

Stress-induced hydrogen movement and the partial molal volume of hydrogen in AISI 4340 steel

S. M. TOY

Interscience Laboratory, 4190 Manuela Avenue, Palo Alto, CA 94306

Stress-induced movement of hydrogen to the high tensile region in AISI 4340 steel was measured at room temperature and 202 °C. A neodymium hydrogen detection method was used to determine the location and concentration of hydrogen. The AISI 4340 stress rings with local hydrogen content up to 0.69 ppm and loaded to $16.87 \times 10^3 \text{ kg cm}^{-2}$ did not fail, whereas a stress ring with 0.73 ppm did fail for the test condition cited. The predicted hydrogen concentration versus fracture time curves at constant tensile stress indicated a good agreement with the stress ring test data.

The partial molal volume of hydrogen, \bar{v}_H , was calculated to be 2.47 cm^3 per g-atom for AISI 4340 steel, which was greater than the reported value for alpha iron at 2.0 cm^3 per g-atom. Knowing the value \bar{v}_H and the hydrogen content for equation $RT \ln C_\sigma / C_0 = \bar{v}_H \sigma / 3$ the increase of hydrogen concentration by a given applied stress can be calculated. © 1999 Kluwer Academic Publishers

1. Introduction

Ultrahigh-strength structural martensitic steels are susceptible to hydrogen embrittlement. The influence of hydrogen on the ductility of the ultrahigh-strength steels depend not only on the concentration of hydrogen but also on its ability to diffuse under a concentration gradient or stress gradient. The objective of this study was to determine the stress-induced hydrogen movement in AISI 4340 by revealing the hydrogen location and concentration with the neodymium hydrogen detection method for metals [1–3].

The partial molal volume of hydrogen is one parameter that describes the elastic interaction between the solute and the stress fields about inclusions, dislocations, and cracks. The partial molal volume is important in the elucidation of phenomena such as hydrogen embrittlement and hydrogen yield point. A knowledge of this quantity has been measured for AISI 4340 steel. The hydrogen concentration in the steel alloy was determined by neodymium hydrogen detection method described by Toy [4].

The method used to investigate hydrogen embrittlement of AISI 4340 high-strength aircraft steels during manufacturing was to perform hydrogen embrittlement stress ring tests. Hydrogen evolution and partial molal volume, \bar{v}_H , of AISI 4340 were determined from these steel rings and compared with the permeation test data reported in the literature (Table I). These investigations indicated that stress did not influence the diffusion coefficient, but it increased the hydrogen concentration in the lattice. A similar effect was observed by Beck *et al.* [5].

2. Douglas hydrogen embrittlement stress ring

The stress ring was prepared from a 6.985-cm piece of ladle vacuum degreased annealed CFE-4340 condition C-4 Mil S5000C, Republic Steel Heat No. 8070801. The round bar stock met Douglas material specification (DMS) 1830. The chemical analysis is given in Table II. The Douglas hydrogen embrittlement stress ring was prepared according to Fig. 1 and heat treated to $16.87 \times 10^3 \text{ kg-cm}^{-2} / 19.68 \times 10^3 \text{ kg-cm}^{-2}$ ($260 \times 10^3 \text{ PSI} / 280 \times 10^3 \text{ PSI}$ or $260 \text{ KSI} / 280 \text{ KSI}$ according to Douglas process specification [DPS] 5.00).

The stress ring was polished on one end, where the face would be under maximum stress, and then loaded to $16.87 \times 10^3 \text{ kg-cm}^{-2}$ (240 KSI) using a cadmium-plated mild steel spacer 6.414 cm in length. A deflection of 0.508 cm produces $16.87 \times 10^3 \text{ kg-cm}^{-2}$ (240 KSI) according to strain gauge measurement [6]. The stress ring was then placed in a metal evaporator to deposit neodymium on its polished face. The stress ring was removed. The coated polished face was covered with an aluminium foil to protect the surface. An aluminium-backed, high-temperature, pressure-sensitive adhesive tape was used to seal the area. A flexible hydrogen detection tape conceived and developed by the author at Douglas was placed on the opposite end of the stress ring (Fig. 1).

Zinc chromate putty was used to form a containment dam on the top of the stress ring, where the stress was the least. The dam prevented any acid from running down the stress ring. Several drops of 50% sulfuric acid solution were placed inside the dam area (Fig. 2).

TABLE I Partial molal volumes of hydrogen in various metals*

| | | | |
|---------|------|----------|-----|
| Pd | 1.73 | Ta | 9.4 |
| Beta-Ti | 4.1 | Alpha-Fe | 2.0 |
| Beta-Zr | 5.3 | Nb | 4.5 |

* Calculated from data in "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958-1965) * \bar{v}_H (cm³ per g-atom_H) in host lattice of metals.

TABLE II Chemical analyses of elements (wt %)

| | | | |
|----|-------|----|------|
| C | 0.400 | Si | 0.25 |
| Mn | 0.78 | Cr | 0.84 |
| P | 0.011 | Ni | 1.70 |
| S | 0.011 | Mo | 0.22 |

3. Nomenclature and calculation of partial molal volume of hydrogen \bar{v}_H

Nomenclature designates "A_s" as the reaction site area (cm²), "B" as normal mobility (g-sec-atom_H/cm-dyne), "C" as hydrogen concentration (g-atom_H/cm³-atom_{Fe}), "C₀" as hydrogen concentration under a hydrostatic condition ($\sigma_h = 0$), "C_σ" as hydrogen concentration under hydrostatic condition (σ_h), "D" as normal diffusivity (cm²/sec) (diffusion coefficient of hydrogen in alpha iron at 201.7°C, $D = 6.75 \times 10^5$ cm²-sec), "J" as flux of solute (g/cm²-sec), "J_C" as $J_T - J_\sigma$, "J_H" as flux of hydrogen, "J_σ" as $J_T - J_C$, "J_T" as total flux, $J_C + J_\sigma$, "K" as Boltzman constant (dyne-cm²/°F), "ρ" as density of specimen (g/cm³), "σ_h" as hydrostatic component, 1/3 applied stress (dyne/cm²), "σ_H" as hydrostatic component, 1/3($\sigma_{xx} + \sigma_{yy} + \sigma_{zz}$), "t" as time (sec), "T" as neodymium film thickness (cm), "U" as chemical potential (cm²-dyne/g-atom_H), "Grad U" as gradient chemical potential, "U_H" as chemical potential of hydrogen, "U⁰" as chemical potential of dissolved hydrogen at zero stress, " \bar{v}_H " as partial molal volume of hydrogen (cm³/g-atom_H), "ΔX" as point distance

where triaxial stress is located beneath the metal surface (cm), and "X_L" as diffusion length (cm).

