EFFECTS OF HIGH-PRESSURE HYDROGEN ON STEELS

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INTRODUCTION

Hydrogen embrittlement of steels is hardly a new subject, but the effects of high-pressure hydrogen have been treated in detail only more recently and to a much more limited extent. Thus, most investigations of hydrogen embrittlement have been concerned with hydrogen in metals, while for the high-pressure hydrogen problem, we are more concerned with metals in (in contact with) hydrogen. I believe there is a difference and, certainly, different mechanisms of embrittlement are at least possible.

To help understand the possible differences in effects and because the thinking on the high-pressure hydrogen effects is influenced by the great amount of work on the effects of hydrogen in metals, I will first briefly discuss the hydrogen-in-metals embrittlement and then look at the effects of high-pressure hydrogen on steels and other metals. This should also help in evaluating the significance of the different kinds of investigations that have been performed.

We should note that hydrogen is a unique material. The hydrogen atom is the smallest; thus, it goes into metals interstitially and atomically. It diffuses relatively rapidly inside the metal and enters and leaves a metal readily at rather low temperatures.

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EMBRITTLEMENT BY HYDROGEN IN METAL

Hydrogen concentrations well under 1 part per million (ppm) have caused embrittlement of high-strength steels. Table 1 shows some methods of hydrogen absorption. High-temperature reactions between metals and H_2O and also H_2S and pickling solutions will produce atomic hydrogen that is absorbed into the metal, and have resulted in cracking of massive steel ingots.

TABLE 1. METHODS OF HYDROGEN ABSORPTION

- Chemical Reaction With Aqueous Solution

  $$H_2O + M \rightleftarrows MO + 2H$$

- Cathodic Reaction

  $$H^+ + 1\ e \rightleftarrows H$$

- Chemical Absorption Onto Metal Surfaces

  $$1/2\ H_2 \rightleftarrows \underline{H}\ (m)$$

  $$K_p = \frac{a\underline{H}}{(H_2)^{1/2}}$$

  or

  $$a\underline{H} = K_p\ (H_2)^{1/2}$$

  If $a\underline{H}$ is linear with concentration

  $$H_{concentration} = K'\ (H_2)^{1/2}\ \text{Sieverts Law}$$

A prime example of hydrogen embrittlement by cathodic reaction is the numerous failures of Cd-plated, high-strength steel parts with the hydrogen introduced during plating. High equivalent hydrogen pressures can be developed by electrochemical means. Most studies of hydrogen in metals have used electrolytic introduction of hydrogen, a few have used quenching from high temperature.

For the absorption of hydrogen from the gas, the hydrogen must react to atomic hydrogen at the surface, there is very little atomic hydrogen in hydrogen gas at normal temperatures.

Table 2 shows the different kinds of hydrogen absorbers among metals. There are various types of hydrogen embrittlement, and I am trying to eliminate those that are not pertinent to our main topic of embrittlement of steels in high-pressure hydrogen. Thus, no hydride is formed in iron as in titanium. Also, for ambient temperature storage, no high-temperature reactions, such as hydrogen with carbon in steels, occur that can produce methane at high pressures that can produce cracking. In alloy steels, hydrides of hydride-forming alloying elements could form.

TABLE 2. TYPES OF ABSORPTION

- Endothermic Absorption
  - ΔH is positive. Solubility increases with increasing temperature.
  - Characterized by low hydrogen solubility--generally no hydride phase
  - Examples: iron, nickel, chromium, molybdenum, and their alloys
- Exothermic Absorption
  - ΔH is negative. Solubility decreases with increasing temperature
  - Characterized by high hydrogen content. H/M atom ratio between 1 and 3 at room temperature
  - Examples: zirconium, titanium, uranium, vanadium, columbium, and tantalum

Now let us consider the nature and theories of embrittlement by hydrogen in iron alloys. The embrittlement of steel was first reported in 1926 by Pfeil. Since then, over 1500 papers have been published on the subject. Thus, hydrogen embrittlement of steel is now well investigated, if not well understood. There have been several, extensive, recent reviews (Ref. 1 through 5).

Embrittlement by hydrogen in steel can most easily be defined by effects that hydrogen produces on the mechanical properties of the steel. The embrittlement appears as a decreased tensile ductility (reduction in area) in a tensile test, a decrease in notch tensile strength, and as a delayed failure in a static loading test.

Embrittlement by hydrogen has the following general characteristics:

1. Hydrogen must be present in the metal. If the hydrogen is removed from hydrogenated specimen, the ductility returns.
2. Embrittlement is enhanced by slow strain rates and elevated temperatures (within limits). These variables normally affect embrittlement in the opposite manner. This strongly indicates that embrittlement is paced by hydrogen diffusion.
3. Hydrogen has no significant effect on yield strength or elastic properties.
4. Hardness is unaffected by hydrogen.
5. Fracture stress is lowered by hydrogen.
6. Ductility is reduced in proportion to hydrogen content of steel up to 5 ppm, above which ductility is at a constant low value.
7. Embrittlement occurs in temperature range from -100 to +100 C (-150 to +210 F) with maximum effect at or just below room temperature.
8. As shown in Fig. 1 (Ref. 6), the effect of hydrogen becomes more severe as the strength level of the steel increases.
9. Electron microscopy has shown that, as with most notched specimens, the crack nucleates below the surface in hydrogenated, notched, steel specimens.

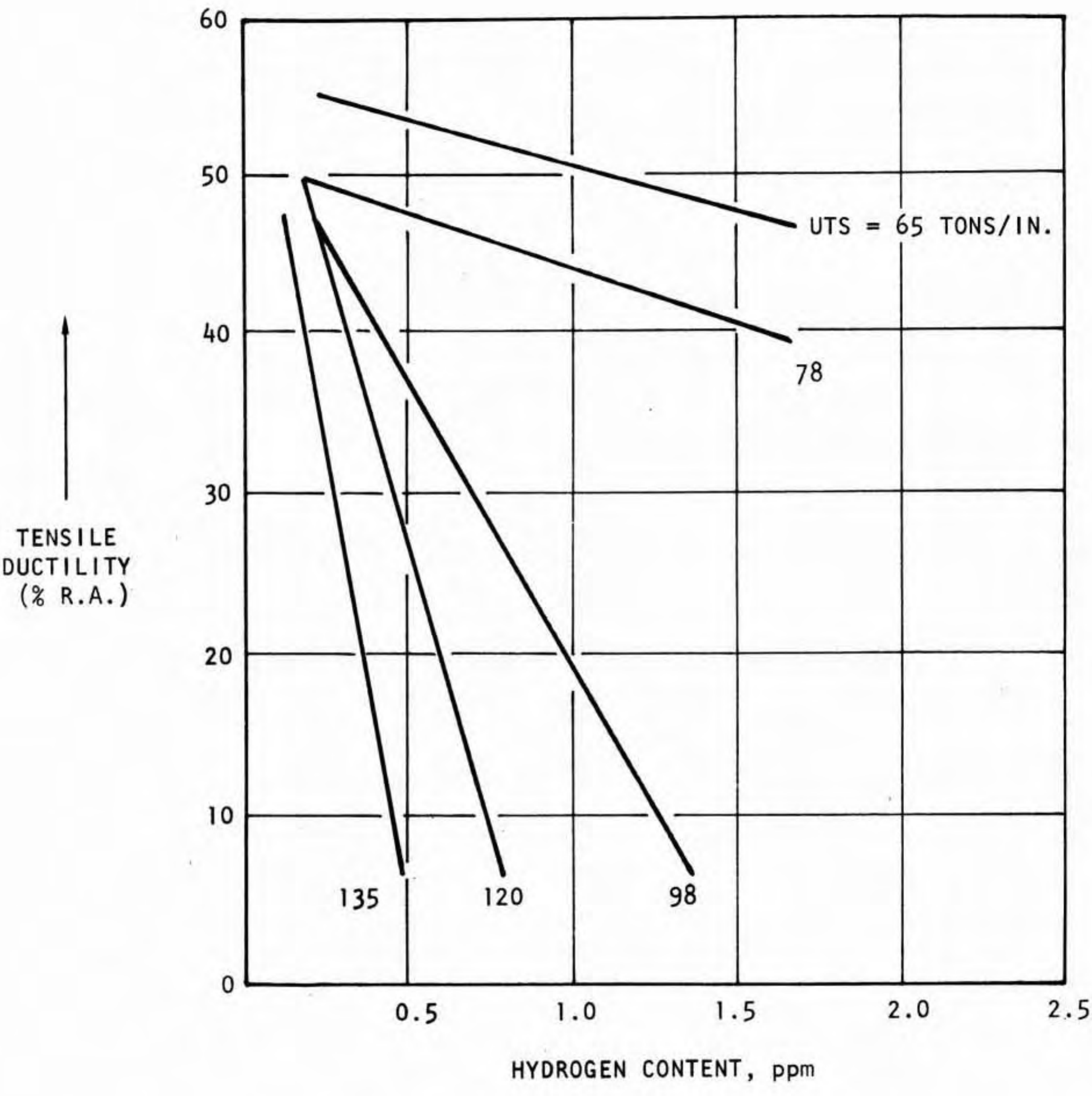


Figure 1. The Effect of Hydrogen Content on the Tensile Ductility of High Strength Steel

The nature of the delayed failure caused by hydrogen is shown in Fig. 2. The characteristics of this delayed failure are:

1. Notch tensile strength may be less than normal and directly reflects loss of ductility due to hydrogen.
2. Delayed failure may occur over wide range of applied stress.
3. There is only a slight dependence of time to failure upon applied stress.
4. There is a minimum critical stress value below which failure does not occur.
5. Notch strength, rupture time, and lower critical stress increase with decreasing hydrogen concentration.
6. Rupture and lower critical stress increase with decreasing crack severity. It is believed that there is no effect of crack severity per se but gives required critical stress for given hydrogen concentration.
7. Lower critical stress decreases as strength level of steel increases. The lower strength steel blunts the notch.

