

## HYDROGEN ABSORPTION IN WELDMENTS OF OVERLAID CLADED PRESSURE VESSEL

Ronnie Higuchi Rusli

Graduate Program of Engineering, University of Indonesia  
Visiting Research Scientist Pressure Vessels Division, Sumitomo Steel Industries, Ltd., Japan

E-mail: ronnie\_rusli@yahoo.com

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### Abstract

Cracks was found in type 347 stainless steel internal attachment welds of a reactor for a high temperature, and high pressure hydrogen service. One of the possible causes of cracking is low cycle fatigue cracking induced by repetition of thermal stress to embrittled weld metal. Type 347 weld metal loses its ductility by presence of sigma phase and hydrogen.

*Keywords: desulfurization, hydrogen embrittlement, hydrocracking, martensitic, weldment*

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### 1. Introduction

The reactor pressure vessels (PV) was commonly used for high temperature high pressure H<sub>2</sub>-H<sub>2</sub>S environment operation such as hydro cracking and hydrodesulfurizing processes. PV usually weld overlaid inside the wall with combination of type 309-310, 321 and 347 attached with stainless steel internals on the inside surface of PV chrom-molybdenum base metal. These stainless steels absorb high amount of hydrogen during the reactor operation in a petrochemical plant of a refinery.

Although austenitic steels are hardly embrittled by such a low hydrogen concentration, in some other cases causes sever embrittlement to most martensitic high strength steels. Remarkable embrittlement of austenitic steels may be observed substantially in metals which contained several percent of delta ferrite for prevention of hot cracking. Nonetheless this may cause a higher susceptibility to hydrogen embrittlement [1].

Recently, in a direct desulfurization reactor which operated for about three years under high temperature, and high pressure hydrogen of approximately 330 to 450°C, which produced high amount of hydrogen [2] was examined by taking sample from its overlaid cladding within the PV (see drawing).

In this paper, the cause of the cracking in the internal stainless weld metals and its countermeasures were analyzed and discussed.

### 2. Methods

#### *Cracks in the Internal Attachment Welds of a Direct Desulfurization Reactor.*

Figure 1 shows cracks which were found in a type 347 stainless steel attachment weld of a direct desulfurization reactor operated at hydrogen gas pressure of approximately 13.70 MPa and at temperatures of 320 to 455°C. The cracks originated in type 347 fillet weld which attached a type 321 stainless steel block to the inner surface of the reactor which was weld overlaid by type 310 and 347 steels. Most of the cracks propagated through the type 347 weld overlay and terminated at the boundary of type 347 and 310. The cracks were associated with delta ferrite and sigma phase in type 347 weld metals. And the cracked weld metals occluded high amount of hydrogen.

It is clearly shown in Figure 1, that the cracks show straight propagation along with dendritic structure in type 347 stainless steel weld metals without any noticeable branching that appears in the stress corrosion cracking process. From this it may indicated that the cracking has close relation to the ductility loss of the weld metals due to hydrogen absorption.

Consequently, bend test methods were conducted on specimens taken from type 347 weld overlay. Test results are shown in Table 1, which are:

- (1) As received specimens which still contained 30 ppm hydrogen 6 month after the shut down broke with small bent angle.