An elastic tensile stress decreases as the elastic compressive stress increases the chemical potential of the interstitial solute. In this case hydrogen was introduced as the solute. If the stress yield has a non-vanishing hydrostatic component, $\sigma_H = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, where they are the principle stresses and if the lattice is elastically isotropic, the dissolved hydrogen expands the lattice equally in all directions. The equation for chemical equilibrium in accord to Oriani [7] may be simplified to

$$RT \ln \frac{C_\sigma}{C_0} = \frac{1}{3} \bar{v}_H \sigma,$$

where C_σ is the hydrogen concentration at a point at which the stress system has a hydrostatic component σ_h . C₀ is the component and is the hydrogen concentration under condition of $\sigma_h = 0$.

For the chemical potential of hydrogen in an elastic stress field the hydrostatic component is

$$U = U^0 - \bar{v}_H \sigma_H,$$

where U⁰ is the chemical potential of dissolved hydrogen at zero stress. Both U and U⁰ refer to the same hydrogen concentration, since grad U is the fundamental driving force for diffusion. The flux of solute is

$$J = -BC \text{ grad } U = -D \text{ grad } U + \frac{DU}{RT} \bar{v}_H \text{ grad } \sigma_H,$$

where B and D are normal mobility and diffusivity, respectively, and where we assume that U and C are related through a composition independent coefficient.

$$J_T = J_C + J_\sigma,$$

where J_T is the total flux.

$$J_T = -\frac{D \Delta C}{\Delta X}$$

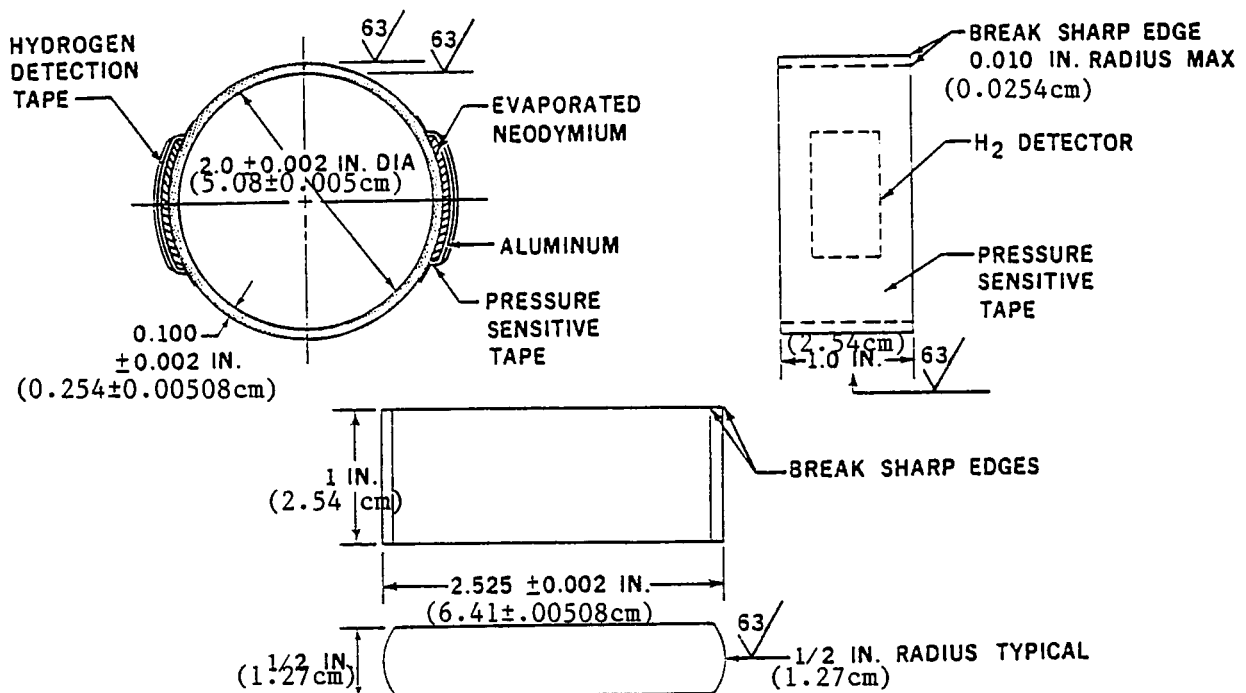


Figure 1 Hydrogen embrittlement ring.