All brittle failure involve initiation and propagation of a crack. Electrical resistance measurements have been used (Ref. 1) to study crack initiation and growth of hydrogenated steels. Three stages were found:

Stage 1. Incubation Period--If the strain rate is so high that the specimen fractures in less time than the incubation period, then hydrogen embrittlement will not be detected, thus conventional tensile tests may not detect susceptibility to delayed failure. Incubation is strongly influenced by the hydrogen content but not by the applied stress. The temperature dependence of the incubation time indicates that the activation energy is the same as that for the diffusion of hydrogen.

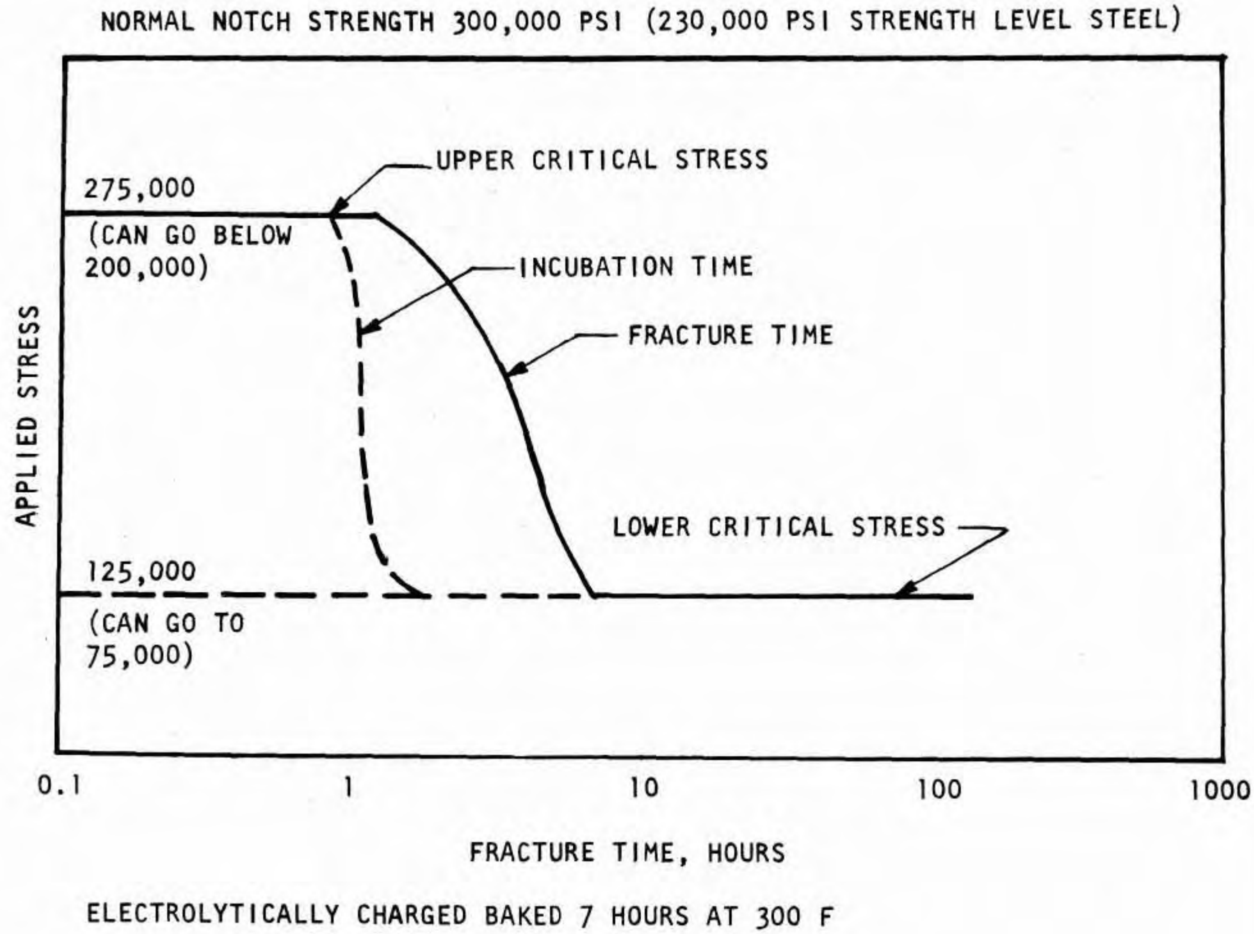


Figure 2. Delayed Failure in Steel

Stage 2. Slow Crack Growth--It appears that average hydrogen concentration is not sufficient to propagate crack, thus must wait for localized increased of hydrogen concentration in front of crack. Thus, slow crack growth is discontinuous--have series of crack initiations. Low-temperature resistance studies clearly showed stepwise crack growth.

Stage 3. Catastrophic Failure--When cross section is sufficiently reduced, the final, very brittle catastrophic failure occurs.

Although general agreement exists on the necessity for the segregation of hydrogen during deformation, there is considerable divergence of opinion on the mechanism of embrittlement. There is the "pressure theory" originally proposed by Zapffe (Ref. 7), subsequently modified by de Kazinsky (Ref. 8), Garofalo et al. (Ref. 9), Bilby and Hewitt (Ref. 10), and Tetelman and Robertson (Ref. 11 and 12). This theory proposes that hydrogen embrittlement results from the precipitation of hydrogen gas at defects such as inclusions, and the expansion of microcracks and voids due to the gas pressure.

In the spirit of the Griffith analysis of fracture, it has been suggested by Petch and Stables (Ref. 13) that hydrogen lowers the fracture stress via absorption on interior surfaces. Adsorption is presumed to lower the surface energy and therefore the fracture stress. This, then, would resemble liquid metal embrittlement.

Troiano et al. (Ref. 1) have suggested that hydrogen diffuses to regions of high triaxial stress, in front of a notch or crack, and then acts to reduce the cohesive strength of the metal lattice.

EFFECTS OF HIGH-PRESSURE HYDROGEN ON STEELS

Now, let us turn to the effects of high-pressure hydrogen on steels. First, let us look at some service failures.

FAILURES FROM HIGH-PRESSURE HYDROGEN

Service failures that have been attributed to high-pressure hydrogen have most often been failures of bourdon tubes. Bourdon tubes have been found to fragment within an hour or so of filling with hydrogen at pressures of 800 to 1000 atm (11,800 to 14,700 psi), Ref. 14. Failures have been reported (Ref. 15) after room temperatures exposure to hydrogen for times as short as 1 minute and at pressures as low as 2/3 full scale even though these gages were completely checked with oil and helium at full scale pressure.

Dodge (Ref. 16) reported that an intensifier which had been used repeatedly to pump oil at 4000 atm (58,800 psi) and several times to compress nitrogen to the same pressure, failed within minutes when used to compress hydrogen at not over 3000 atm (44,100 psi).

Several failures have been reported to occur when pressure vessels were pressurized with high-pressure hydrogen. Bridgman (Ref. 17) found that a Cr-V steel vessel used to contain hydrogen at 9000 atm (132,000 psi) developed submicroscopic fissures which later developed into cracks visible to the eye, although the vessel had previously withstood liquids at 25,000 atm (368,000 psi) pressure without damage.

Poulter (Ref. 18) reported that a 200-cu ft hydrogen cylinder, presumably with 2000 psi maximum pressure, failed after being in service 25 years. Examination of other hydrogen cylinders that had not failed showed small cracks extending from the inside surface to a depth of 25 percent of the wall thickness. Nitrogen vessels in service about the same length of time did not contain cracks.

Recently, failures occurred at Aerojet General Corporation in 1300-cu ft, 5000-psi hydrogen storage vessels. Aerojet General Corporation had seven vessels in service at 5000 psig, four containing hydrogen and three containing nitrogen. Four failures, all in 1-inch nozzles in hydrogen-containing vessels, occurred.

Some months ago a failure occurred at NASA-MTF (Mississippi Test Facility) of a large, 6000-psi rated vessel. The failure occurred during initial pressurization when the pressure reached 5850 psi. The vessel had been hydrotested at 10,080 psi.

MECHANICAL TEST PERFORMED IN HIGH-PRESSURE HYDROGEN

The preponderance of tests performed in high-pressure hydrogen have been carried out at elevated temperatures to study hydrogen attack on or decarburization of steel; these tests are not applicable to our problem. Hydrogen embrittlement, as such, is most severe at ambient temperatures. Thus, the collection of elevated temperature data plotted by Nelson, i.e., the Nelson curves (Ref. 19), showing safe operating conditions, are not applicable for predicting low-temperature compatibility of hydrogen with steels.

Room temperature, high-pressure hydrogen tests were reported by the duPont Chemical Company in 1952 (Ref. 20). Room temperature burst tests were performed using oil and hydrogen as the pressurizing media. The results showed that pressure vessels suitable for operation under oil at pressures in excess of 7000 atm (103,000 psi) failed in a brittle fashion under hydrogen at pressures as low as 2000 atm (29,400 psi) and in periods of time as short as a few minutes. With stainless-steel lined vessels provided with continuous, shallow, spiral grooves to prevent hydrogen pressure buildup between the liner and vessel, it was found that the hydrogen pressure required for failure was the same as the oil pressure required for failure. The use of such stainless-steel liners for periods up to several months was successful in eliminating brittle rupture.

In the early 1950's, Dodge and co-workers, Van Ness and Perlmutter (Ref. 21 and 22), began the most extensive attack up to that time on the high-pressure hydrogen problem. However, all of their experiments consisted of exposing specimens to high-pressure hydrogen, then removing them from the hydrogen environment, and flexing or tensile testing to failure. More than 50 metals were exposed to hydrogen at pressures between 7300 and 60,000 psi. Armco Iron was among the most seriously embrittled. After 40 days in hydrogen at 7300 psi, the number of flexures to fracture decreased to 20 as compared to 62 for an unexposed sample.

Recently, Van Ness and Ansell and co-workers (1963 to 1965) and Hofmann and Rauls (1961 to 1965) performed mechanical tests in high-pressure hydrogen atmospheres. These tests yielded the most valuable information to that time.

