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RECENT ACTIVITIES
ON
HIGH TEMPERARTURE HYDROGEN ATTACK

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ABSTRACT

Existing C-0.5Mo steel in hydrogen service is still our concern in industries. High Temperature Hydrogen Attack (HTHA) has been one of the major problems in petroleum and petrochemical industry because of its effect. Since the original Nelson Curves was suggested in 1949 to define the operating limits for steels used in hydrogen service to avoid HTHA, a number of research and investigation activities on HTHA have been carried out mainly in The United States and Japan.

In USA, API summarized these data as Publication 941 – “Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants” in 1970 and, since then, it has been widely used for material selection in hydrogen service, operation and maintenance in petroleum and petrochemical plants. In Japan, some organizations such as JSM, JPVRC and PVT have been tackling HTHA problems since 1970’s, and they suggested some assessment procedures for HTHA. Importance is how to evaluate this equipment to keep plant integrity.

This paper summarizes the research and investigation activities related to HTHA, including the general information about HTHA.

Key words: HTHA, High Temperature Hydrogen Attack, Carbon steel, C-0.5Mo steel,
Low alloy steel, API, JSM, JPVRC, PVT

INTRODUCTION

HTHA has been observed in petroleum refining and petrochemical equipment used in the environment with high hydrogen pressures at elevated temperatures. This attack is caused by the ingress of hydrogen into steel. Hydrogen atoms react with dissolved carbons or carbides in steel and form methane gas in accordance with the following chemical reaction.

$$4H + C \rightarrow CH_4 \quad \text{or} \quad 4H + MC \rightarrow CH_4 + 3M \quad \text{(M: metals)}$$

This gaseous methane forms voids mainly on grain boundaries or inclusions as shown in Figure 1, and the increase of gaseous methane pressure in the voids may result in the formation of micro fissure, blistering or cracking as shown in Figures 2 and 3. The attacked material significantly deteriorates its mechanical properties in tensile strength and ductility, and finally causes catastrophic failures.

It has been well known that the operating limit on HTHA could be summarized using two parameters; operating temperature and hydrogen pressure. Schuyten first suggested this theory on carbon steel [1], and Nelson also investigated HTHA cases of the other materials and proposed the first Nelson Curves in 1949 [2]. This Nelson Curves was introduced in American Petroleum Institute Publication (API Publ. 941) in 1970. The Curves has been revised several times after new damage cases had been reported and the current API 941 is the sixth edition as a Recommended Practice (RP). The activities on HTHA in The United States have been mainly along with this API.

The research and investigation works on HTHA also have been carried out in Japan. Japan Society of Materials (JSM) carried out the user survey on HTHA and proposed to establish a HTHA assessment parameter including operating time in addition to operating temperature and hydrogen pressure. And Japan Pressure Vessel Research Council (JPVRC) established a task group on hydrogen attack on C-0.5Mo steel and proposed Pw and Pv parameters to evaluate HTHA. Other than JSM and JPVRC, a private research working group, Pressure Vessel Technology (PVT), had their own activities related to HTHA.

This paper introduces the activities on HTHA, focusing on the achievements in The United States and Japan.

ACTIVITIES IN THE UNITED STATES

Since Nelson proposed the original Nelson Curves in 1949, this has been widely utilized in The United States. Industrial experience and experimental data have been collected and the curves were revised several times mainly based on HTHA experiences of users. API has played a significant role on this activity.

API Subcommittee on Corrosion and Materials published the first issue of Publication 941 – Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants in 1970. API Publ.941 summarizes the results of experimental tests and industrial data acquired from operating plants to establish the practical operating limits for carbon steel, 0.5Mo steels and low alloy steels on HTHA. The Nelson Curves has been revised when new damage data had been available. The most remarkable revision was for 0.5Mo, including C-0.5Mo, steels. The operating limit for 0.5Mo steels had existed until 1990, however, it was removed from the Nelson Curves in the fourth edition of API Publ.941. This was because a number of HTHA cases under the operating limit curve for 0.5Mo steels had been reported and the reliability of 0.5Mo curve was in doubt. Other than 0.5Mo steels, the case histories of 1.25Cr-0.5Mo and 2.25Cr-0.5Mo steels were also reported in detail in the fifth edition in 1997. This issue is currently the newest one and authorized as a Recommended Practice (RP). Figure 4 shows the current operating limit curves. This issue also mentions about HTHA of 0.5Mo steels in Appendix A with the reference data, including the summary of experience as shown in Figure 5.