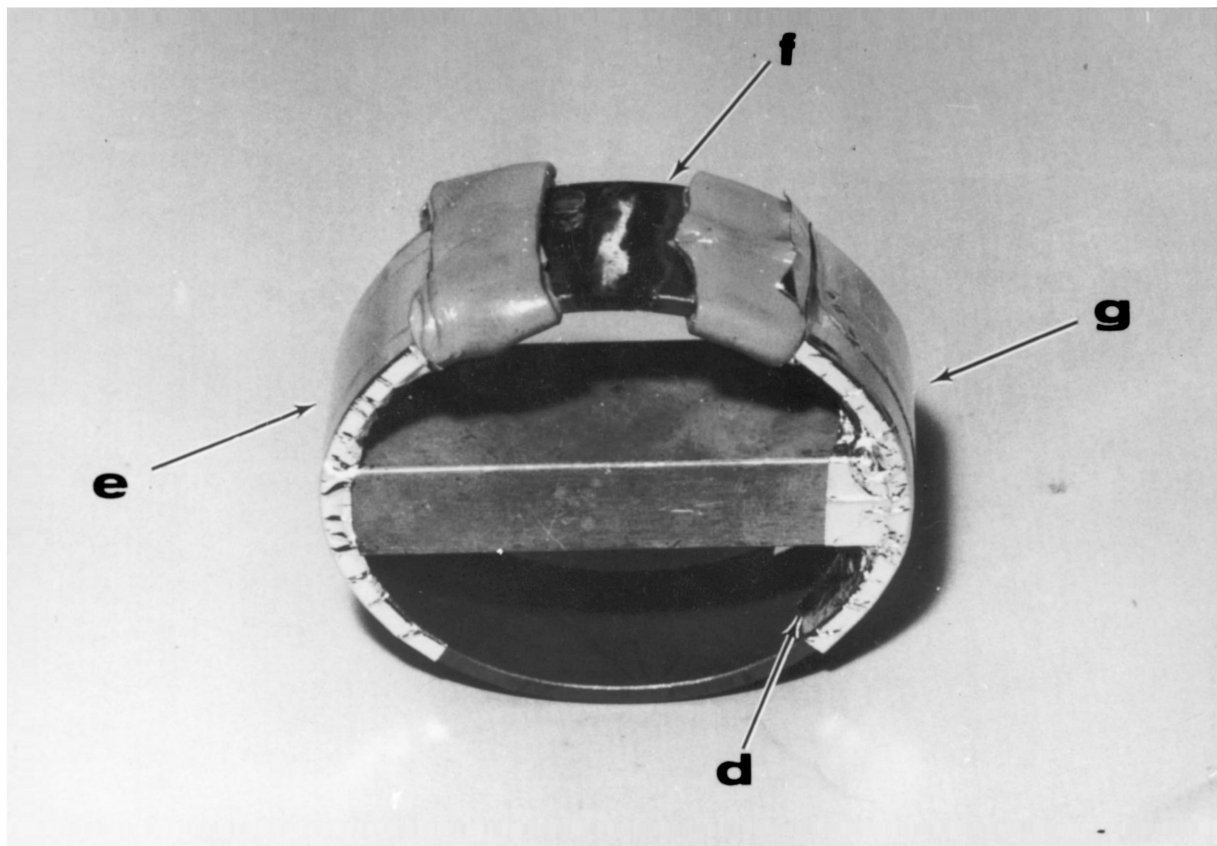


Figure 2 Stressed hydrogen embrittlement ring. (f) Sulfuric acid, (g) direct evaporation of neodymium, (e) flexible hydrogen tape, (d) alternate location to deposit acid.

$$J_{\sigma} = \frac{DC}{Rt} \bar{v}_H \frac{\Delta\sigma}{\Delta X}$$

If one determines $J_T = J_C + J_{\sigma}$ and $J_C = J$, then J_{σ} can be calculated.

4. Experimental data on AISI 4340 steel and calculations

The AISI 4340 hydrogen embrittlement stress rings were all loaded to $16.87 \times 10^3 \text{ kg-cm}^{-2}$ (240 KSI).

Stress ring No. 3 was baked at 201.7°C for 24 h. After the sample was cold, the flexible hydrogen detection tape was removed. Examination of the tape at magnification $7\times$ and $100\times$ indicated the hydrogen had diffused to the area of maximum stress (Figs 3 and 4). The stress ring did not fail and local hydrogen content was determined to be 0.42 ppm where the hydrogen had segregated (Fig. 4).

Stress ring No. 2 was held at room temperature for 2 days without failure. Examination of the directly evaporated neodymium-coated and polished face revealed microcracks that had formed in the neodymium film. The hydrogen position (cracked face) is indicated by many fine lines of neodymium dihydride reaction sites receding in number away from the crack (Figs 5 and 6).

The surface of stress ring No. 1 was not polished and had neodymium evaporated on it. This stress ring was baked out at 148.9°C for 12 h and then held at room temperature for an additional 16.5 h. No failure

occurred in this test. The very rough surface made it difficult to resolve the neodymium dihydride reaction sites optically and to interpret the results (Fig. 7).

Stress ring No. 3 failed at room temperature over the weekend. Using a reasonable average time-to-failure of 24 h, the local hydrogen content of this stress ring No. 3 was determined to be 0.73 ppm. This stress ring surface was also rough, but scanning electron micrograph of the neodymium-coated surface revealed the neodymium dihydride reaction sites and the surface roughness (Fig. 8).

4.1. Sample calculation of hydrogen content

Let the diffusion coefficient D equal $3.2 \times 10^{-7} \text{ cm}^2/\text{s}$ at room temperature. The neodymium film thickness T equals 102.6 nm. Then the diffusion length X_L is

$$X_L = (Dt)^{1/2},$$

where t is time in seconds. For 24 h

$$X_L = (3.2 \times 10^{-7} \times 24 \times 3600)^{1/2} = 0.166 \text{ cm}$$

From the scanning electron micrograph photoprint the diameter of the neodymium dihydride reaction site, d , is determined to be $6.26 \times 10^{-5} \text{ cm}$, so the reaction area $A = 3.03 \times 10^{-9} \text{ cm}^2$. The weight of iron, W_{Fe} , is

$$\begin{aligned} W_{\text{Fe}} &= \rho X_L A_s \\ &= (7.87)(0.116)(3.03 \times 10^{-9}) = 3.95 \times 10^{-9} \text{ g} \end{aligned}$$

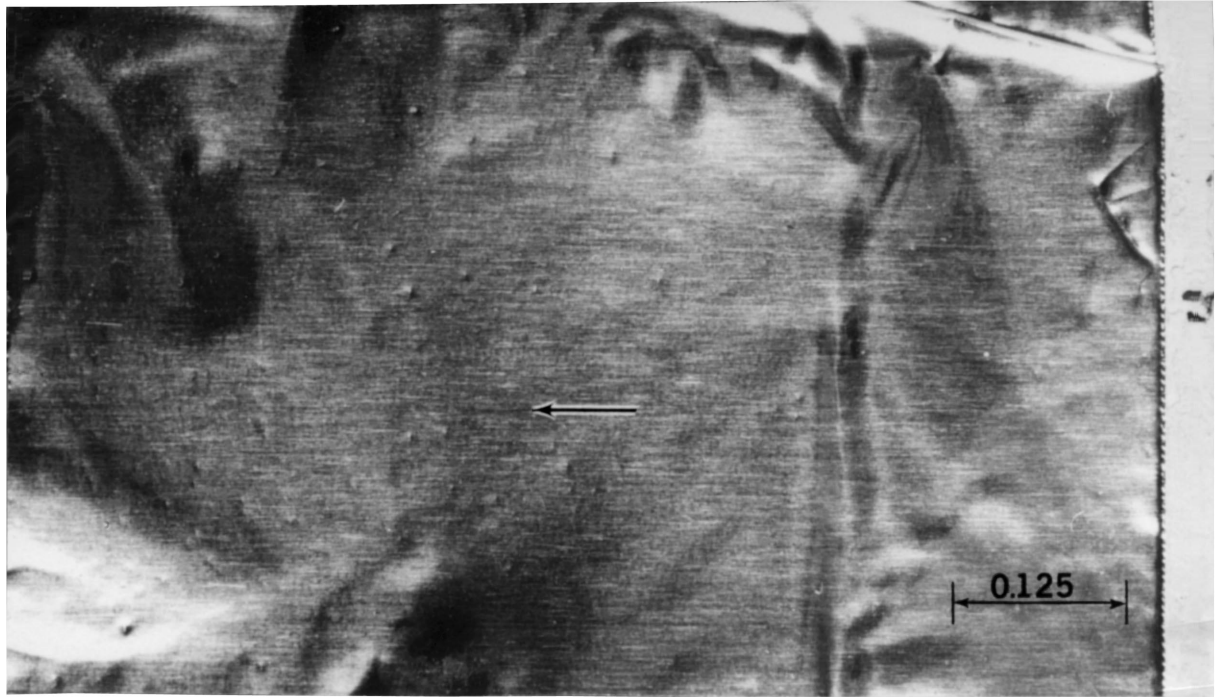


Figure 3 Stress ring No. 3, low magnification. Baked at 201.7°C for 24 hours. At the hydrogen detection tape removed from the ring, arrow points to the hydrogen segregation.