Some results from Cavett and Van Ness (Ref. 23) are shown in Table 3. The test specimens were notched. The test sequence consisted of holding for 24 hours at pressure before the stress was applied followed by tensile testing to failure in the same high-pressure hydrogen environment. The tests lasted about 2 minutes from the time stress was applied until the samples failed. Also, stress rupture tests were performed which lasted 3 to 8 days. There was only a small decrease in the ultimate strength as a result of holding under stress in hydrogen. Other results were as follows: Delayed failure was observed when the applied stress was sufficiently low when specimens were first loaded in tension, and only then subjected to high-pressure hydrogen. Specimens subjected to higher stresses frequently failed while pressure was being applied.

The relative loss of strength due to hydrogen was approximately the same at 80 and 250 F.

High-strength 4140 steel showed a 63 percent reduction in its notched tensile strength (362,000 to 135,000) due to hydrogen at 80 F at a pressure of only 2000 psi.

TABLE 3. MECHANICAL TESTS IN HIGH-PRESSURE HYDROGEN AND NITROGEN

	Room Temperature Unnotched Properties Tested in Air			Room Temperature Notched Tensile Properties		
Material	Yield, ksi	Ultimate, ksi	Percent Elongation	Ultimate in 10,000 psi Nitrogen, ksi	Ultimate in 10,000 psi Hydrogen, ksi	Percent Decrease Strength From 10,000 psi Nitrogen to 10,000 psi Hydrogen
Low-Strength 4140	127	135	21	241	204	14
High-Strength 4140	212	228	8.7	362	89	75
C 1025 Steel	47	65	32.6	106	80	25
Precipitation Hardened K Monel	---	139	8.7	251	113	55
Annealed K Monel	47	100	40.1	144	105	27

Some results from Hofmann and Rauls (Ref. 24) are shown in Fig. 3. The percent reduction of area decreased from about 62 percent (for Ck 22N, a plain carbon steel containing 0.22 percent C) when tested in air at ambient pressure to about 28 percent when tested in hydrogen at a pressure of 150 atm (2200 psi). Even at 10 atm hydrogen pressure, there was a significant decrease in ductility.

Hofmann and Rauls (Ref. 24) also showed that the presence of 1 percent O_2 in H_2 at 130 atm (1910 psi) total pressure completely eliminated the embrittling action of hydrogen. Argon and purified nitrogen additions to hydrogen did not affect the degree of embrittlement. However, the addition of 5 percent nitrogen which was not purified partially eliminated the embrittling effect of hydrogen probably because of the oxygen contained in the nitrogen.

Steinman, Van Ness and Ansell (Ref. 25) performed similar tests on 4140 at the two strength levels using two different types of notched specimens. Both notches were relatively dull with the sharper corresponding to that used by Cavett and Van Ness. Tests were performed in hydrogen at a pressure of 10,000 psi and air following hydrogen exposure. The results are shown in Tables 4 through 7.

TABLE 4. EFFECT OF 10,000 PSI HYDROGEN ON LOW-STRENGTH 4140 SHARP NOTCH

Testing Conditions	Fracture Strength	Percent Change in Strength
In Air, Room Temperature	261,246	(Control Sample)
Soaked in Hydrogen, Room Temperature	215,025	18 percent loss
Soaked in Hydrogen, Room Temperature, Hydrogen Removed, Aged for 3 Hours	255,750	2 percent loss
In Air, -321 F	361,186	38 percent gain
Soaked in Hydrogen for 2 Hours, Room Temperature, Fractured at -321 F	377,513	4 percent gain; relative to specimen in air at -321 F

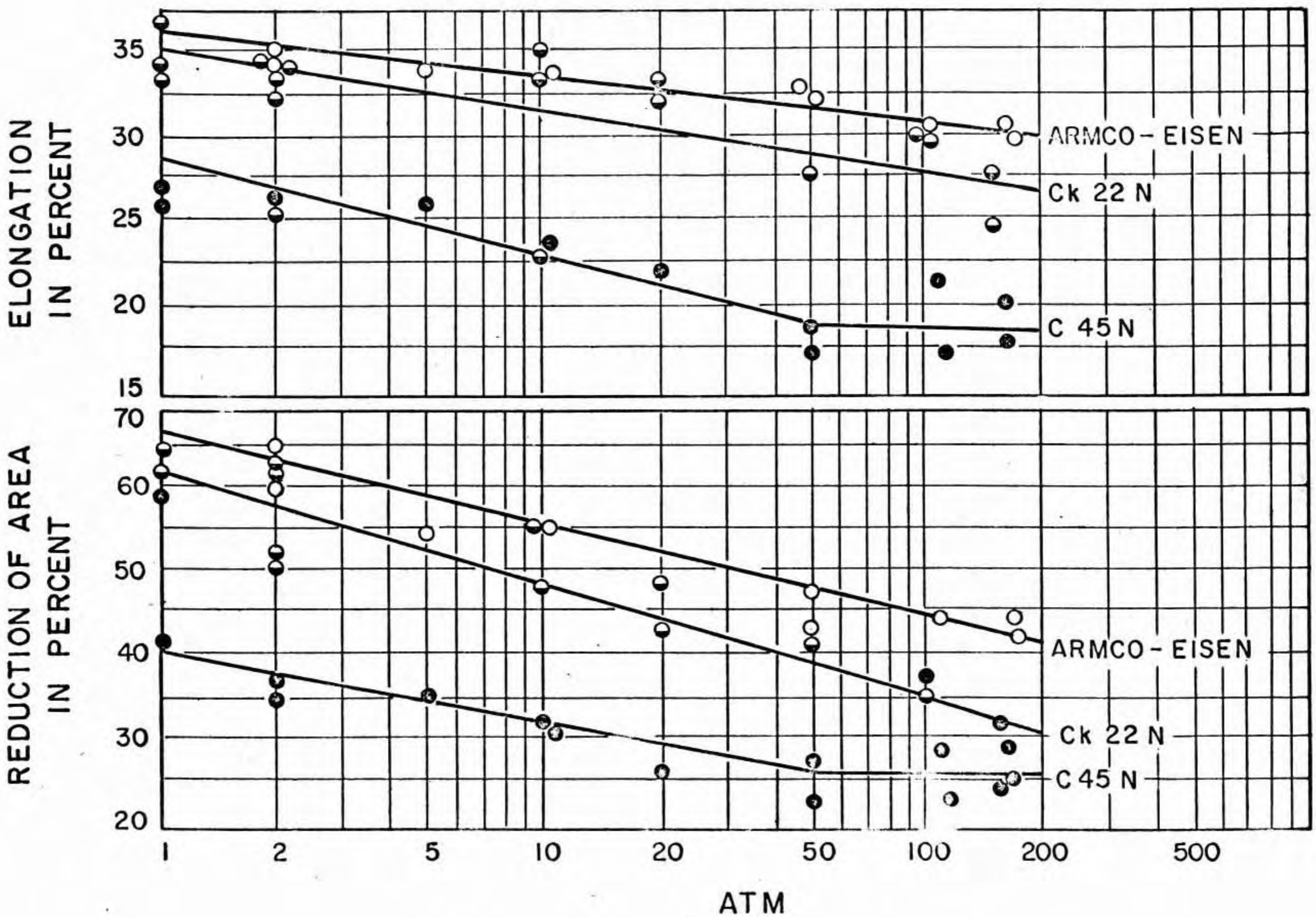


Figure 3. Ductility of Steel in High-Pressure Hydrogen

TABLE 5. EFFECT OF 10,000 PSI HYDROGEN ON HIGH-STRENGTH 4140-SHARP NOTCH

Testing Conditions	Fracture Strength	Percent Change in Strength
In Air, Room Temperature	375,085	(control sample)
Soaked in Hydrogen, Room Temperature	121,694	68 percent loss
Soaked in Hydrogen, Room Temperature Hydrogen Removed, Failed Immediately	196,627	47 percent loss
Stressed to 175,000 psi, Room Temperature, Then Failed When 4000 psi Hydrogen Admitted	188,000	50 percent loss
Stressed to 125,000 psi, Room Temperature, Then Failed When 4800 psi Hydrogen Admitted	140,000	63 percent loss
Stressed to 75,000 psi, Room Temperature, Then Failed When 10,000 psi Hydrogen Admitted	106,600	72 percent loss
In Air at -321 F	265,319	29 percent loss
Soaked in Hydrogen, Room Temperature Fractured at -321 F	237,930	10 percent loss, relative to specimen in air at -321 F
Brought to -321 F, Then Soaked in Hydrogen	247,514	7 percent loss, relative to specimen in air at -321 F
Brought to -321 F, Then Stressed to 197,000 psi, Then Failed When 10,200 psi Hydrogen Admitted	228,962	14 percent loss, relative to specimen in air at -321 F

TABLE 6. EFFECT OF 10,000 PSI HYDROGEN ON LOW-STRENGTH 4140-DULL NOTCH

Testing Conditions	Fracture Strength	Percent Change in Strength
In Air, Room Temperature	287,458	(control sample)
Soaked in Hydrogen, Room Temperature	254,481	11 percent loss
Fractured Immediately After Admission of Hydrogen, Room Temperature	251,867	12 percent loss
Soaked in Hydrogen, Room Temperature, Hydrogen Removed, Fractured Immediately	278,373	3 percent loss
Stressed to 180,000 psi, Room Temperature, Hydrogen Admitted Then Stressed to Failure	264,005	8 percent loss

TABLE 7. EFFECT OF 10,000 PSI HYDROGEN ON HIGH-STRENGTH 4140-DULL NOTCH

Testing Conditions	Fracture Strength	Percent Change in Strength
In Air, Room Temperature	377,062	(control sample)
Soaked in Hydrogen for 5 Minutes, Room Temperature	240,187	36 percent loss
Soaked in Hydrogen, Room Temperature	177,419	52 percent loss
Soaked in Hydrogen, Room Temperature, Hydrogen Removed, Fractured Immediately	309,774	17 percent loss

The degree of embrittlement decreased when the specimen was removed from the hydrogen atmosphere prior to fracturing. Embrittlement decreased with increase in time after removal from the hydrogen atmosphere before fracturing the sample. It was also found that samples fractured in hydrogen with and without prior soaking had about the same degree of embrittlement.

