UNIVERSITI TEKNIKAL MALAYSIA MELAKA

# EFFECT OF CHROMIUM CARBIDE ($Cr_{23}C_6$) FORMATION ON MICROSTRUCTURE AND CORROSION PASSIVITY BEHAVIOR OF AISI 304 STAINLESS STEEL

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) with Honours.

By

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FACULTY OF MANUFACTURING ENGINEERING

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# UNIVERSITI TEKNIKAL MALAYSIA MELAKA

## BORANG PENGESAHAN STATUS TESIS*

TAJUK: **EFFECT OF CHROMIUM CARBIDE ($Cr_{23}C_6$) FORMATION ON MICROSTRUCTURE AND CORROSION PASSIVITY BEHAVIOR OF AISI 304 STAINLESS STEEL**

SESI PENGAJIAN: 2009/2010

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Signature :
Author's Name : SITI FAIZAH BINTI MAD ASASAARI
Date : 16th April 2010

# APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) with Honours. The member of the supervisory committee is as follow:

……………….………………………………

**(DR. MOHD WARIKH BIN ABD. RASHID)**

# ABSTRACT

This project aimed to study the effect of chromium carbide, $Cr_{23}C_6$ formation on the microstructure and corrosion resistance behavior of AISI 304 stainless steels in 3.5 % NaCl solution. Five specimens of AISI 304, 15 mm x 15 mm x 2 mm each size with various heating time, 5 seconds, 10 seconds, 20 seconds, 40 seconds, and 60 seconds respectively are used. All specimens are immersed in 3.5 % NaCl solution, for cyclic potentiodynamic polarization technique with a scan rate of 0.5 mV/s, then, the corrosion behavior of AISI 304 was analyzed. The $Cr_{23}C_6$ formation on the microstructure of AISI 304 to resist pitting corrosion is studied by exposed the specimens to the heating time and five different pH solutions which is pH 3, pH 5, pH 7, pH 9, and pH 12. The number of $Cr_{23}C_6$ formation is high at 60 s of heating time by observing on the optical microscope. X-ray diffraction (XRD) analysis is used to study the $Cr_{23}C_6$ formation that presence on the structure of AISI 304. The increase in number and size of $Cr_{23}C_6$ performed in the structure of AISI 304, the corrosion resistance of the specimens decrease. At high heating time and more acidic solution, the pitting corrosion attack is increased. Based on the cyclic polarization scan, it is clear that at 60 s, the value of high potential stress is 0.325 V, decreases from 0.420 V as performed by 5 s heating time. While for the effect of pH solution, specimen immersed in pH 3 shows the lowest potential, 0.32 V as performed by specimen number one.

# ABSTRAK

Projek ini bertujuan untuk mempelajari pengaruh pembentukan kromium karbida, $Cr_{23}C_6$ terhadap mikrostruktur dan perilaku rintangan pengaratan bagi keluli tahan karat AISI 304 dalam larutan 3.5 % NaCl. Lima spesimen AISI 304 bersaiz 15 mm x 15 mm x 2 mm dipanaskan pada pelbagai masa pemanasan iaitu 5 saat, 10 saat, 20 saat, 40 saat, dan 60 saat. Kesemua spesimen telah direndam dalam larutan 3.5 % NaCl dengan kadar imbasan sebanyak 0.5 mV/s bagi teknik kitaran potentiodinamik polarisasi. Dengan itu, perilaku pengaratan bagi AISI 304 dianalisis. Pembentukan $Cr_{23}C_6$ pada mikrostruktur AISI 304 dipelajari untuk menangani pengaratan bopeng yang terdedah pada spesimen apabila didedahkan dengan masa pemanasan yang berbeza dan lima larutan pH yang berbeza iaitu pH 3, pH 5, pH 7, pH 9 dan pH 12. Jumlah pembentukan $Cr_{23}C_6$ adalah tinggi pada masa 60 saat dengan mengamati pembentukannya pada mikroskop optik. Analisis pembelauan X-ray (XRD) digunakan untuk mengkaji pembentukan $Cr_{23}C_6$ yang hadir pada struktur AISI 304. Peningkatan jumlah dan saiz $Cr_{23}C_6$ pada struktur AISI 304 menunjukkan rintangan pengaratan semakin menurun. Pada masa pemanasan yang tinggi dan keadaan berasid, serangan pengaratan bopeng meningkat. Berdasarkan imbasan kitaran polarisasi, jelas menunjukkan bahawa pada masa pemanasan 60 saat, nilai potensi stres menurun sebanyak 0.325 V dari 0.420 V iaitu ketika 5 saat masa pemanasan. Manakala, untuk pengaruh larutan pH, spesimen yang direndam pada pH 3 menunjukkan potensi terendah iaitu 0.32 V untuk spesimen nombor satu.