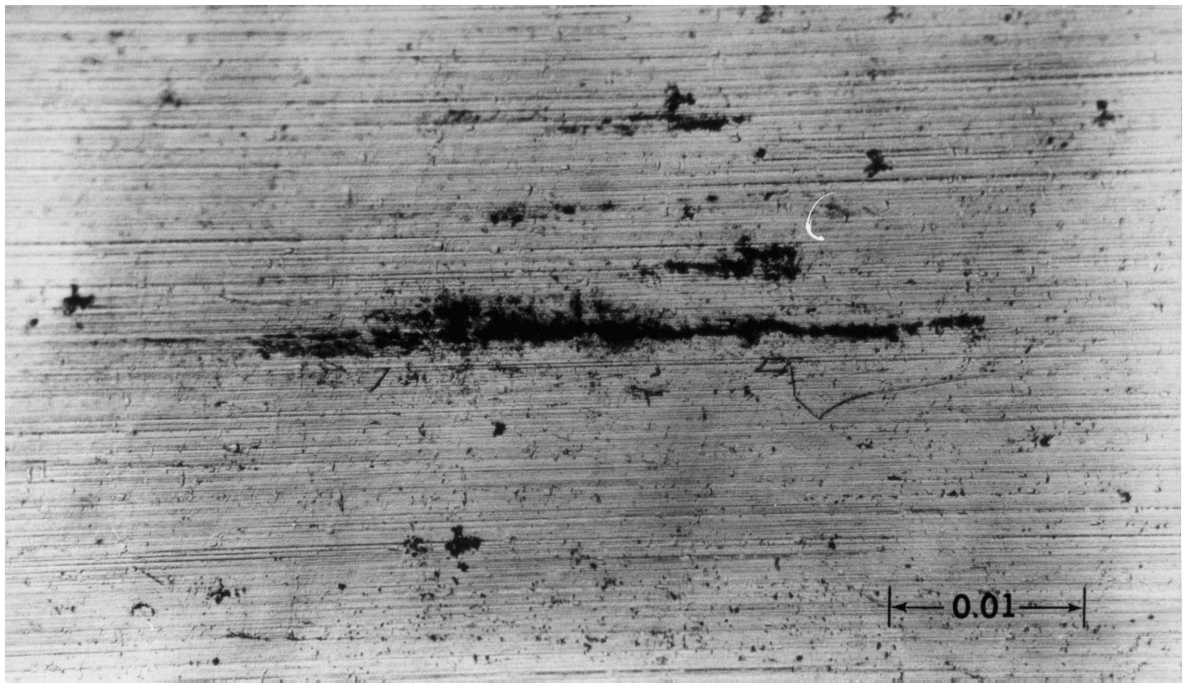


Figure 4 Stress ring No. 3, high magnification. Hydrogen segregation at maximum tensile stress area, hydrogen content is 0.42 ppm and no failure.

The weight of neodymium, W_{Nd} , is

$$\begin{aligned}
 W_{Nd} &= \rho T A_s \\
 &= (6.8)(1.026 \times 10^{-5})(3.03 \times 10^{-9}) \\
 &= 2.12 \times 10^{-13} \text{ g}
 \end{aligned}$$

The weight of hydrogen, W_H , is

$$W_H = W_{Nd} \frac{M_W(H)}{M_W(Nd)}$$

$$= 2.12 \times 10^{-13} \frac{(2)}{(144.2)} = 2.86 \times 10^{-15} \text{ g}$$

Hydrogen content in ppm

$$= \frac{W_H}{W_{Fe}} \times 10^6$$

$$= \frac{2.68 \times 10^{-15} \times 10^6}{3.95 \times 10^{-9}} = 0.73$$

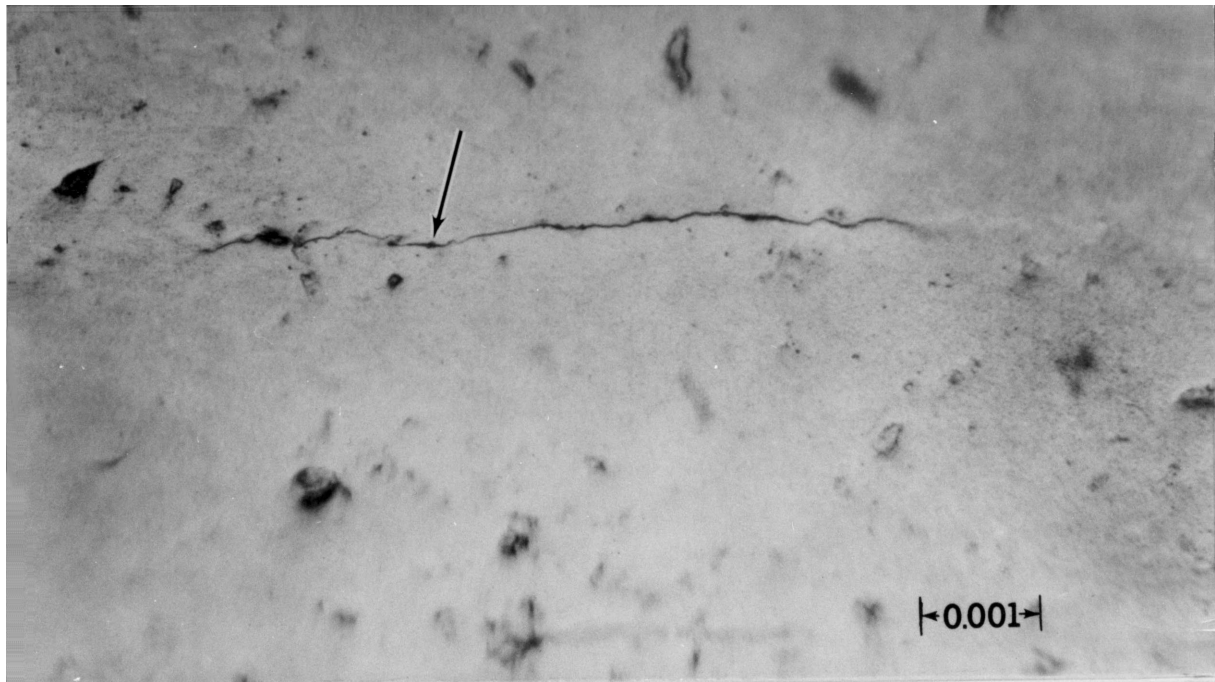


Figure 5 Stress ring No. 2. Hydrogen content is 0.69 ppm at crack in the neodymium film, after 2 days at room temperature.