PROGRAM CONDUCTED AT ROCKETDYNE

A program on the effects of high-pressure hydrogen on storage vessel steels was conducted at Rocketdyne under NASA funding (Ref. 26).

Three steels which have been used in the construction of large, welded, high-pressure hydrogen storage vessels were investigated. The chemical compositions of the test materials are given in Table 8 and the mechanical properties in Table 9.

Specimens were taken from welded plates which in thickness, weld procedure, heat treatment and, in fact, in every way possible, simulated plates used in the construction of pressure vessels. The plates were fabricated by pressure vessel manufacturers; A-302 by Taylor Forge and Pipe Works, T-1 by Struthers Wells Corp., and A-212 by American Bridge Division of United States Steel Corp. Notched and unnotched specimens of parent and weld metal were tested in hydrogen at pressures of 10,000, 7500, 5000, and 3000 psi with hold periods of 1, 10, and 100 days.

The cylindrical test specimens were 9 inches long and 0.306 inch in diameter, and were threaded for 1 inch on each end. The specimens were machined to a 16-rms surface finish from a thin slab near the surface of the test plate, which simulates the surface that would be in contact with the gas in a storage vessel. The unnotched specimens contained 1-inch long, 0.250-inch diameter reduced sections. The notch used was a 60-degree V notch placed midway along the specimen. The specimen diameter at the bottom of the notch was 0.150 ±0.001 inch, and the root radium was $0.0046\,^{+0.0002}_{-0.0001}$ inch, resulting in a stress concentration factor of approximately 4.2.

TABLE 8. CHEMICAL COMPOSITION OF PARENT METAL AND WELD METAL OF WELDED STEEL PLATES*

Element	A-302-56 Gr. B Modified With Nickel			A-517-64 (T-1)		A-212-61 Gr. B-FB	
	Parent Metal**	Longitudinal Weld	Girth Weld	Parent Metal	Weld Metal	Parent Metal	Weld Metal
C	0.25	0.14	0.07	0.13	0.08	0.32	0.07
Mn	1.31	2.00	1.93	0.91	1.34	0.75	1.02
Si	0.27	0.03	0.55	0.19	0.29	0.23	0.32
Cr	--	0.32	0.26	0.64	0.32	<0.05	<0.05
Ni	0.63	2.63	2.43	1.11	2.28	<0.10	<0.10
Mo	0.56	0.53	0.64	0.49	0.55	0.02	0.44
Cu		0.30	0.12	0.26	0.43	0.06	0.13
V		0.03	0.07	0.06	0.27	0.06	0.07
P	0.016	0.009	0.010	0.009	0.008	0.016	0.014
S	0.021	0.009	0.010	0.025	0.008	0.020	0.025
B	0.003			0.006	0.002		

*Certified report of chemical analysis performed by Materials Testing Laboratories
**Data obtained from Taylor Forge & Pipe Works

TABLE 9. MECHANICAL PROPERTIES OF PARENT METAL AND WELD METAL TAKEN FROM THE SURFACE OF THE PLATES

Material	Condition	Yield Strength	Ultimate Strength		Percent Reduction of Area,		Percent Elongation
		Unnotched, psi	Unnotched, psi	Notched, psi	Unnotched	Notched	
A-302-56 Gr. B Modified With Nickel	Parent Metal Longitudinal Direction	98	114	210	68	17	21
	Parent Metal Transverse Direction	87	106	194	62	9	27
	Longitudinal Weld	101	115	215	65	11	23
	Longitudinal Weld Heat-Affected Zone	-	-	207	-	12	-
	Girth Weld	104	117	218	53	6	17
	Girth Weld Heat-Affected Zone	-	-	243	-	3	-
A-517-64 (T-1)	Parent Metal Longitudinal Direction		111*	191*	49	3	18
	Parent Metal Transverse Direction	109	118	214	66	7	25
	Longitudinal Weld		104*	197*	62	11	17
	Longitudinal Weld Heat-Affected Zone	-	-	202*	-	1	-
	Girth Weld	96	116		64		17
	Girth Weld Heat-Affected Zone	-	-		-		-
A-212-61T	Parent Metal Longitudinal Direction	38	73	112	56	12	37
	Longitudinal Weld	64	77	146	53	11	17
	Longitudinal Weld Heat-Affected Zone	-	-	133*	-	11	-

*Strength in 10,000-psi helium

Parent metal specimens were prepared with the long specimen dimension parallel to the longitudinal and long transverse rolling directions. Specimens also were taken normal to the longitudinal and girth welds, so that the weld region came within the gage length of unnotched specimens, or a notch was placed in the weld or in the heat-affected zone.

Apparatus

The apparatus used for conducting tensile tests on specimens in high-pressure hydrogen was patterned after the one developed at Rensselaer Polytechnic Institute. Each 9-inch long tensile specimen was held inside a cylindrical, high-pressure test cell with the specimen ends extending out of the test cell through Teflon sliding seals, as shown in Fig. 4. A plug was screwed into each end of the test cell, forcing brass rings against the Teflon rings which, in turn, were forced against the specimen to form a gas-tight seal between the specimen and the test cell. The test cells were made of 316 stainless steel. A tensile load was applied to each specimen by means of a spring, as shown in Fig. 5. The threaded specimen ends that extend out of a test cell, and which are attached to ball and socket joints connected to the top and bottom pull rods, were used for self-aligning. The tensile load was applied by compressing the spring and was determined by measuring spring deflection with dial gages across the spring length. The spring was deflected by means of a nut riding on a thrust bearing for the tests performed on the A-302 specimens, which were the first specimens tested. For the tests on the T-1 and A-212 specimens, a hydraulic ram (Fig. 6) was used for compressing the spring.

Considerable care was taken in calibrating the specimen loading system. The springs were calibrated with a Baldwin Universal Tensile Testing Machine. Such calibrations were made before and after the 100-day hold tests and approximately every 45 days while conducting the 1- and 10-day hold tests. The complete loading system was calibrated by using a load cell in place of a tensile specimen on the spring loading device. The

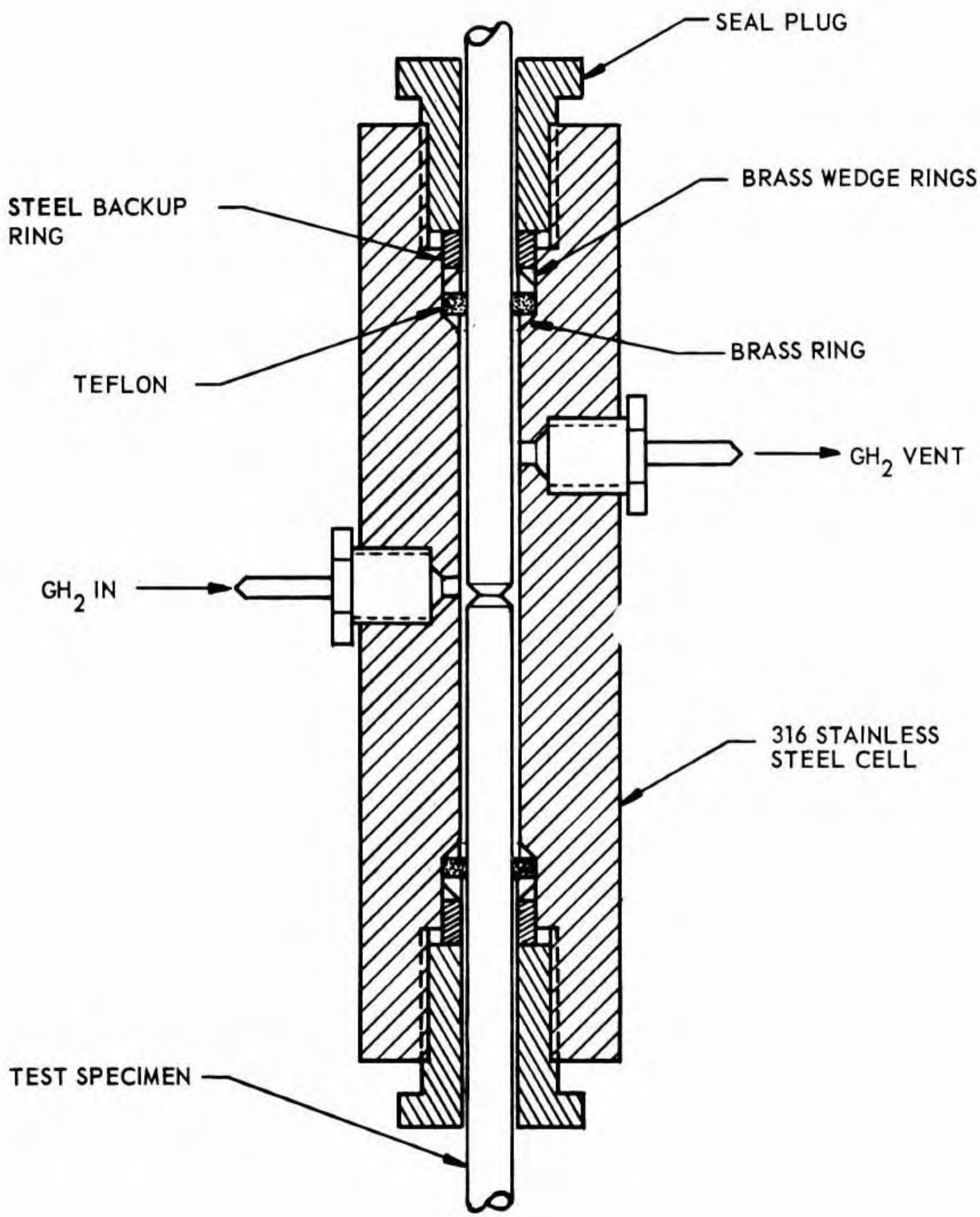


Figure 4. Test Cell With Specimen (Full Scale)

