UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EVALUATION ON EMBRITTLEMENT PHENOMENA FOR WELDED PRESSURE VESSEL STEEL EXPOSED TO HYDROGEN

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

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Date	:	16 April 2009

APPROVAL

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

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(Mr. Mohamad Haidir bin Maslan)

ABSTRACT

Pressure vessel especially welded pressure vessel steel often failed catastrophically due to hydrogen embrittlement. Some examples of pressure vessels case histories of failure cases are due to hydrogen embrittlement phenomena. In accordance to that reason, evaluation on embrittlement phenomena of welded pressure vessel exposed to hydrogen must be carried out. ASTM A516 Gr 70 carbon steel which is commonly used for pressure vessel is selected for the study. The specimens are submerged arc welded in X-groove type. Electrolysis is carried out to expose the specimen towards hydrogen at three different exposure times which are 5 hours, 7 hours and 17 hours. As comparison, non-hydrogenated specimens are tested. In weldment, there are three main zones; base metal (BM) zone, heat affected zone (HAZ) and weld metal (WM) zone. However, microstructure and mechanical tests are only done on BM and HAZ as they have greater tendency to cause failures due to hydrogen embrittlement. Optical microscope and Scanning Electron Microscope (SEM) analysis are used to study the microstructure of the specimens. From the experiment, the difference between BM and HAZ overall microstructure, grain size and shape are clearly observed. Dislocations are more severely occur in the HAZ region and the hardness of the specimens is increased by the increasing of cathodic charging time. The complexity of HAZ microstructures in a slim region is expected to cause the dislocation in the specimens' structure and initiate the cracks. Long hydrogen exposure times could cause the decrement in some important properties of the specimens which lead to hydrogen damages.

ABSTRAK

Dandang bertekanan terutamanya dandang tekanan besi berkimpal seringkali gagal dengan dahsyat disebabkan oleh perapuhan hidrogen. Beberapa contoh kes sejarah kegagalan dandang bertekanan adalah disebabkan oleh fenomena perapuhan hidrogen. Bertepatan dengan alasan itu, taksiran ke atas fenomena perapuhan dandang bertekanan besi berkimpal terdedah kepada hidrogen perlu dijalankan. Besi karbon ASTM A516 Gr 70 yang mana biasa digunakan untuk dandang bertekanan telah dipilih untuk kajian ini. Spesimen-spesimen telah dikimpal separa cantum dalam alur jenis X. Electrolisis telah dijalankan untuk mendedahkan spesimen kepada hidrogen pada tiga masa pendedahan yang berlainan iaitu 5 jam, 7 jam dan 17 jam. Sebagai perbandingan, spesimen tidak terhidrogenasi telah dikaji. Dalam pengimpalan, terdapat tiga zon utama; logam spesimen (BM), zon terkesan haba (HAZ), dan zon kimpalan(WM). Bagaimanapun, ujian mikrostruktur dan mekanikal hanya dijalankan ke atas BM dan HAZ disebabkan mereka lebih cenderung untuk menyebabkan kegagalan berpunca daripada perapuhan hidrogen. Mikroskop optik dan analisis Mikroskop Imbasan Electron (SEM) digunakan untuk mengkaji mikrostruktur spesimen-spesimen. Daripada eksperimen, perbezaan diantara keseluruhan mikrostruktur, saiz bijian dan bentuk bijian BM dan HAZ dapat diperhatikan dengan jelas. Kehelan adalah lebih ketara terjadi di dalam bahagian HAZ dan kekerasan spesimen-spesimen adalah bertambah berdasarkan penambahan masa pngecasan katodik. Kekompleksan mikrostruktur HAZ di dalam kawasan yang sempit telah disyaki menyebabkan kehelan di dalam struktur spesimen-spesimen dan memulakan keretakan. Masa pendedahan hidrogen yang lama boleh menyebabkan penurunan di dalam beberapa sifat-sifat penting spesimen-spesimen yang membawa kepada kerosakan hidrogen.