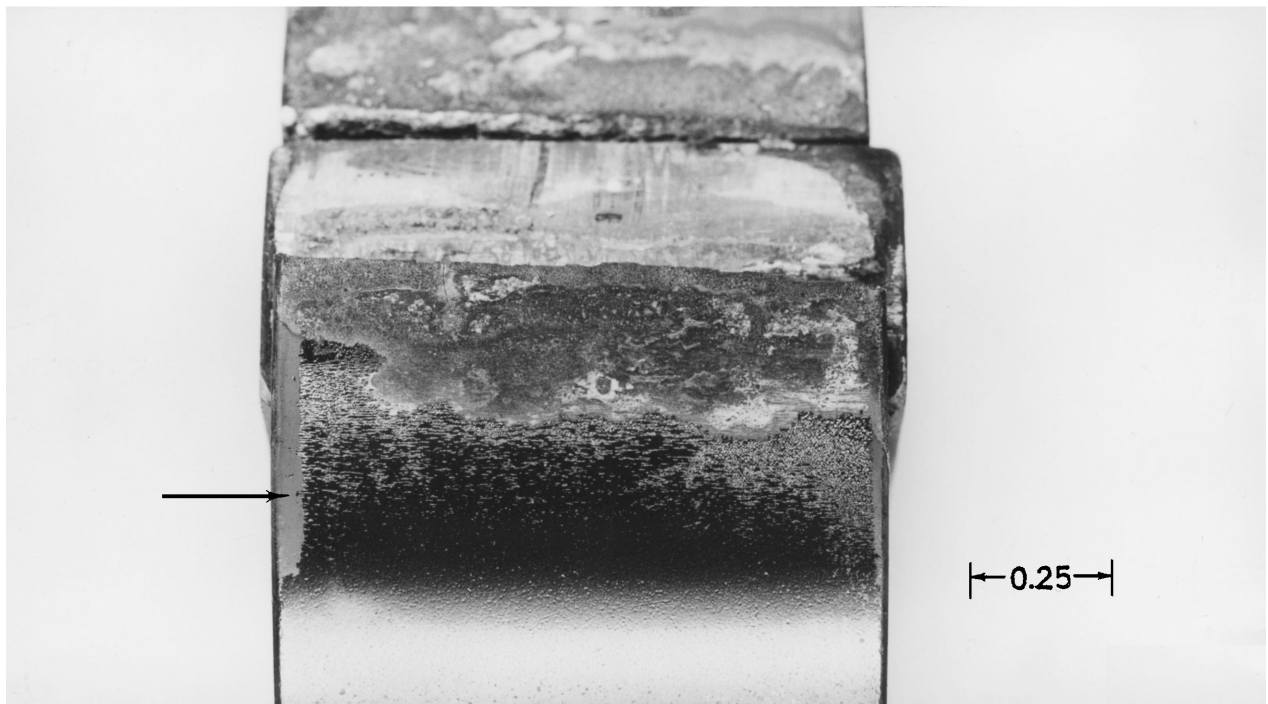


Figure 6 Stress ring No. 2 test continued. Cracked within 16 hours after placing acid on the compression side of the ring at maximum stress.

4.2. AISI 4340 results and discussion and calculation of its partial molal volume

Direct evidence of stress-induced hydrogen movement at room temperature and at 201.7°C during hydrogen bakeout was revealed by neodymium hydrogen detection methods developed and applied on the hydrogen embrittlement stress rings. Observation of microcracks in the neodymium coat on stress ring No. 2 with 0.69 ppm hydrogen, before actual mechanical rupture, suggests the direction of a possible beginning of stress corrosion damage. Toy and Phillips [2] reported that microcracks formed in the neodymium-coated (250 grade) 18 nickel maraging steel weldment specimen

can reveal the stress corrosion-susceptible microstructural features located beneath them in the steel. A comparison of the predicted hydrogen concentration versus fracture time survey at constant tensile stress with the stress ring test data indicates a good agreement (Fig. 9). These curves were derived by combining Troiano notch tensile test data [8] on AISI 4340 steel with the author's hydrogen evolution test data on cadmium-plated 300 M (DPS 9.28 baked at 201.7°C ± 8.3°C) in an evacuated glass reactor tube (Figs 10 and 11).

The determination of the local hydrogen content at these stress-induced hydrogen sinks can form the basis for predicting future service life of AISI 4340 parts.