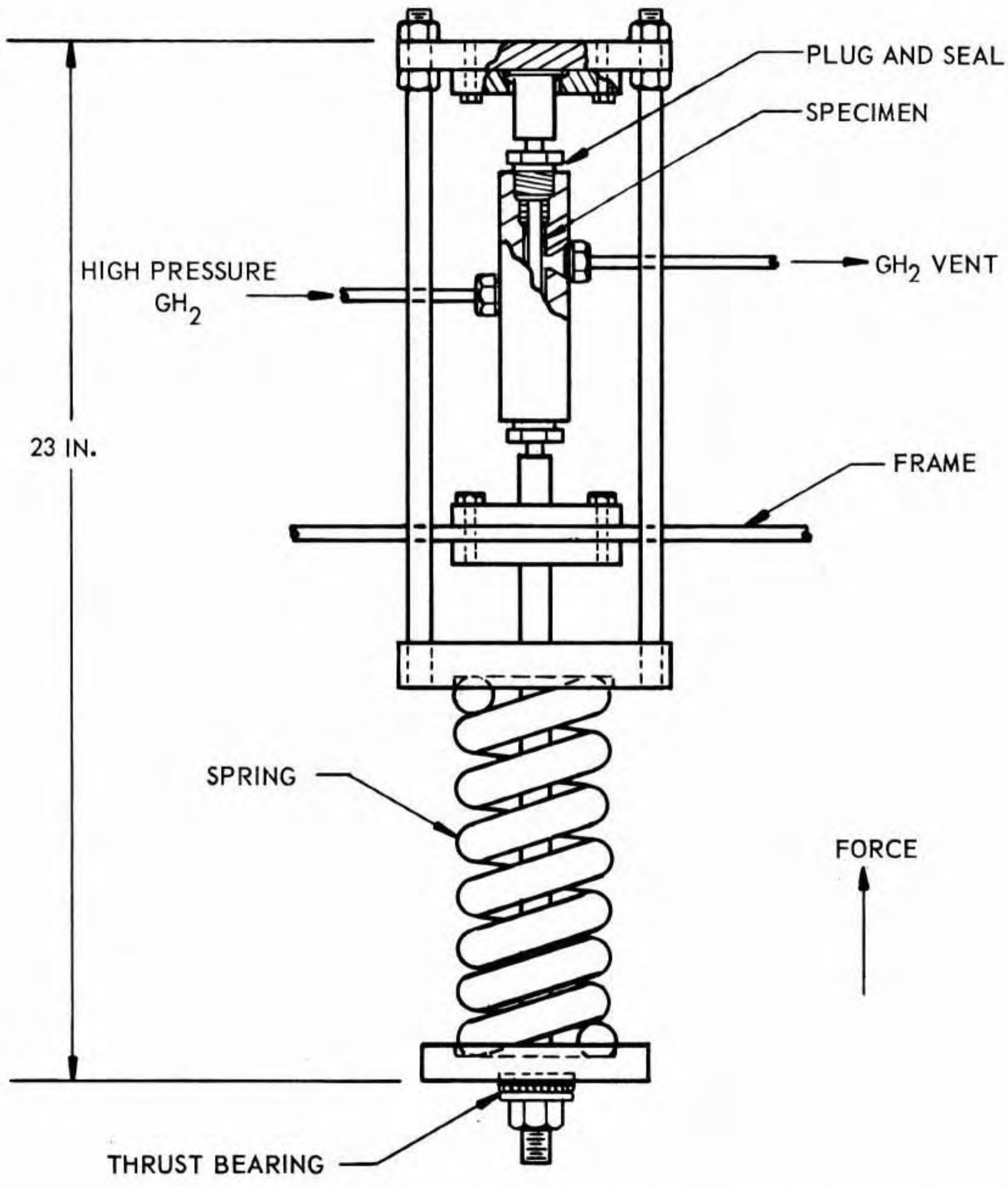


Figure 5. Test Vessel and Static Loading Device

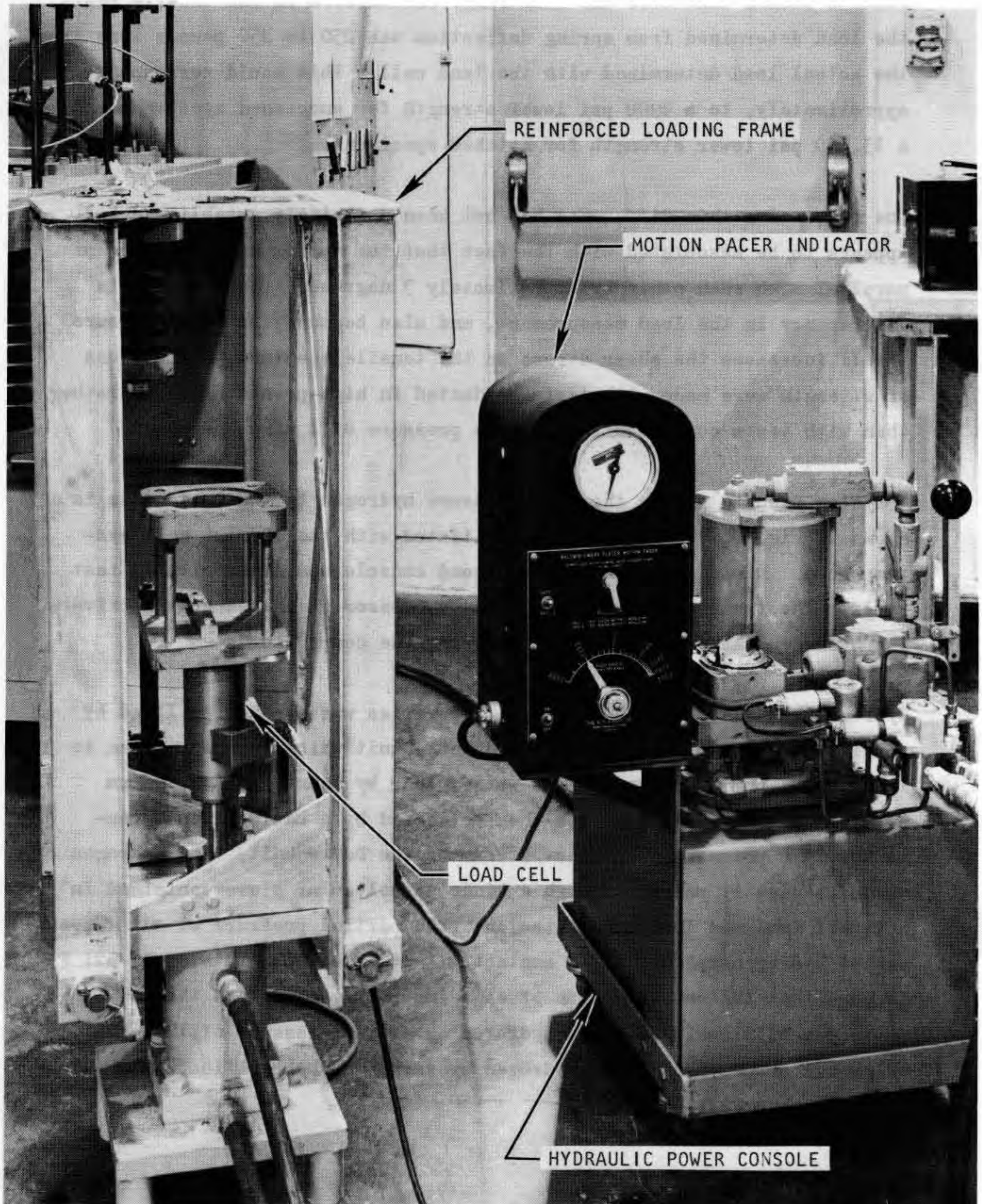


Figure 6. Hydraulic Loading Device

results showed that over the load range encountered in the tensile tests, the load determined from spring deflection was 230 to 250 pounds less than the actual load determined with the load cell. This would correspond, approximately, to a 4900 psi lower strength for unnotched specimens and a 13,500 psi lower strength for notched specimens.

The reason for this difference has not been definitely established but appears to be associated with the fact that the spring ends were out of parallel with each other by approximately 3 degrees. Because of this discrepancy in the load measurement, and also because the high pressure itself increases the shear stress on the tensile specimen, comparisons of strength were made with tests conducted in high-pressure helium rather than with tests conducted in air at a pressure of 1 atmosphere.

A system used to supply the high-pressure hydrogen to the test cells is shown in Fig. 7. The program was initiated with the 10-test cell system shown. During the program, a second console was added with 12 test cells. The two systems used a single compressor which fed both receivers. The hydrogen was purified before entering the compressor.

Hydrogen with less than 5 ppm total impurities was further purified by passing the gas through an Engelhard DeOxo unit which removed oxygen to less than 1 ppm by conversion to water vapor by means of a palladium catalyst. The water vapor was then collected by a BaO desiccant contained in a pressure vessel downstream of the DeOxo unit. The hydrogen was subsequently passed through a Linde 5A molecular sieve contained in a vessel immersed in liquid nitrogen. The partial pressure of all gases except hydrogen and helium in contact with the molecular sieve at -321 F is such that the concentration of each impurity gas is less than 50 parts per billion (ppb) for a hydrogen or helium pressure of 1000 psi, which was about the minimum hydrogen pressure in the purification system during pressurization.