DEDICATION

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LIST OF ABBREVIATIONS

AC	-	Alternating Current
AIDE	-	Adsorption-induced dislocation emission
AHW	-	Atomic Hydrogen Arc Welding
ASME	-	American Society of Mechanical Engineers
ASTM	-	American Society of Testing and Materials
AWS	-	American Welding Society
BCC	-	Body Cubic Centered
BIF	-	Brittle intergranular fracture
BM	-	Base Metal
CTTW	-	Contact Tip to Work
CVN	-	Charpy V-Notch
DBTT	-	Ductile to Brittle Transition Temperature
DC	-	Direct Current
DCEN	-	Direct Current Electrode Negative
DCEP	-	Direct Current Electrode Positive
ESO	-	Electrode Stick-Out
GDS	-	Glow Discharge Spectrometer
GMAW	-	Gas Metal Arc Welding
GTAW	-	Gas Tungsten Arc Welding
HAZ	-	Heat Affected Zone
HB	-	Hydrogen Blistering
HE	-	Hydrogen Embrittlement
HEDE	-	Hydrogen-enhanced decohesion
HELP	-	Hydrogen-enhanced localized plasticity
LPG	-	Liquefied Petroleum Gas
MEA	-	Monoethandamine
PAW	-	Plasma Arc Welding
PPIC	-	PETRONAS Petrochemical Industrial Complex

PV	-	Pressure Vessel
PWHT	-	Post weld heat treatment
SAW	-	Submerged Arc Welding
SCC	-	Stress Corrosion Cracking
SEM	-	Scanning Electron Microscope
SMAW	-	Shielded Metal Arc Welding
TIG	-	Tungsten Inert Gas Welding
UTeM	-	Universiti Teknikal Malaysia Melaka
UTM	-	Universal Testing Machine
UTS	-	Ultimate Tensile Strength
VHN	-	Vickers Hardness Number
WM	-	Weld Metal
YS	-	Yield Strength

CHAPTER 1

INTRODUCTION

1.1 Background

Hydrogen is one of the mostly known environment which surrounds in human daily lives. It contained in water (H_2O), use as fuel including rocket fuel, filling balloon, preparing others useful chemical such as hydrochloric and methanol, and others. However, it also has a wide range of harmful effects on metals; known as hydrogen damages. Occurrences of hydrogen had caused several damages on pressure vessels, since a few decades ago.

Hayes (1996) stated six case histories of pressure vessels failures within 1963 to 1984 in her research study. Three of the failures were clearly caused by hydrogen; John Thompson ammonia converter pressure vessel for ICI Immingham (1965), Robert Jenkins pressure vessel (1970) and Union Oil Co. Amine absorber tower (1984). Both failures at John Thompson and Robert Jenkins pressure vessels were initiated by crack at the heat affected zone (HAZ) of weldment. The probable cause of the original crack was hydrogen cracking. Meanwhile, Union Oil Co. Amine absorber pressure vessel failure was caused by the hydrogen blistering which later formed four cracks at the HAZ. According to Hayes study, it can be concluded that hydrogen penetration is more sensitive towards the HAZ rather than the base metal and the fusion zone. Another case of failure is on December 13, 1984, at the Las Piedras Refinery, Venezuela in which a crack was found in the heat affected zone about 1-1.5 inches from weld and fatigue is dominantly occurred due to hydrogen embrittlement (Abduh, 2008).

Hydrogen damages can be classified into several types and one of them is Hydrogen Embrittlement (HE). HE occurred when hydrogen is absorbed into the material and results in reduction of its mechanical performance. Propagation of hydrogen atoms into metals will cause severe failures. It can be initiator to others problems and corrosion of the metals as well. Hydrogen could be developed from water vapor in atmosphere, melting metal process, electrolysis in electroplating, welding and others.

Reduction of the mechanical properties such as decreasing in ductility and loss in tensile strength are the main problem occurred from HE. Hence, microscopic examination is carried out in order to study in detail the embrittlement process that causes reduction of materials properties. Microstructure of ASTM A516 metal specimens exposed to hydrogen at three different exposure times will be further observed and explained throughout this research.

Pressure vessel is a closed container used for liquid or gases storage at high pressure. ASTM A516 is one of the steel commonly used for pressure vessel at low and moderate temperature. In this study, welded pressure vessel specimen is used for the determination of hydrogen adsorption effects. The pressure vessel has broad application such as liquid and gases storage in oil refinery, diving cylinder, LPG gas storage and others. Welded pressure vessel has different properties than non-welded pressure vessel and it will be explain in detail throughout this thesis.

1.2 Problem Statement

Pressure Vessel steel had been designed so that it capable to operate in the elevated temperature and high pressure environmental service application. However, due to long time exposure to hydrogen environment, hydrogen embrittlement occurred and significantly embrittled the steel. As the pressure vessel is welded, the tendency of hydrogen embrittlement occurs in the weld part could be slightly different from the vessel steel part, because of the differences in chemical composition and some other factors. Hence, an investigation is carried out to check the durability of pressure vessel starting with the crack inspection of two types of samples; hydrogen exposed steel and non-hydrogen exposed steel, and then each type of samples are divided into two distinct parts; base metal and heat affected zone. Weld metal will not included in detail for this study as there is very little and almost none failure cases regarding to the weld metal. The microstructure of each samples are evaluated to analyze the differences of hydrogen embrittlement by means of different exposure times. Elements in the samples are determined by using Energy Dispersive X-ray Microanalysis (EDX) which also known as Energy dispersive Spectroscopy (EDS).