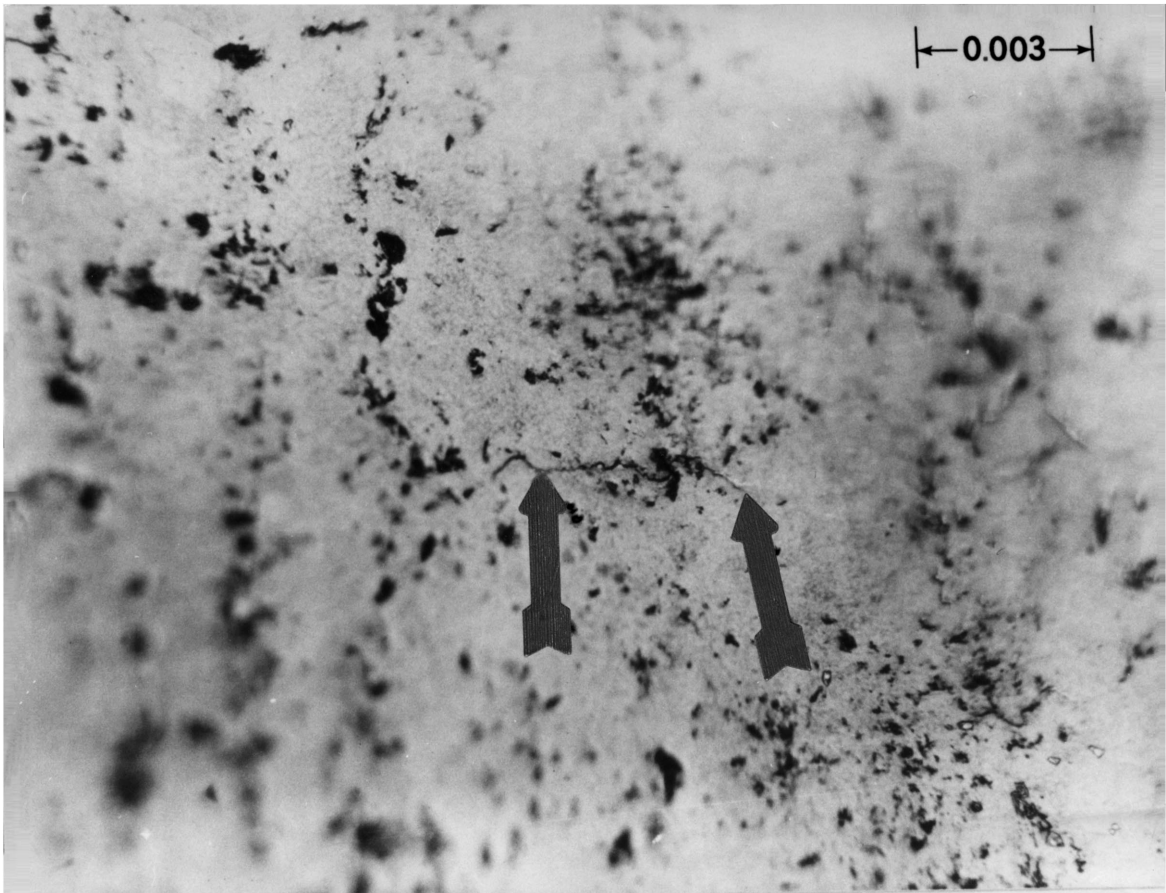


Figure 7 AISI 4340 steel ring No. 1. Hydrogen introduced by acid source, baked out at 148.89°C for 12 hours and held for 16-1/2 hours at room temperature has no failure with small cracks in the neodymium film.

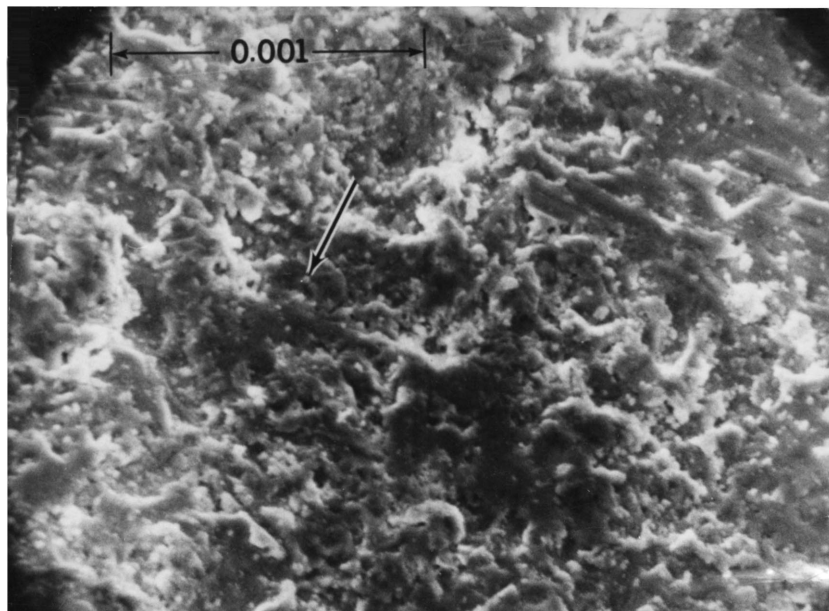


Figure 8 Neodymium coated hydrogen embrittlement stress ring No. 3. AISI 4340 steel failed at room temperature in less than 2-1/2 days. Hydrogen content is 0.73 ppm.

By comparing the maximum hydrogen content, C_m , determined for catastrophic failure from Fig. 9 and the determined AISI 4340 test media rate of hydrogen accumulation, $\Delta C/\Delta t$, one can calculate the time-to-failure for a given stress by dividing $(C_m - C_i)$ by $(\Delta C/\Delta t)$, where C_i is the initial hydrogen content before exposure to the corrosion test media.

The experimental data on hydrogen evolution from AISI 4340 steel at $18.28 \times 10^3 \text{ kg-cm}^{-2}$ to $19.68 \times 10^3 \text{ kg-cm}^{-2}$ (260–280 KSI) under no stress and an applied tensile strength of $9.14 \times 10^3 \text{ kg-cm}^{-2}$ (130 KSI) at 201.7°C give $J_T = 3.2 \times 10^{-7} \text{ g/cm}^2\text{-s}$ and $1.09 \times 10^{-10} \text{ g/cm}^2\text{-s}$ at $t=0$; therefore, $J = 2.7 \times 10^{-11} \text{ g/cm}^2\text{-s}$ (Fig. 12).

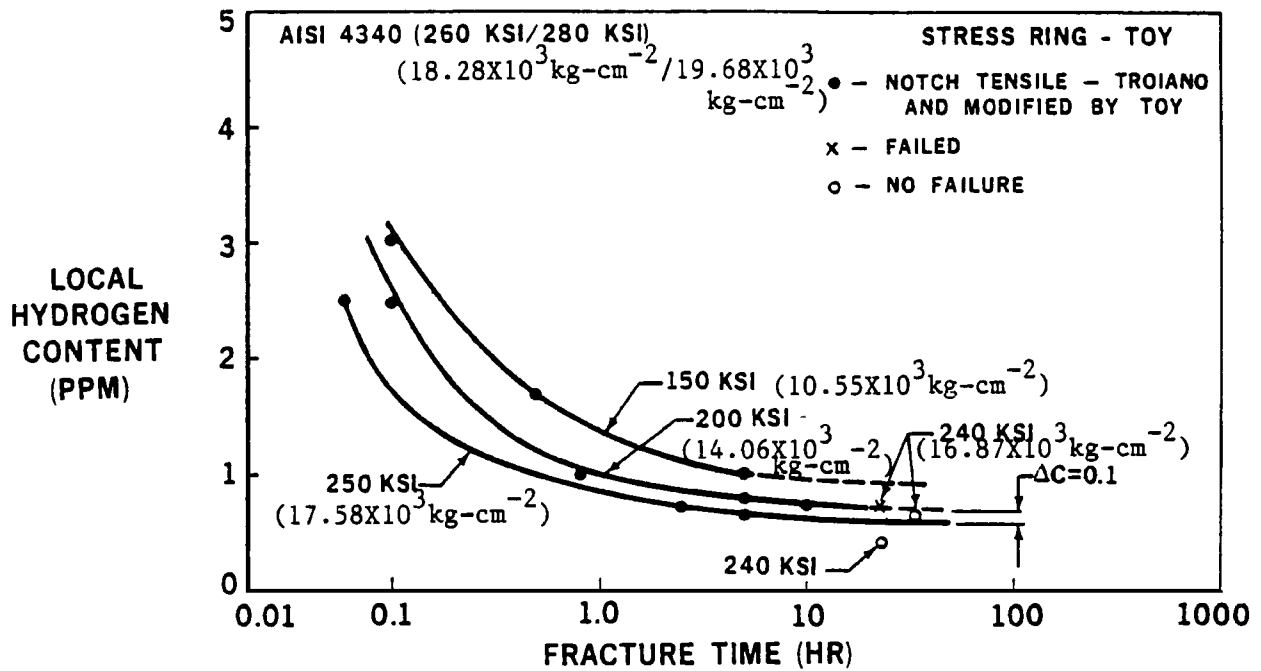


Figure 9 Predicted hydrogen concentration versus fracture time at constant tensile stress.