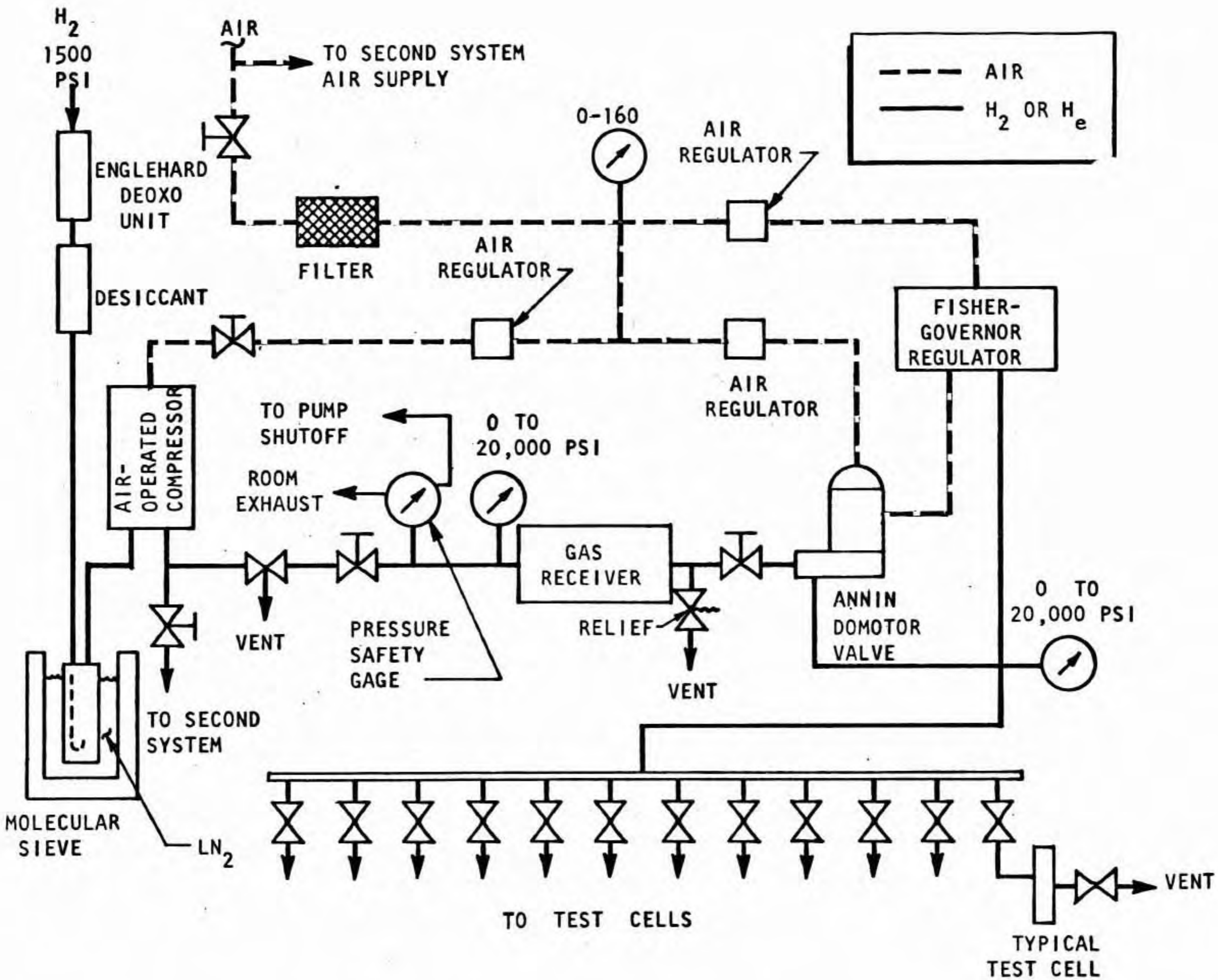


Figure 7. Schematic for High-Pressure Gaseous Hydrogen System

This hydrogen purity, however, was not maintained after leaving the purification apparatus. Following the 100-day tests on the A-302 specimens, the oxygen and nitrogen content in the storage vessel was 200 and 930 ppm, respectively. It was necessary to pump 17 times for the 100-day tests and, with each pumping the impurity concentration evidently increased.

After improving flushing procedures and enclosing the compressor in a box containing a flowing argon purge, the 1-day tests on the T-1 specimens were performed, and the hydrogen gas in the storage vessel was analyzed as less than 0.5 ppm oxygen, 2 ppm nitrogen, and 16 ppm argon.

After purification, the hydrogen was pressurized to 15,000 psi in the storage vessels by means of a Haskel Model AG152, which is an air-operated, nonlubricated gas compressor with 20,000 psi maximum pressurization capability. The pressure is regulated to the test cells in the first system by means of a Fisher Governor Type 4160 regulator which has a 20,000 psi maximum inlet pressure and 3000 to 15,000 psi outlet pressure range. This regulator controls an Annin Domotor Valve Model 5060 (Wee Willie) which is air activated by means of a pneumatic line connected to the Fisher Governor regulator. The pressure for the 10,000 psi tests was controlled between 9600 and 10,600 psi during the hold period. It is estimated that the pressure varied within 10,000 ±100 psi over 50 percent of the time.

Before a specimen was tested to failure, the hydrogen pressure was set at the desired pressures, i.e., 10,000, 7500, 5000, or 3000 psi. The variation from that level was less than 50 psi.

Procedure

The procedure followed for all tests in high-pressure hydrogen consisted of thoroughly purging the system of foreign gases by pressurizing with purified helium to 10,000 psi and depressurizing to approximately

1 atmosphere pressure. This was then followed by three 10,000 psi pressurizing and depressurizing cycles with purified hydrogen. For tests performed at 3000, 5000, and 7500 psi hydrogen pressure, the system was pressurized to 3000, 5000, or 7500 psi, respectively, instead of 10,000 psi for the helium and hydrogen pressure cycles. Six hydrogen pressure cycles were used for the 3000 psi tests, five cycles for the 5000 psi tests, and four cycles for the 7500 psi tests. The hydrogen gas pressure was then brought up to the desired level and the load was applied and maintained for 1, 10, or 100 days. At the end of the holding period the hydrogen pressure was adjusted to the desired level and the specimens were loaded to failure and the fracture stress noted.

The hold stress for all unnotched specimens was either 75 percent of the yield strength or 5 percent above the yield strength (0.2 percent offset). The hold stress for the notched specimens was 25 percent below or 5 percent above the stress, above which there was a significant departure from linearity on the stress strain curve.

A dynamic friction load of 76 pounds was subtracted from the applied load of specimens tested in 10,000 psi hydrogen and helium. This friction value was based on the force needed to move a tensile specimen through the vessel with the sliding seals tightened to approximately the same tightness (60 ft-lb) required to hold 10,000 psi helium and hydrogen.

The tensile load exerted by the pressure inside the test vessel was added to the applied load in calculating the stress.

The ductilities of the specimens tested in the various environments were also determined. The percent elongation of unnotched specimens was measured between punch marks placed 2 inches apart outside of and bridging the 1-1/4 inch reduced section. It was assumed that essentially all of the elongation took place in the reduced section so that the percent elongation was equated to the change in distance between the punch marks divided by 1-1/4 inches times 100. It was decided best not to place marks of any kind in the reduced section because of the effect they might have on the results. The reduction of area of unnotched specimens was determined by measuring the cross sections of the specimens with a micrometer before and after testing. The reduction of area of notched specimens was determined by using an optical comparator to measure the cross section of the notch before and after testing.

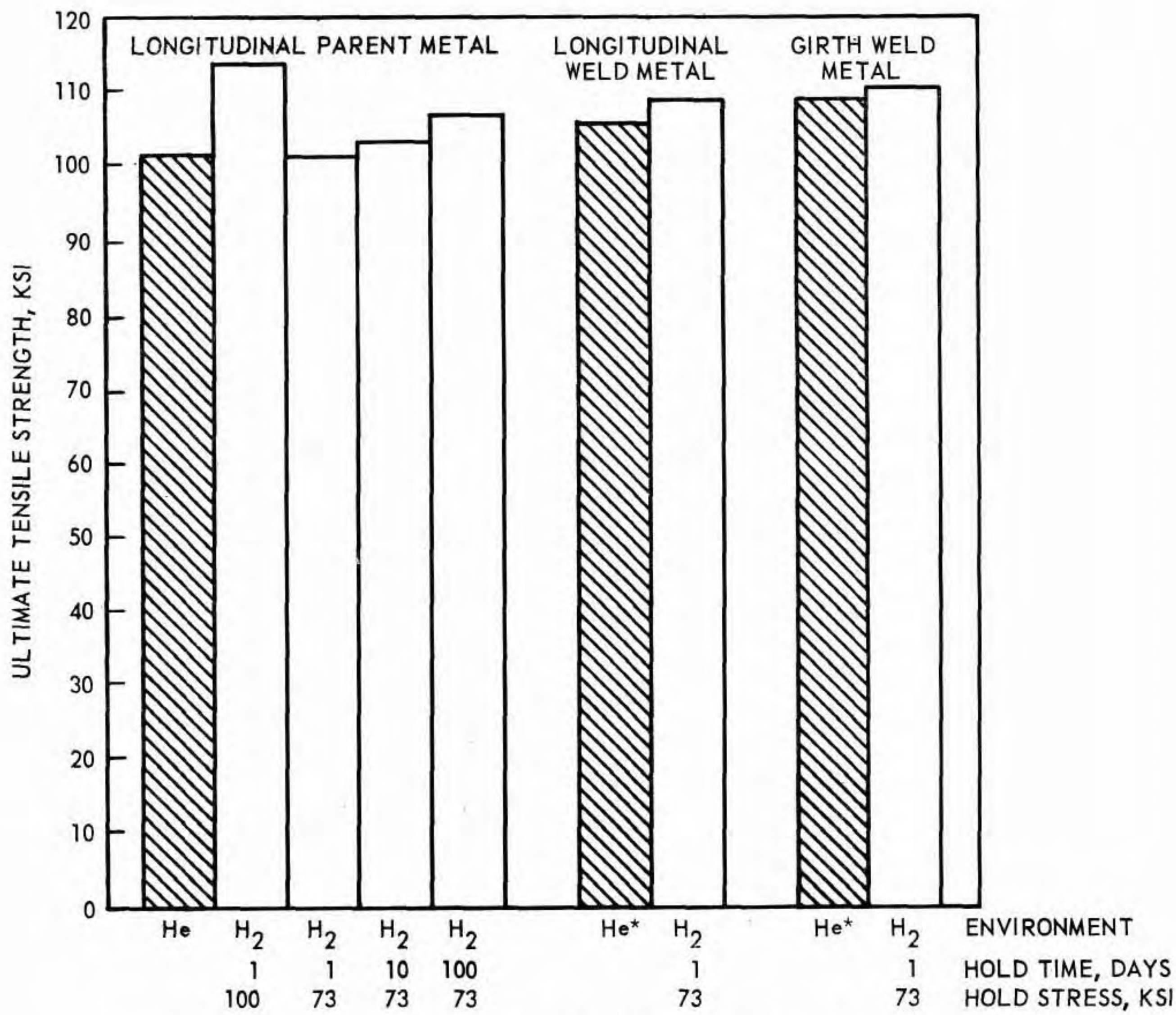
A number of specimens were examined by optical and electron metallography and electron fractography.