# DEDICATION

*Dedicated to my beloved family and friend*

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# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| AISI | - | American Iron and Steel Institute |
| ANSI | - | American National and Standard Institute |
| ASTM | - | American Society for Testing and Materials |
| SAE | - | Society for Automotive Engineers |
| UNS | - | Unified Numbering System |
| SEM | - | Scanning Electron Microscopy |
| OM | - | Optical Microscope |
| EDS | - | Energy Dispersive X-Ray Spectroscopy |
| XRD | - | X-ray Diffraction |
| EBDS | - | Electron Backscatter Diffraction |
| DC | - | Direct Current |
| CR | - | Corrosion Rate |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| $E_{corr}$ | - | corrosion potential |
| $E_{pit}$ | - | pitting potential |
| $E_{rep}$ | - | repassivation potential |
| $i_{app}$ | - | applied current density |
| $i_{corr}$ | - | current density |
| $\beta_a$ | - | anodic Tafel slope |
| $\beta_c$ | - | cathodic Tafel slope |
| $i_{ox}$ | - | oxidation current density |
| $I_{ox}$ | - | oxidation current |
| $F$ | - | Faraday's constant (96,487 C/gram) |
| $n$ | - | number of electrons |
| $A$ | - | surface area |
| $I$ | - | circuit current |
| $t$ | - | time in Coulombs (C) |
| $d$ | - | metal or alloy density |
| $n_i$ | - | number of electron of component $i^{th}$ element of alloy |
| $f_i$ | - | mass fraction of component $i^{th}$ of alloy |
| $M_i$ | - | atomic weight of element $i^{th}$ of alloy |
| $EW$ | - | equivalent weight |
| $pH$ | - | - log $a$ ($H^+$) |
| HCl | - | hydrochloric acid |
| $H_2SO_4$ | - | sulfuric acid |
| NaCl | - | sodium chloride |
| SiC | - | silicon carbide |
| S1 | - | specimen one |
| $C$ | - | capacitance |
| V | - | voltage |
| $T$ | - | temperature ($^oC$) |
| $M$ | - | molar |
| wt % | - | weight percent |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Stainless steels are an important class of alloys. Their importance is revealed in a wide range of applications that rely on their use. From low end applications, like cooking utensils and furniture, to very sophisticated ones, such as space vehicles (Lo, K.H., *et al*., 2009), the use of stainless steels is crucible. Stainless steels are used for consumer products, machinery, architectural and military applications, and for equipment in the petroleum, chemical, aerospace, power, and process industries. In fact, the omnipresence of stainless steels in our daily life makes it impossible to specify their applications. In order to impart stainlessness to steels, chromium (Cr) must be added to at least about 11 wt% (Lo, K.H., *et al*., 2009). At this Cr level, an adherent, self-healing chromium oxide can form on the steel surface in relatively benign environments. Stainless steel type 304 containing 18 % chromium, 8 % nickel and also known by the UNS Number S30400 (Schweitzer, P.H., 2007), they do in fact suffer from certain types of corrosion. Corrosion can cause a variety of problems, depending on the applications (Steinberg, A.M., 2008). Corrosion is an expensive process which leads to enormous damage for modern industrial societies. The serious consequences of the corrosion process have become a problem of worldwide significance where due to this problem, more cost had been use for research and development of corrosion engineering as to control corrosion on the material. Hence, this study will introduce the fundamentals and the electrochemical basis of the corrosion of metals in an aqueous environment and the corrosion passivity behavior on AISI 304.