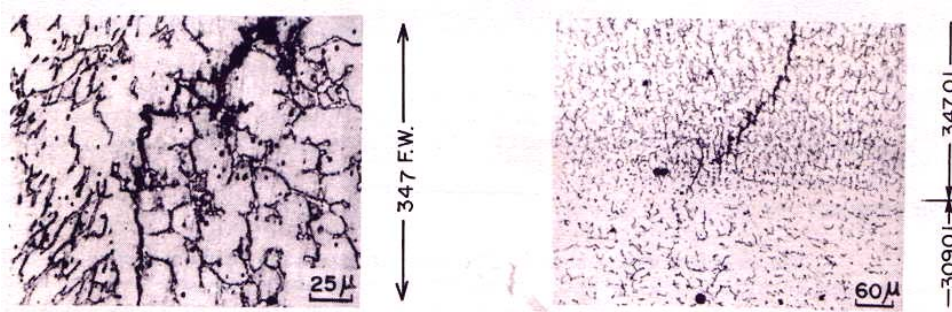


Figure 1. Cracks in internal attachment weldment

Table 1. Surface bend test results

Location	As Received Delta Ferrite: 2.7% Hydrogen: 29 ppm	1) Hydrogen Outgassed Delta Ferrite: 2.7% Hydrogen: 1 ppm	2) Desigmatized Delta Ferrite: 10% Hydrogen: 4 ppm	Remarks
Center of Bend	75°, Break	180°, No Break	180°, No Break	1) 630°C x 3 hr at 10 <sup>-3</sup> ~10 <sup>-4</sup> Torr 2) 900°C x 2 hr Water Quenched 3) Test Specimen : 4 x 25 x 70 (mm) Bend Radius : 10 mm <sup>R</sup>
	5 5°, Break	180°, No Break	180°, No Break	

- (2) Dehydrogenated specimens with 1.25 ppm hydrogen and the same ferrite content as the case (1) Bent 180° bent angle without cracking.
- (3) Desigmatized specimens with 10% ferrite were also bent 180° without cracking.

Test result shown in Table 1 illustrated sever loss ductility of a type 347 weld metal due to hydrogen

**Hydrogen Embrittlement of Austenitic Stainless Steel Weld Metals**

From the above results, it may be considerable that hydrogen embrittlement is one of the most important factors for the cracking of weld metals in this reactor [2]. In order to study the behavior of hydrogen embrittlement of the stainless weld metals, several austenitic stainless steels were prepared, and tested after hydrogen charging.

Type 347 weld metals containing various amounts of delta ferrite are used for the major portion of this investigation. And the other austenitic weld metals and casting are also used. All of the weld metals are prepared by strip weld overlay on the 100 mm thick 2 1/4Cr-1Mo steel forging.

The cast test blocks used are 12 kg ingots made by vacuum induction melting. Test blocks and location of test specimens are presented in Figure 2.

**Hydrogen absorption of type 347 weld metals**

It is well known that the degree of hydrogen embrittlement is closely related to hydrogen content in the steel. Consequently, prior to the mechanical testing of hydrogenated weld metals, the effects of temperature and partial pressure of hydrogen gas, and their relation is given as the following equation.

Results are shown in Figure 3 and 4. According to Sievert's law, hydrogen absorption or solubility in metals is dependent on the temperature and partial pressure of hydrogen gas, and their relation in given as the following equation.

$$[H] = K \sqrt{PH_2} \exp (- Q / 2RT) \tag{1}$$

- where, [H] : Absorbed hydrogen ppm
- PH<sub>2</sub> : Hydrogen partial pressure
- Q : Heat of solution

It is clear in Figure 3 and 4, hydrogen absorption in type 347 weld metals is also in good agreement with Sievert's law, that is absorbed hydrogen content is strongly affected by hydrogen pressure and temperature. But effect of delta ferrite content, up to 12%, on hydrogen absorption of type 347 weld metals is not so clear.