Results

A-302. The effect of exposure of the unnotched A-302 specimens to 10,000 psi hydrogen for 1, 10, and 100 days with different hold stresses are shown graphically in Fig. 8. Generally, the tensile strengths of unnotched A-302 specimens were not greatly affected by exposure to hydrogen. The ductilities of unnotched specimens exposed to 10,000 psi hydrogen are shown in Fig. 9. There was no effect of exposure to 10,000 psi hydrogen on the percent elongation of the parent metal specimens oriented in the longitudinal direction.

However, there was an appreciable decrease of ductility as measured by reduction of area due to exposure of unnotched specimens to high-pressure hydrogen. For the parent metal specimens, this ductility appears to decrease with increased duration of exposure. Holding at 100,000 psi caused less embrittlement than holding at 73,000 psi and the higher holding stress resulted in an increase of strength. The two specimens exposed for 100 days each had 40 percent reduction of area. The longitudinal and girth weld were more embrittled than the parent metal..

The lower ductility of the specimens tested in high-pressure hydrogen was accompanied by surface cracking (Fig. 10). Surface cracks form perpendicularly to the direction of the applied stress in the necked-down region, and can be seen without the aid of magnification. No such cracks occur in specimens tested in air or in 10,000 psi helium.



* AS DETERMINED ON UTM MINUS 11,000 PSI TO ADJUST FOR TESTING IN SPRING-LOADED DEVICE WITH 10,000-PSI PRESSURE

Figure 8. Ultimate Tensile Strength of A-302-56 Gr. B Modified With Nickel, Unnotched Specimens in 10,000 psi Hydrogen and Helium

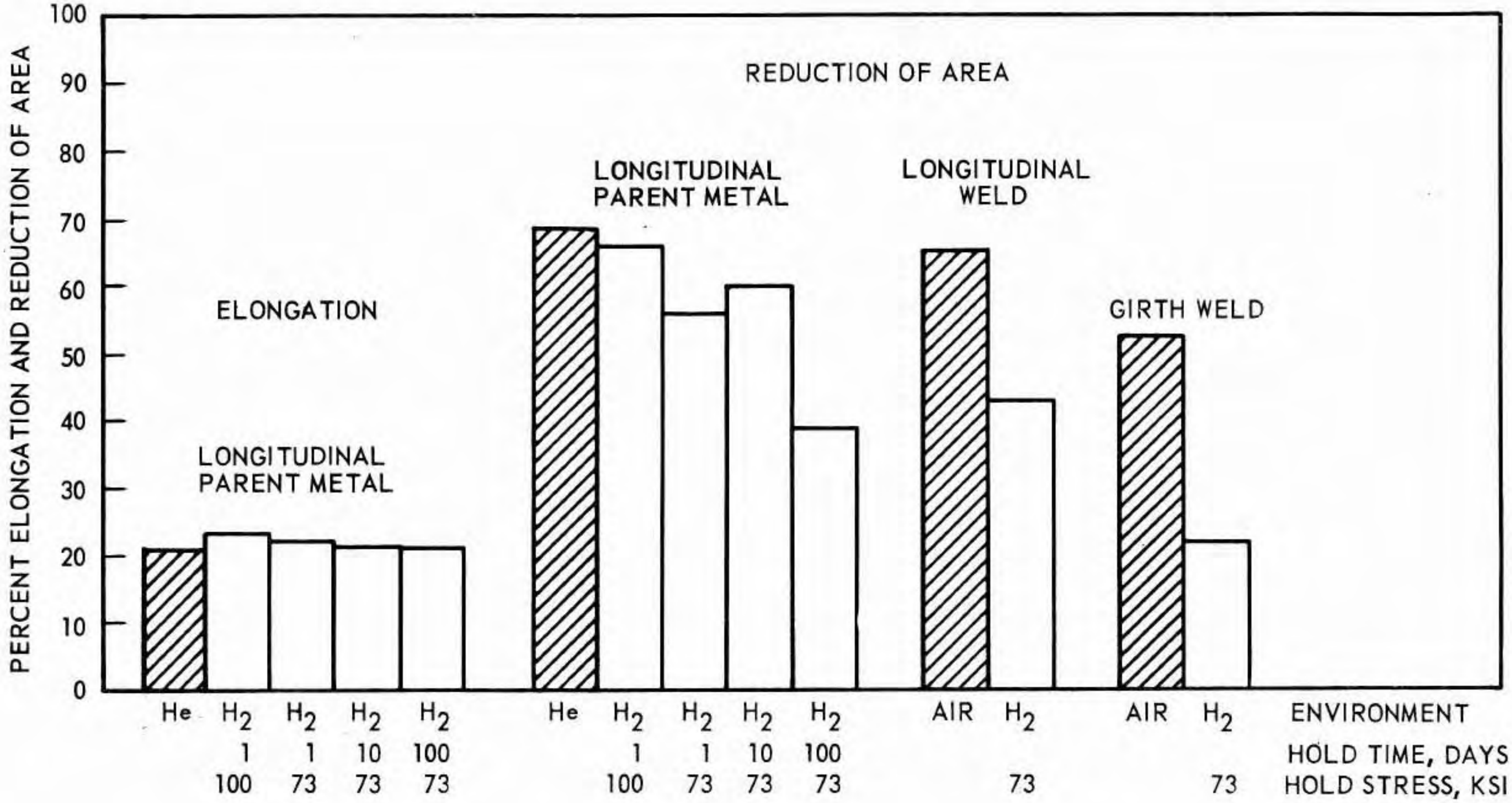
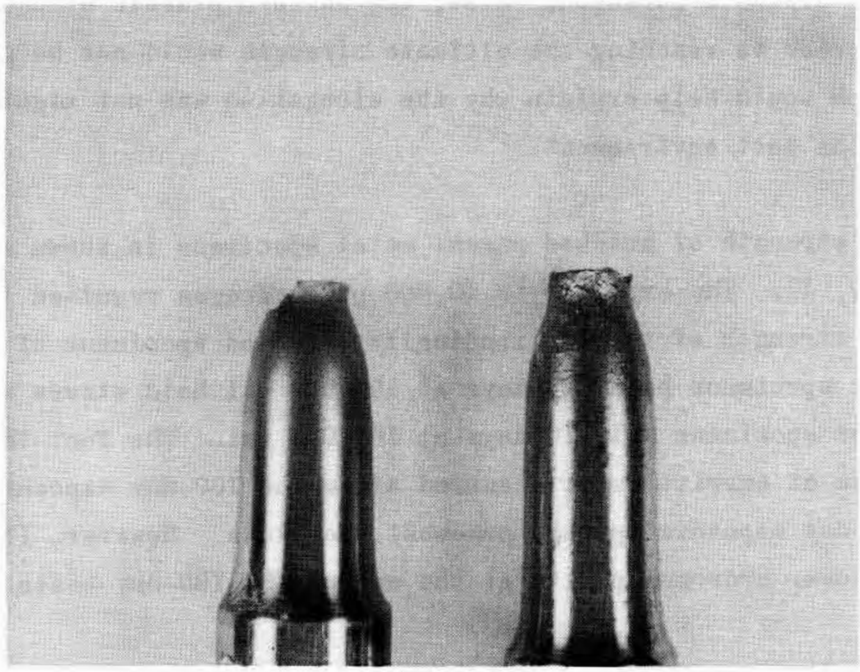


Figure 9. Ductility of A-302-56 Gr. B Modified With Nickel Unnotched Specimens in Air, 10,000-psi Hydrogen and Helium



3X

Photomacrograph

Figure 10. A-302-56 Longitudinal Parent Metal: Left Specimen Tested in 10,000 psi Helium; Right Specimen A-63 Tested in 10,000 psi Hydrogen; 1-Day Hold

Surface cracking was present only in the necked-down region, which suggests that the specimens must have almost reached their ultimate strength before the cracks formed, and in which case the cracks would not have much effect on the ultimate strength. Also, the uniform plastic elongation that occurs prior to reaching the ultimate strength would not be greatly reduced, which would help explain why the elongation was not significantly affected by the test environment.

The ultimate strength of notched parent metal specimens is shown graphically in Fig. 11. The exposure to 10,000 psi hydrogen resulted in a reduction in strength of the longitudinally oriented specimens of between 6 percent for specimens held 100 days at 109,000 psi hold stress and 16 percent for specimens held 10 days at 109,000 psi. The fact that a smaller degree of embrittlement occurred after the 100-day exposure than after the 10-day exposure appears somewhat anomalous. However, it may be due to a lower hydrogen purity at the end of the 100-day tests.

The two notched parent metal specimens that were tested in 10,000 psi hydrogen after holding unstressed for 15 minutes in the hydrogen atmosphere had a 24 percent average reduction of strength. This is a greater degree of embrittlement than was encountered for the specimens held in hydrogen under load.

The notched parent metal specimens oriented in the transverse direction had no significant reduction of strength from the 10,000 psi hydrogen. The ultimate strengths of the notched longitudinal weld specimens are shown in Fig. 12. Specimens with the notch in the longitudinal weld metal were significantly affected by the 10,000 psi hydrogen, and the longer the exposure to hydrogen (with the 109,000 psi hold stress), the greater the reduction of strength. The ultimate strength after the 100-day exposure averaged 145,000 psi which corresponds to a 28 percent average reduction of notched strength. Again, holding at 152,000 psi for 1 day resulted in a lower reduction of notched strength than holding 1 day at 109,000 psi. Specimens notched in the longitudinal weld heat-affected zone were not as embrittled as specimens notched in either the parent metal or the longitudinal weld metal.