In addition to the activities to establish the operating limits for materials used in hydrogen environment, API 941 also reports the inspection methods for HTHA in the fifth edition. It is suggested that inspection for equipment operated near or below the Nelson Curves has low priority, however, C-0.5Mo steel is the notable expectation and periodic inspection is recommended if equipment has been operated above the carbon steel curve. As for inspection techniques for HTHA, several methods were introduced. In API RP941, ultrasonic methods are the most effective in early detection of HTHA of the microfissure stage for base metal. The combined use of a sensitive backscatter method with the velocity ratio, attenuation, and/or spectral analysis is also recommended. For weldment inspection, API RP941 mentions that the early stage detection on HTHA is difficult by means of nondestructive method. Other than nondestructive inspection methods, in-situ metallography is recommended as another effective procedure to detect the early stages of HTHA at the surface of the steel.

API still continues the activity on HTHA in the Subcommittee on Corrosion and Materials, and revisions to the curves will be published as the need arises. They request new information to users to establish more reliable curves, especially for chromium-molybdenum steels not included on the existing chart. The next issue might be published in 2004 with revised inspection section. Technical Basis Document including numerous references and citations, theoretical and modern work and new references is also expected to release in the near future.

Risk Based Inspection (RBI) has been widely used in refining and petrochemical plants recently. API summarized HTHA Technical Module as Appendix I in API Publ.581 – Risk Based Inspection Base Resource Document (BRD/RBI), which is released in May 2000. This technical module can be used when user carried out RBI assessment. In this technical module, a susceptibility to HTHA can be estimated using Pv parameter (later mentioned in this paper) and the effectiveness of some inspection procedures is summarized.

ACTIVITIES IN JAPAN

In Japan, Japan Society of Materials (JSM), Japan Pressure Vessel Research Council (JPVRC) and Pressure Vessel Technology (PVT) Working Group played a significant role in the research activities on HTHA. The followings are introduced their achievements.

JSM

JSM carried out the survey related to hydrogen attack and summarized the data in "Collection and arrangement of High Temperature & Pressure Hydrogen Damage Data in Japan [6] " in 1980. In this survey, JSM investigated users' experience on total eighty (80) items in refineries as well as reviewed literatures published between 1969 and 1979.

JSM compared the Nelson Curves to the industrial experience and revealed that the industrial data of C-0.5Mo in actual plants is not necessarily satisfied with the operating limit on the Nelson curve. JSM also suggested that HTHA susceptibility could be estimated considering an incubation period before incidence of damage using operating time factor along with operation temperature and hydrogen pressure. This suggestion was verified in detail by JPVRC afterwards.

JPVRC

JPVRC established Subcommittee on hydrogen embrittlement in 1978 and eight task groups (TG) have had many activities . As for HTHA, JPVRC investigated about hydrogen attack limit of C-0.5Mo steel in TG4. The remarkable achievement in TG4 was to propose Pw and and Pv parameters to evaluate the HTHA susceptibility of C-0.5Mo steel. The original concept of Pw was suggested by Shewmon et al [5] as the following equation.

$$Pw = 3 \log (P_{H2}) + \log t - (9981/T)$$

P_{H2} : Hydrogen partial pressure (kgf/cm^2)

t : Total operating time (hr)

T : Operating Temperature (K)

JPVRC revealed in their investigation [5] that the critical values of Pw on HTHA of C-0.5Mo steel were the followings;

For base metal Pwcr = -4.80

For HAZ with PWHT Pwcr = -5.25

For HAZ without PWHT Pwcr = -7.90

Nomura et al. traced the above result [6] and showed that Pwcr values were generally between –4.45 and –5.64, which were almost the same as JPVRC's proposal value.

As an expansion of JSM's suggestion, JPVRC also proposed the following Pv parameter;

$$Pv = \log (P_{H2}) + 3.09 \times 10^{-4}\, T (\log t + 14)$$

P_{H2} : Hydrogen partial pressure (kgf/cm^2)

t : Total operating time (hr)

T : Operating Temperature (K)

The critical values of HTHA for C-0.5Mo steel were summarized as below;

For base metal Pvcr = 5.80

For HAZ with PWHT Pvcr = 5.60

For HAZ without PWHT Pvcr = 4.90

Hydrogen attack may be directly detected by nondestructive inspection, however, Pw and Pv parameters are effective to the assumption of incubation period before generating HTHA microfissure even in the case that no HTHA is observed in nondestructive inspection. The concept of Pv parameter proposed through the activities in Japan is now reflected in API publ.581 as previously mentioned in this paper.

JPVRC had already closed TG4, however, it has still carried out the activities related to hydrogen damage. Currently, the activity on Fitness-For-Service on hydrogen embrittlement and temper embrittlement has been progressed in TG8.