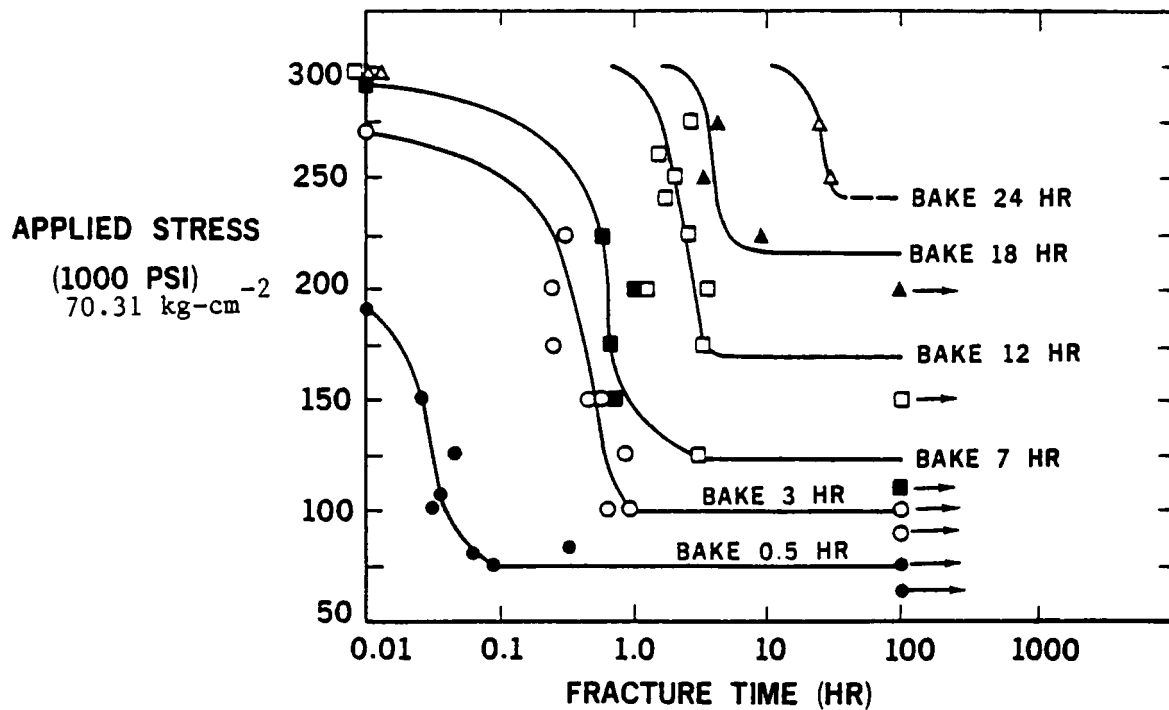


Figure 10 Static hydrogen curves for AISI 4340 steel. Hydrogen concentration varies with different baking times at 201.67°C on sharply notched specimens at 230,000 PSI strength level. ($16.17 \times 10^3 \text{ kg-cm}^{-2}$)

Since $\bar{v}_H = J_\sigma \cdot KT \times \frac{\text{Avogadro's number}}{\sigma_H DC}$,

$= 2.98 \times 10^9 \text{ dynes per cm}$

Let $C = \text{hydrogen (ppm)} \cdot \text{Density}$

$\Delta X = 0.058 \text{ cm}$ point where triaxial stress is located beneath the metal surface

$= 0.41 \times 10^{-6} (7.88)$

$D = 6.75 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 201.7°C

$= 3.14 \times 10^{-6} \text{ g of hydrogen per cm}^3 \text{ of Fe}$

$K = \text{Boltzman constant, dyne-cm}/^\circ\text{F}$

$\sigma_H = 1/3 \text{ applied}$

$J_T = J_C + J_\sigma$

$\sigma_H = \frac{130000 \times 6.894 \times 10^{-4}}{3.0}$

$= -\frac{D\Delta C}{\Delta X} + \frac{DC}{RT} \bar{v}_H \frac{\Delta\sigma}{\Delta X}$

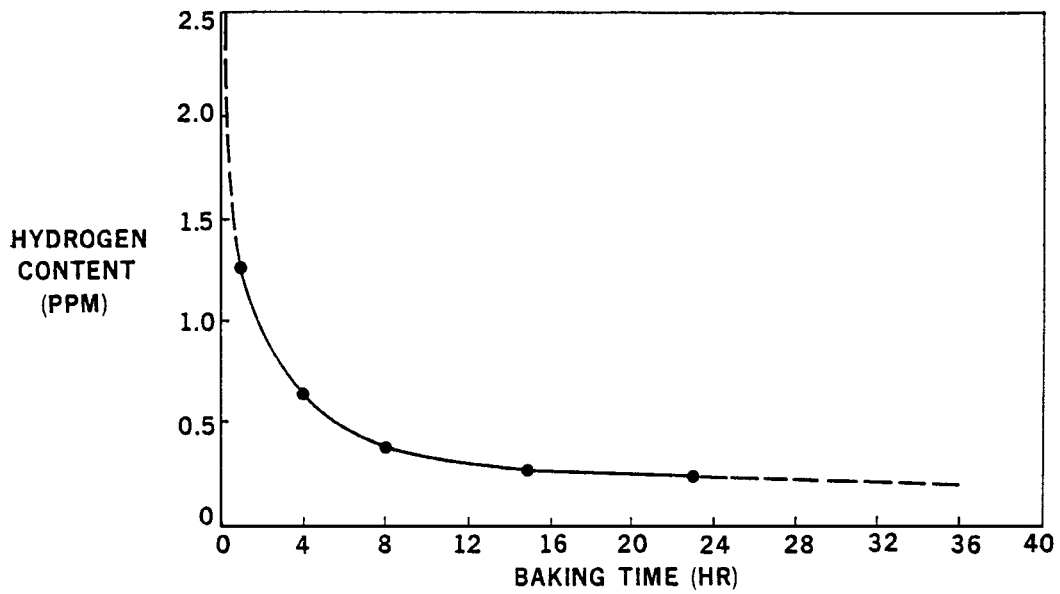


Figure 11 Hydrogen content versus baked-out for cadmium plated 300 M.