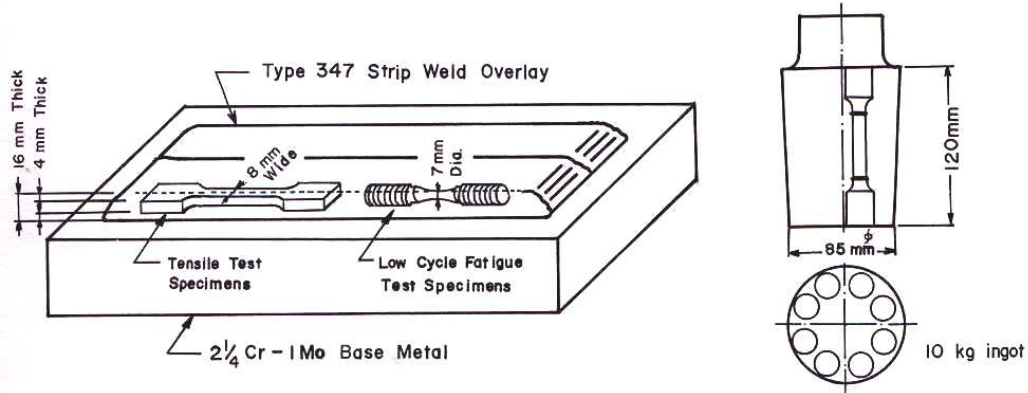


Figure 2. Location of specimens

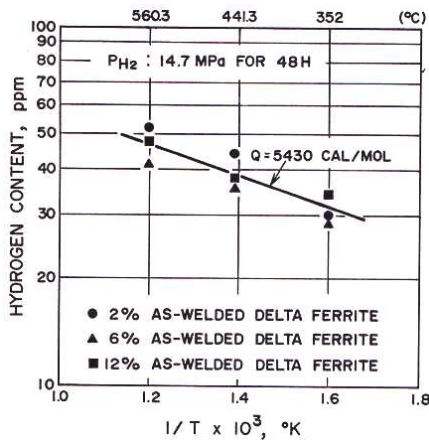


Figure 3. Effect of temperature hydrogen absorption by Type 347 weld metal

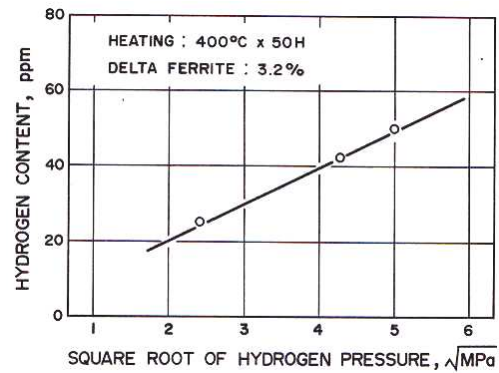


Figure 4. Effect of pressure on hydrogen absorption by Type 347 weld metal

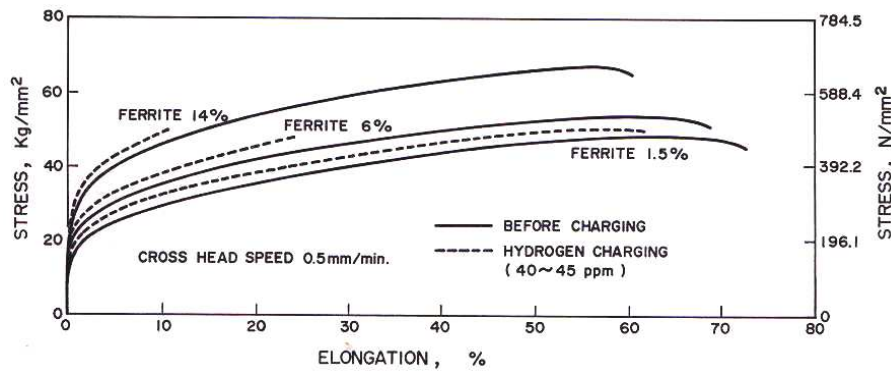


Figure 5. Stress-strain curves of Type 347 castings with different delta ferrite

*Analysis of tensile test on hydrogen charged stainless steels:*

**Stress-strain curves of type 347 steel.** Figure 5 shows stress-strain curves of type 347 castings with different delta ferrite content before and after hydrogen charging. Type 347 castings are embrittled by absorption of 42 to 47 ppm hydrogen. Degree of hydrogen embrittlement in

type 347 casting depends on delta ferrite content. After hydrogen absorption, the yield strength of type 347 casting is higher than that of hydrogen free casting.

**Loss in tensile ductility of the austenitic steels by hydrogen absorption.** The effect of hydrogen content on the tensile ductility was tested on type 347 weld

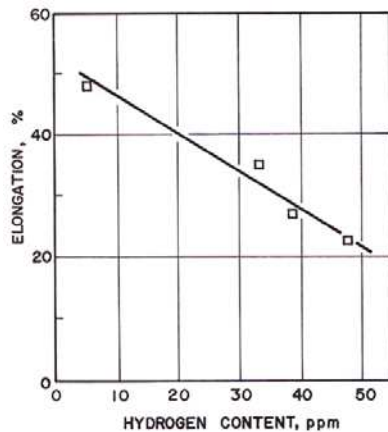


Figure 6. Effect of hydrogen content ductility of a type 347 weld metal; As-weld with 13% delta ferrite

metal specimens. The as-weld metal with 12% delta ferrite was charged with hydrogen under a pressure of 14.7 MPa for 48 h at temperatures between 355 to 555°C. The result obtained is shown in Figure 6, and it was found that the elongation decreased linearly with increase of hydrogen content.

In These experiments, weld metal showed about 22% loss of ductility due to 39 to 59 ppm hydrogen. The forging seems to be less sensitive and the casting to be more sensitive than the weld metal.