## 1.2 Problem Statement

A lot of stainless steel components are used at elevated temperatures. Upon high-temperature exposure, a numerous of phases may precipitate in the various classes of stainless steels especially AISI 304. Some of these phases, like the $Cr_{23}C_6$, may be common to all classes, but some of them are not. High corrosion resistance of AISI 304 is primarily attributed to the passive oxide film formed on its surface that exposed to an aqueous solution and chromium oxide enrichment at the metal film interface (Marcus, P., 2002). Formation of grain boundary carbides, with an attendant decrease in Cr content in their regions, degrades corrosion resistance and is known to be the main culprit for causing sensitization. Susceptibility of the heat applied on stainless steels to intergranular corrosion has been known for a long time (Kokawa, H. and Kuwana, T., 1992), and is principally caused by the diffusion of carbon in the steel to the grain boundaries in the sensitized region. The interrelationship between $Cr_{23}C_6$ and grain boundary irregularity has been studied in detail in several recent works. Hong and Nam (2002) have discovered that grain boundary irregularity occurs before $Cr_{23}C_6$ precipitation and exerts a dramatic effect on its formation in austenitic stainless steels. Based on the previous research, the presents of $Cr_{23}C_6$ in the microstructure of AISI 304 have been affecting the corrosion behavior of this material, which by means, the number of $Cr_{23}C_6$ present will tend to localize corrosion. This occurs at a short distance from the base metal. Chromium carbide precipitates form at the boundaries with the result that regions adjacent to the grain boundaries are depleted of the chromium necessary for passivity. However, the resistance of this passive film is determined by the environmental effects which exposed to the stainless steel. In this study, AISI 304 will be exposed to heat of oxy acetylene at various times and the corrosion resistance of AISI 304 is analyzed as to study the effect of temperature by using electrochemical test. It becomes clear that the best methods to study susceptibilities to this form of corrosion are the electrochemical techniques.

## 1.3 Objectives

(1) To study the effect of chromium carbide ($Cr_{23}C_6$) formation at the grain boundaries of AISI 304 stainless steel.

(2) To study the corrosion behavior of AISI 304 from electrochemical technique due to the temperature effect and pH effect.

## 1.4 Scope of Study

The scope of this project is to study the corrosion passivity behavior of AISI 304 towards electrochemical technique in an aqueous environment. The purpose of electrochemical technique is to investigate corrosion properties of AISI 304 due to the temperature effect and pH effect. Five samples of various pH values are exposed to 3.5 % NaCl solution to study the corrosion behavior of AISI 304 in an acidic, neutral, and alkali solution. The as-received specimens of AISI 304 is exposed to heat of oxyacetylene gas welding and another five specimens ranging from 5 seconds, 10 seconds, 20 seconds, 40 seconds, and 60 seconds also exposed to the same heat of oxyacetylene gas welding to investigate the effect of temperature on microstructure and corrosion properties of this materials. The study will focused on the microstructure of AISI 304 such the present of $Cr_{23}C_6$ formation by using optical microscope (OM) and X-ray diffraction analysis (XRD) is used to determine the peak corresponding to the presence of $Cr_{23}C_6$.

# CHAPTER 2

## LITERATURE REVIEW

This section will reviewed the study of AISI 304 stainless steel properties and the application of electrochemical technique to corrosion research. This literature survey provides information related to corrosion phenomena on passivated metal surfaces and its finding on AISI 304 stainless steel corrosion behavior.

### 2.1 Stainless Steels

The main reason for existence of the stainless steels is their resistance to corrosion. Chromium (Cr) is the main alloying element, and the steel should contain at least 11 percent (Fontana, M.G., 1987). Cr is a reactive element, but it passivates and exhibit excellent resistance to many environments. Stainless steels are characterized by their corrosion resistance, high strength and ductility referred to mechanical properties, and high Cr content. They are called stainless because in the presence of oxygen, they develop a thin, hard, adherent film of chromium oxide that protects the metal from passivation corrosion. Stainless steels generally are divided into five types decomposed of austenitic stainless steel, ferritic stainless steel, martensitic stainless steel, precipitation-hardening, and duplex structure (Kalpakjian, S., 2006). Table 2.1 lists the compositions of stainless steels. The American Iron and Steel Institute (AISI) type numbers shown designate wrought compositions. A recent study by the Society for Automotive Engineers (SAE) and the American Society for Testing Materials (ASTM) resulted in the Unified Numbering System (UNS). UNS numbers are also listed in the Table 2.1 where the letter S identifies stainless steels.