PVT Working Group

A private research working group, PVT, also enthusiastically tackled HTHA problem. PVT was organized in 1975 in order to discuss the matters related to damage mechanisms occurred in pressure vessels. It was grouped by a pressure vessel fabricator, , an engineering contractor and several oil refining companies. Idemitsu was a main contributor among them. The achievements in PVT were summarized in many reports [7] and distributed to the member companies.

Through PVT researches, metallurgical dependency on HTHA was investigated in detail. PVT proposed the procedure to estimate HTHA susceptibility from the correlation between morphology of carbide precipitates and operating temperature difference from Nelson chart or Pv parameter [8] as shown in Figure 6. In addition, some inspection procedures to detect HTHA were tested in PVT working. PVT suggested a total evaluation to assess HTHA susceptibility, using hardness test, metallurgical observation and non-destructive inspection, mainly by UT.

CONCLUSIONS

Research activities on HTHA have been carried out mainly in The United States and Japan. The following remarkable achievements were accomplished through their activities.

(1) The operating limit for HTHA was summarized for Carbon steel, 0.5Mo steels and low alloy steels using two parameters; hydrogen partial pressure and operating temperature. Schyten and Nelson originally suggested this concept, and the operating limit curves have been on API941 since 1970 and widely used in petroleum and petrochemical industry.

(2) API Subcommittee on Corrosion and Materials has been active since they first published API941 – Steels for hydrogen service at elevated temperatures and pressures in petroleum refineries and petrochemical plants. The newly revised one (sixth edition) would be published soon including more information about inspection procedures.

(3) In Japan, JSM, JPVRC and PVT played a significant role on research activities on HTHA. Through their activities, some beneficial data and concepts were suggested.

(4) JSM summarized the results of the survey in 1980 and revealed that the Nelson curve of C-0.5Mo steel was dissatisfied in many cases. JSM also proposed to establish an assessment procedure including operating time factor along with hydrogen pressure and temperature.

(5) JPVRC suggested Pw and Pv parameters to evaluate the incubation time before HTHA microfissure generation in C-0.5Mo steel. The concept of Pv is currently introduced in API Publ.581 and used for Risk Based Inspection.

(6) A private research working group, PVT, tackled pressure vessel degradation problems including HTHA. PVT proposed the procedures to estimate HTHA susceptibility from the correlation between carbides morphology and operating temperature difference below Nelson curve or Pv parameter.

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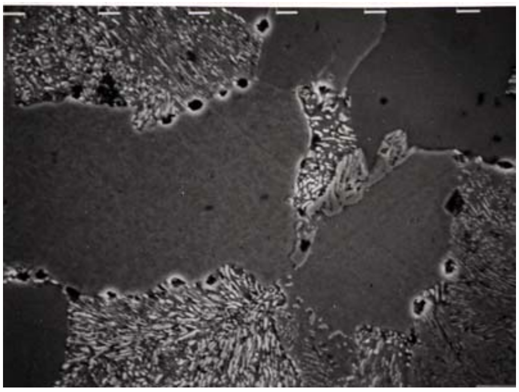