1.3 Research Objective

a) To evaluate the hydrogen embrittlement mechanism.
b) To analyze the microstructure of two distinct zones in the welded pressure vessel steel and to differentiate their properties.

1.4 Research Scope

This study is mainly focused into three major scopes. First is to analyze the welded pressure vessel steel characteristics and its behavior towards the mechanical properties. Microstructure of two out of three distinct zones of the welded pressure vessel steel; base metal (PV steel) and heat affected zone, are further investigated to differentiate their properties. Then, electrolysis is carried out in order to expose the sample towards hydrogen. Finally, the hardness test is done to differentiate the hardness of the zones for the hydrogen exposed and non-hydrogen exposed specimens. Besides three non-destructive tests; optical microscopy test, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Microanalysis (EDX), were also carried out.

CHAPTER 2

LITERATURE REVIEW

Hydrogen Embrittlement is a failure phenomenon where the ductile metal becomes brittle due to hydrogen exposure. National Board Bulletin (January 1986) describes the cause of a monoethandamine (MEA) absorber vessel that ruptured in the state of Illinois in 1984, resulting in 17 fatalities and property damage in excess of $100 million (Schmeilski, 1986). This article is describing the affect of welding factors and corrosion factors that contributed to the rupture. Besides that, hydrogen adsorption is investigated over MEA adsorption as another possible factor. Several type of hydrogen damage will be further investigated especially damages which occurred at room temperature. Metallurgical of two different zones in welded pressure vessel of ASTM A516 Gr. 70 will be observed. The following literature review attempt to explain in detail each component included in this research.

2.1 Hydrogen Damage

Hydrogen damage is a metal degradation processes cause by the interaction with hydrogen gases (Fontana, 1986). The hydrogen atom is the smallest of all atoms and hydrogen attack is similarly insidious and hidden from the simple inspection techniques. Hydrogen is present practically everywhere, in the atmosphere, several kilometers above the earth and inside the earth. Engineering materials are exposed to hydrogen and they may interact and resulting various kinds of the structural damage. Damaging effects of hydrogen in metallic materials have been known since 1875 when W. H. Johnson reported that some remarkable changes are produced in iron by the action of hydrogen and acids (Hayes, 1996). During the intervening years many similar effects have been observed in the different structural materials like steels, aluminum, titanium, zirconium, etc. Because of the technological importance of hydrogen damage, many people explored the nature, causes and the control measures of hydrogen related degradation of metals. Hardening, embrittlement and internal damage are the main hydrogen damage processes in metals. **Figure 2.1** schematically shows the mechanism of the degradation begins with the formation of free hydrogen atom at the steel surface. Technically, the hydrogen atoms are developed from the sulphide attack of the process medium at the steel surface. As a result of electrochemical reaction, hydrogen atoms are generated and the steel surfaces are corroded.

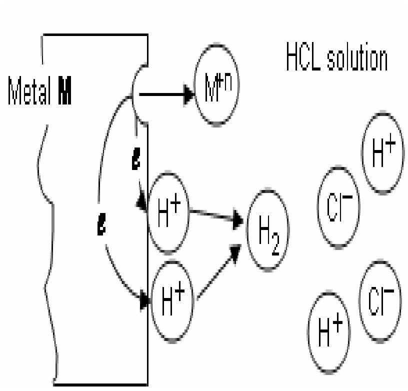


Figure 2.1: Electrochemical reactions occurring during corrosion of metal M in hydrochloric acid (Fontana, 1986)

The process variables for hydrogen occurrence are; (a) Acidic environment with acidity of pH 4.0 and below has greater tendency for hydrogen damage with the presence of H_2S. However, if both H_2S and cyanide are present, hydrogen damage can occur at acidity level above the pH 7.0. (b) Normally, H_2S level above 50ppm is required for the attack. Meanwhile, in the presence of cyanide, H_2S threshold level for the attack is reduces remarkably. (c) Basically, hydrogen damage takes place at two temperature regions which are temperatures at the ambient and slightly above 26^oC-150^oC and at the elevated temperatures. At elevated temperature, moisture does not required to develop the damage.