### 3. Results and Discussion

**Possible mechanism for the cracking in type 347 weld metals.** From the above results, it is recognized that type 347 weld metals which absorbs high amount of hydrogen show remarkable embrittlement which was associated with delta ferrite and sigma phase in austenitic matrix. However, even at high amount of hydrogen absorption type 347 weld metals still have remained several percent of ductility, and it is difficult to crack them by only single tensile loading [3]. So, possibility of stress corrosion cracking, hydrogen delayed failure and low cycle fatigue cracking has been studied.

**Stress corrosion cracking and Hydrogen delayed failure.** A careful study revealed no evidence of stress corrosion cracking in the weld overlay or surrounding material. Notched tensile specimens were tested under sustained load at room temperature to determine delayed cracking characteristics. Type 347 weld metal with 50 ppm hydrogen showed no signs of the delayed cracking even though at high applied stress.

**Cracking by low cycle fatigue.** The low cycle fatigue behavior of a type 347 weld metal with 15% as-welded ferrite was also investigated. Pour glass shaped

specimens with 7 mm minimum diameter were taken from the overlaid weld metal as shown in Figure 2. With diametral strain controlled, zero-tension low cycle fatigue tests were conducted with frequencies of 5 to 10 cycles per minute.

The relationship between plastic strain range ( $\Delta\epsilon_p$ ) and the number of cycles to failure (N) was obtained equation (2).

$$\Delta\epsilon_p \cdot N^\alpha = a \cdot \epsilon_f \dots\dots\dots (2)$$

- where,
- $\Delta\epsilon_p$  : Plastic strain range
  - N : Number of cycles to failure
  - $\alpha, a$  : Constants
  - $\epsilon_f$  : True fracture ductility  
 $= \epsilon_n \cdot 100 / 100 - RA$   
 RA : Reduction of areas %

The constants  $\alpha$  and  $a$  differ for as-welded and post-weld heat treated samples. For as-welded,  $\alpha$  and  $a$  are 0.405 and 0.755 respectively; for post-weld heat treated, they are 0.530 and 0.693 respectively.

The initiation of fatigue cracks was investigated using polished flat specimens (Figure 2). Microscopic observation revealed that minute cracks formed after only a few cycles at stresses lower than the yield strength. A specimen taken from type 347 weld metal with 15% as-welded ferrite, heat treated and hydrogen charged was stressed repeatedly from 0 to 0.92 times the yield strength. The crack was found in a sigma rich area and outlined the sigma phase. It appears cracking occurs when the sigma phase separates from the gamma matrix.

**Preventive measure for the cracking.** It is recognized from Equation (2) that a small strain range and large tensile ductility are desirable for improved life (N). Strain range can be kept low by decreasing thermal stress levels and avoiding stress concentrates. Internals made of a Cr-Mo steel and weld overlaid by stainless steel (instead of solid stainless steel internals) can reduce thermal stress [4]. The corner radius on internal attachments should be smooth and as large as possible to minimize stress concentration. Internals attached to the reactor wall should be designed to allow easy access for welding in order to minimize weld defects. Crack arrest at the boundary between the type 309 and type 347 suggests that a lighter construction should be always considered in designing internal attachments

Reduced as-welded ferrite contents favor improved tensile ductility in the hydrogen charged type 347 weld metal [5-6]. However, some ferrite is required to prevent hot cracking during solidification of the weld metal. In practical applications a range of 3 to 7% as-welded ferrite is desirable.

Sigmatization of as-welded delta ferrite by post-weld heat treatment significantly decreases the tensile ductility of a type 347 weld metal. Elimination of such a heat treatment may be beneficial when it does not result in a harmful hardened base metal.

#### 4. Conclusion

In type 347 stainless steel weldments which attached internals on the wall of a direct desulfurization reactor, cracks were found after its high temperature, high pressure hydrogen service.

Preliminary investigation revealed sever loss of tensile ductility of a type 347 stainless steel weld metal due to presence of sigma phase and hydrogen absorption.

Through various studies carried out, the following results are obtained: (1) Low cycle fatigue type cracking associated with loss of tensile ductility due to sigma and hydrogen is considered as a possible cause of the cracking; (2) In order to prevent the cracking, control of the amount of sigma phase in type 347 weld metals and decrease of the strain amplitude imposed to the internal attachment weldments are suggested.

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