**Table 2.1**: Chemical compositions of stainless steels (Fontana, M.G., 1987)

| AISI Type | UNS Number | Carbon Content (%) | Chromium Content (%) |
|---|---|---|---|
| 304 | S 30400 | 0.08 maximum | 18 - 20 |
| 316 | S 31600 | 0.10 maximum | 16 - 18 |

### 2.1.1 AISI 304 Stainless Steel

The most common stainless steel used in industries is AISI 304 stainless steel. Type 304 stainless steel is a T 300 series stainless steel austenitic. AISI 304 stainless steel is the most common austenitic grades, containing approximately 18 percent chromium and eight percent nickel. It is used for chemical processing equipment, for food, dairy, and beverage industries, for heat exchangers, and for the milder chemicals. It has high corrosion or oxidation resistance due to the chromium content, it has a deep drawing quality, excellent toughness, low temperature properties responding well to hardening by cold working and it is easy to clean, fabrication and has a beauty appearance.

#### 2.1.1.1 Mechanical, Thermal and Electrical Properties of AISI 304

Table 2.2 lists mechanical properties of AISI 304. The high strength materials exhibit good strength. High hardness is desirable for wear and some applications where resistance to corrosion is required. The austenitic steels retain good ductility and impact resistance at very low temperatures. Stainless steel, an alloy of Cr, nickel (Ni) and iron (Fe), requires at least 12 % Cr for passivity. If stainless steel is heated to a high temperature such as 425 degree celcius ($^{o}$C), chromium carbide precipitates will start to form along grain boundaries, leaving a zone depleted of Cr. The precipitates will dissolve back into the grain structure when heated above 850 $^{o}$C and fast cooled to room temperature.

**Table 2.2:** Mechanical properties of AISI 304 (Fontana, M.G., 1987)

| Material | Condition | Tensile strength, $lb/in.^2$ | Yield point, $lb/in.^2$ 0.2 % offset | Elongation, % in 2 in. | Hardness | |
|---|---|---|---|---|---|---|
| | | | | | Rockwell | Brinell |
| Type 304 | Annealed | 85,000 | 35,000 | 55 | B80 | 150 |

### 2.1.1.2 Effect of Alloying Compositions

Table 2.3 shows the chemical composition of AISI 304 which decomposed of chromium, manganese, silicon, carbon, and nickel. The element that can influence the corrosion behavior and properties of AISI 304 is discussed.

**Table 2.3:** Chemical composition of AISI 304 stainless steels (Schweitzer, P.A., 2006)

| **Element** | Carbon | Manganese | Silicon | Chromium | Nickel |
|---|---|---|---|---|---|
| **Weight %** | 0.08 maximum | 2.00 maximum | 1.00 maximum | 18 - 20 | 8 - 10 |

**Chromium**

Chromium is commonly added to steel to increase corrosion resistance and oxidation resistance or to improve high temperature strength. It is added for wear resistance and most importantly for corrosion resistance of AISI 304. Chromium has a tendency to increase hardness penetration. When five percent chromium or more is used in conjunction with manganese, the critical quenching speed is reduced to the point that the steel becomes air hardening. Chromium can also increase the toughness of steel, as well as the wear resistance.

**Nickel**

Nickel is used as alloying compositions in AISI 304 to improve low-temperature toughness and to increase hardenability. It appears to reduce the sensitivity of a stainless steel to variations in heat treatment and to distortion and cracking during quenching. Nickel is particularly effective when used in combination with chromium and molybdenum in producing AISI 304 that has high strength, toughness and hardenability.

**Manganese**

Manganese always present in steels to reduce the negative effects of impurities carried out forward from the production process for example sulfur embrittlement (Schweitzer, P.A., 2006). Manganese combines with sulfur to form manganese sulfides stringers. It considered having a detrimental effect on the general corrosion resistance of stainless steels. Manganese also used in stainless steels in order to improve hot ductility and increase the solubility of nitrogen and is used to obtain high nitrogen contents in austenitic stainless steels.

**Carbon**

Carbon is the most important single alloying element in steel. Toughness and ductility are reduced by increases in carbon content. The hardness of AISI 304 stainless steel is increased by raising the carbon content of stainless steel.