Figure 1　SEM fractograph of HTHA voids on grain boundaries

Figure 2　Blistering observed on C-0.5Mo nozzle flange used in Platformer unit

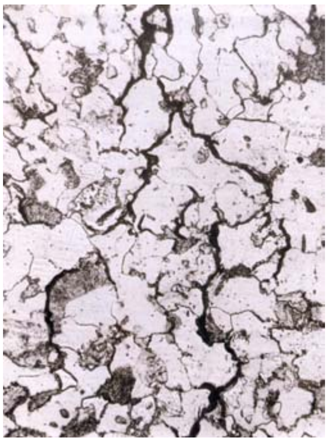

Figure 3　Photomicrograph of intergranular cracking caused by HTHA

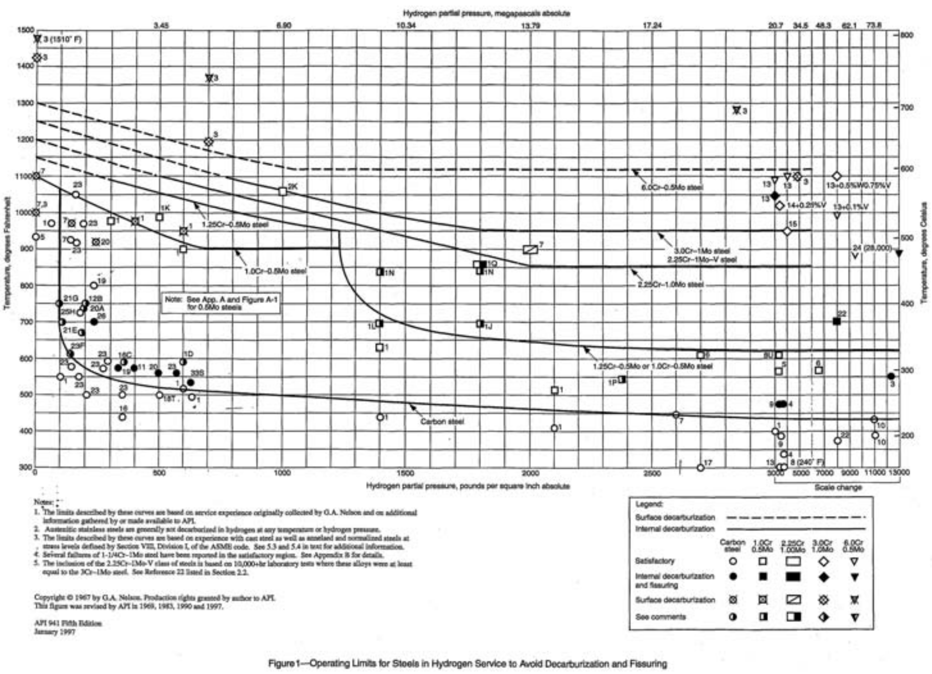

Figure 4　Current operating limit curves in API RP941

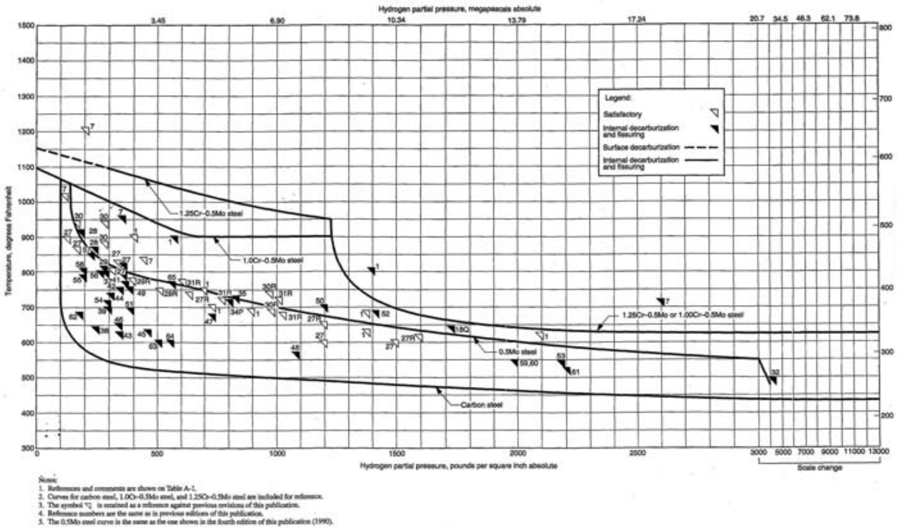

Figure 5　Experience with 0.5Mo steels in high temperature hydrogen service

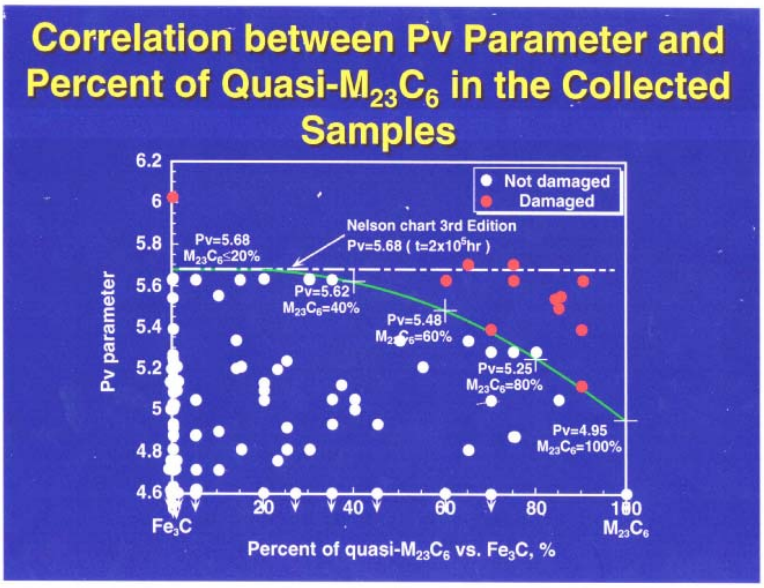

Figure 6　Correlation between Pv parameter and secondary carbides on HTHA