referring to austenitic stainless steels and the 400 series covering the ferritic and martensitic stainless steels. Because of their high chromium and nickel content, austenitic stainless steel is one of the most corrosion resistant of the stainless steel group that provide fine mechanical properties.