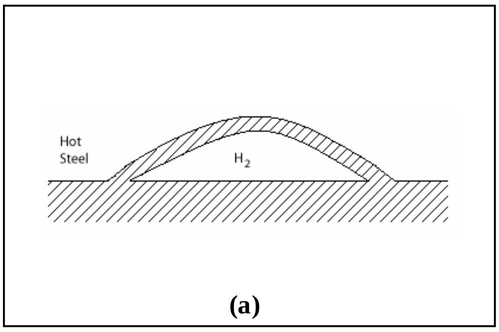
2.1.1 Classification of Hydrogen Damage

As stated earlier, hydrogen damage will takes place at the two temperature region; elevated temperatures and at the ambient and slightly above. Ambient hydrogen damage, also known as wet Hydrogen Sulfide (H_2S) damage can be classified in terms of a number of distinct classes as shown in **Table 2.1**.

Table 2.1: Some examples of hydrogen damages at two different temperatures ranges.

Low / Moderate	Elevated
i) Hydrogen Embrittlement	i) Decarburization
ii) Hydrogen Blistering	ii) Hydrogen Attack
iii) Stress Corrosion Cracking	

Stress corrosion cracking is a class of corrosion which is typically develops in hard spots of weld; cracking occur in weld metal itself (Mostert & Sharp, 2005). In SCC, the ductile metal is said to be failed in the brittle manner or known as ductile to brittle transition. Two main conditions must be correlated in SCC are stress is being applied towards the metal together with the presence of hydrogen. Meanwhile, hydrogen blistering (HB) results from the penetration of hydrogen same as HE, instead the effect of the penetration of hydrogen towards the material physical. In HB, hydrogen gas nucleates at the internal defects and inclusions, forming voids which eventually generate enough pressure to locally rupture the metal (Fontana, 1986).



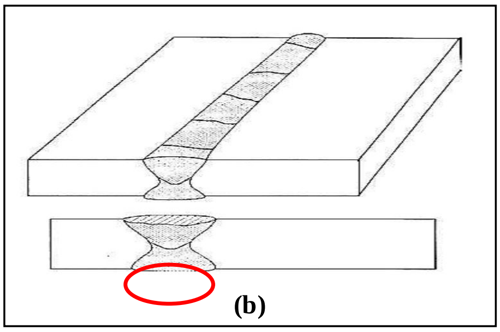


Figure 2.2: (a) Hydrogen blistering. **(b)** SCC in weld metal. (Mostert and Sharp, 2005)

Both of the corrosion types shown in **Figure 2.2** slightly have potential to be developed in this research. However, more focus are given on the hydrogen embrittlement as the main hydrogen damage assumed to develop rather than both stated earlier. Furthermore, hydrogen embritlement is more prevalent at room temperature and decreases with the increasing temperature (Kim, 2002).

2.1.2 Hydrogen Embrittlement

Hydrogen embrittlement is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in the reduction of the load bearing capacity of a component. Many metallic alloys such as those of Fe, Ni, Al, Ti, Zr, Ta, Hf, Nb, V, W, Mo and U are susceptible to hydrogen embrittlement and in fact no structural alloy is totally immune to this type of embrittlement (Dayal & Parvathavarthini, 2003). According to Kim (2002), the presence of hydrogen in steel reduces the tensile ductility and causes premature failure under the static loads that depends on the stress and time. The mechanism starts with the single hydrogen atoms diffusing through the metal as shown in **Figure 2.3**.

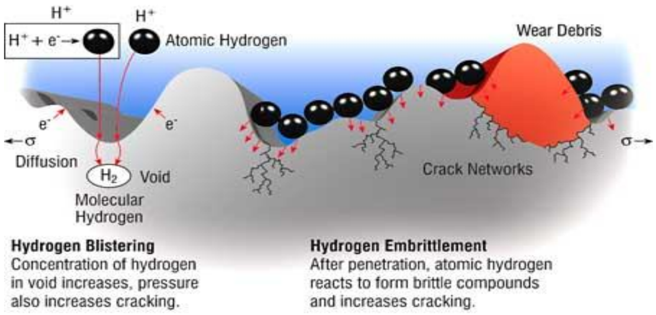


Figure 2.3: Hydrogen atom penetration through metal (Toyer, 2004).

Typical conditions of hydrogen embrittlement are at the pressure of 10^{-6} to 10^{8} N/m^2 and usually observed at -100˚C to 700˚C; most severe near 20˚C as stated by ASTM. Besides that, embrittlement is more severe at low strain rate and in notched or pre-cracked