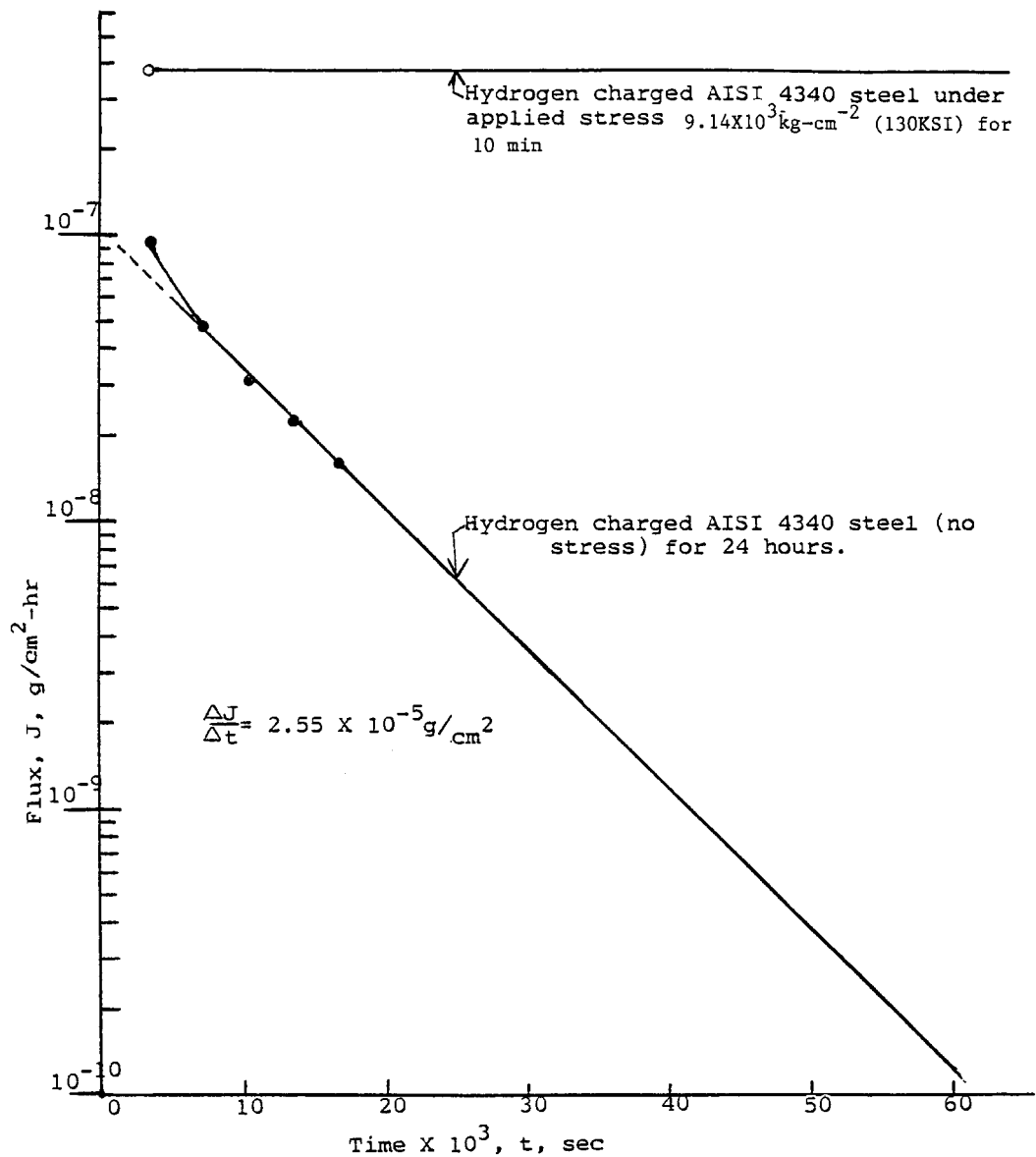


Figure 12 Flux versus time of AISI 4340 steel under no stress and applied stress of 130 KSI at 201.67°C. Hydrogen evolution was determined by hydrogen detection tape for one hour and the hydrogen charging solution was 5% NaCN and 5% NaOH at 10 amp per sq ft.

therefore, $3.8 \times 10 = 1 \times 10 + J_\sigma$

$$J_\sigma = 2.8 \times 10 = \frac{DC}{RT} \bar{v}_H \frac{\Delta\sigma}{\Delta X}$$

$$\bar{v}_H = (\text{Hydrogen in ppm} \times 1.11)(55.4)/100$$

$$= 0.41 \times 1.11 \times 55.4/100$$

$$= 2.47 \text{ cm}^3 \text{ per g-atom in alpha iron, where 1.11 is a conversion factor for hydrogen in ppm to cm}^3 \text{ of hydrogen per 100 g of Fe}$$

5. Summary

Direct evidence of stress-induced hydrogen movement in Douglas hydrogen embrittlement AISI 4340 steel stress rings was revealed at room temperature and at 201.7°C. The hydrogen segregation and hydrogen concentration in high tensile stress region were determined with the neodymium hydrogen detection method for metals conceived and developed by the author at Douglas. The AISI 4340 stress rings with a local hydrogen content up to 0.69 ppm and loaded to $16.87 \times 10^3 \text{ kg-cm}^{-2}$ (240 KSI) did not fail. A stress ring with 0.73 ppm did fail for the test condition cited, however. The bakeout of a stress ring loaded to $16.87 \times 10^3 \text{ kg-cm}^{-2}$ and baked at 201.7°C for 24 hours did not fail. Its local hydrogen content was determined to be 0.42 ppm. Observation of microcracks in the neodymium film directly evaporated on a stress ring No. 2 after a 72-h period at room temperature that did not fail. This result points to the detection of the beginning of the stress corrosion damage.

The predicted hydrogen concentration versus fracture time curves for a constant tensile stress were found to be in good agreement with the stress ring test data. By determining the local hydrogen content required to cause catastrophic failure and the rate of hydrogen con-

tent accumulation from the corrosive test media, it may eventually be possible to predict the service life of AISI 4340 or other steels at a given design load before exposure to the test media.

The partial molal volume of hydrogen, \bar{v}_H , was calculated to be 2.47 cm^3 per g-atom. The hydrogen evolution data were generated from stressed and non-stressed loaded rings. The \bar{v}_H number for martensitic steel was greater than values reported for alpha iron of 1.8 to 2.0 cm^3 per g-atom [7, 9]. Knowing the value and the hydrogen content for the equation $RT \ln C/C_0 = 1/3 \bar{v}_H$ the concentration of hydrogen increase by a given applied stress can be calculated.

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