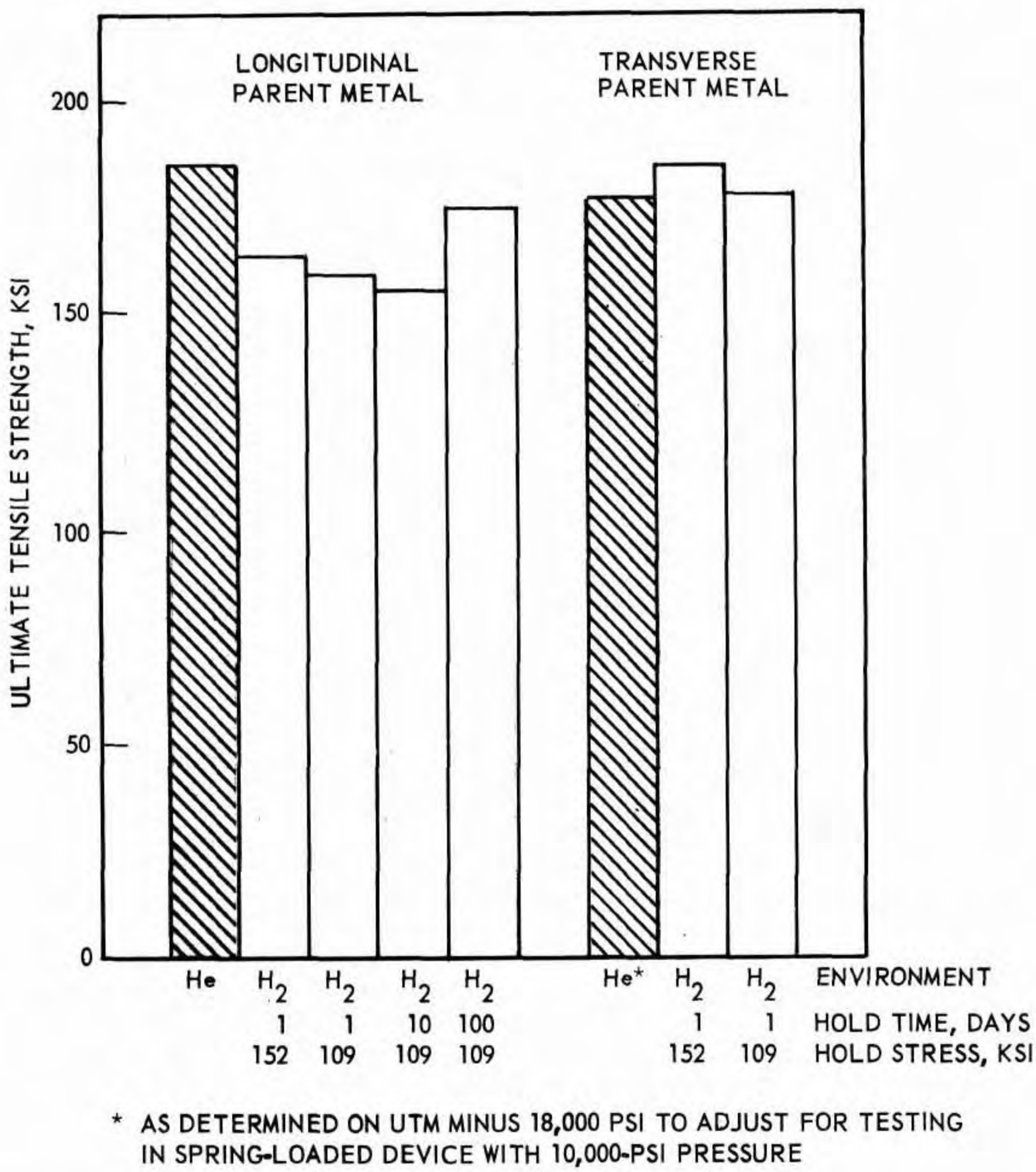


Figure 11. Ultimate Tensile Strength of A-302-56 Gr. B Modified With Nickel Notched Parent Metal Specimens in 10,000 psi Hydrogen and Helium

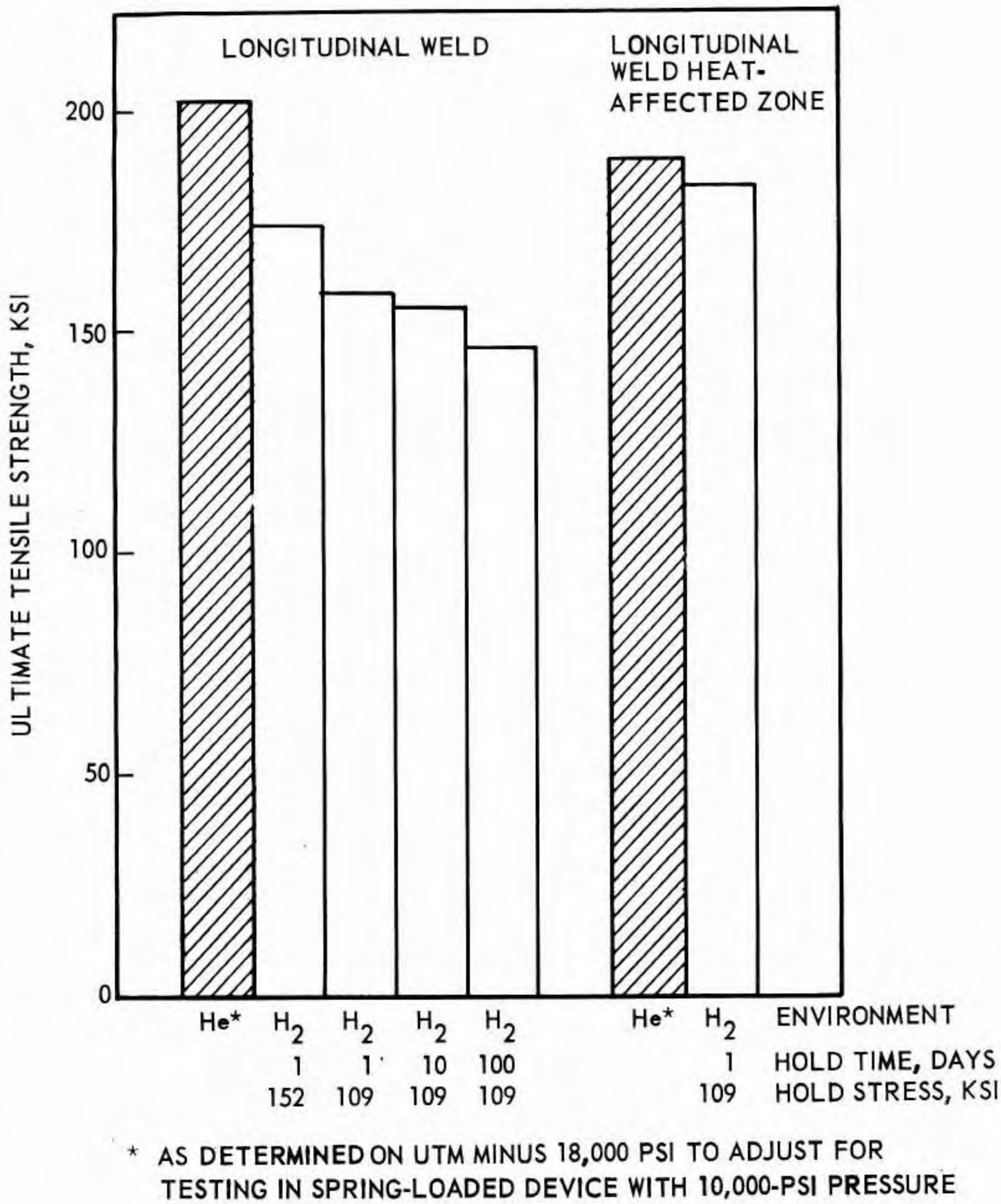


Figure 12. Ultimate Tensile Strength of A-302-56 Gr. B Modified With Nickel Notched Longitudinal Weld Specimens in 10,000 psi Hydrogen and Helium

The two specimens notched in the girth weld metal tested in 10,000 psi hydrogen had as much as a 29 percent reduction of strength for a specimen that broke during preloading (Fig. 13). Three specimens, held 1 day at 109,000 psi stress, had an average ultimate strength of 159,000 psi which corresponds to a 22 percent reduction of notched strength.

Specimens notched in the girth weld heat-affected zone were the type of A-302 specimens most affected by the hydrogen environment. The reduction of notched strength ranged from 29 percent for two specimens held 100 days at 109,000 psi hold stress to 60 percent for a specimen that broke during preloading in hydrogen.

The ductility of the notched A-302 specimens, as measured by reduction of area, is plotted in Fig. 14 for the parent metal specimens and in Fig. 15 for specimens notched in the weld metal and the heat-affected zone. The percentage reduction of ductility resulting from testing in the hydrogen environment was even greater than the reduction of strength.

No specimens broke during the hold period except two which were tested early in the program and which were subjected to extraneous forces. One failed when an accidental increase in the hydrogen pressure occurred during a test, and the other failed because it was subjected to a shock when a specimen in an adjacent cell was fractured.

It is interesting to note that two notched parent metal specimens that were tested in 10,000 psi hydrogen after holding for 15 minutes in hydrogen, with the only load being that due to pressure, had only a 0.8 percent average reduction of area, which is much lower than for any of the other parent metal specimens tested in 10,000 psi hydrogen.

To determine the effect of hydrogen pressure on the mechanical properties, tensile tests also were performed at 3000, 5000, and 7500 psi hydrogen pressure after holding 1 day at this pressure on notched longitudinal parent and longitudinal weld metal specimens. The results are plotted

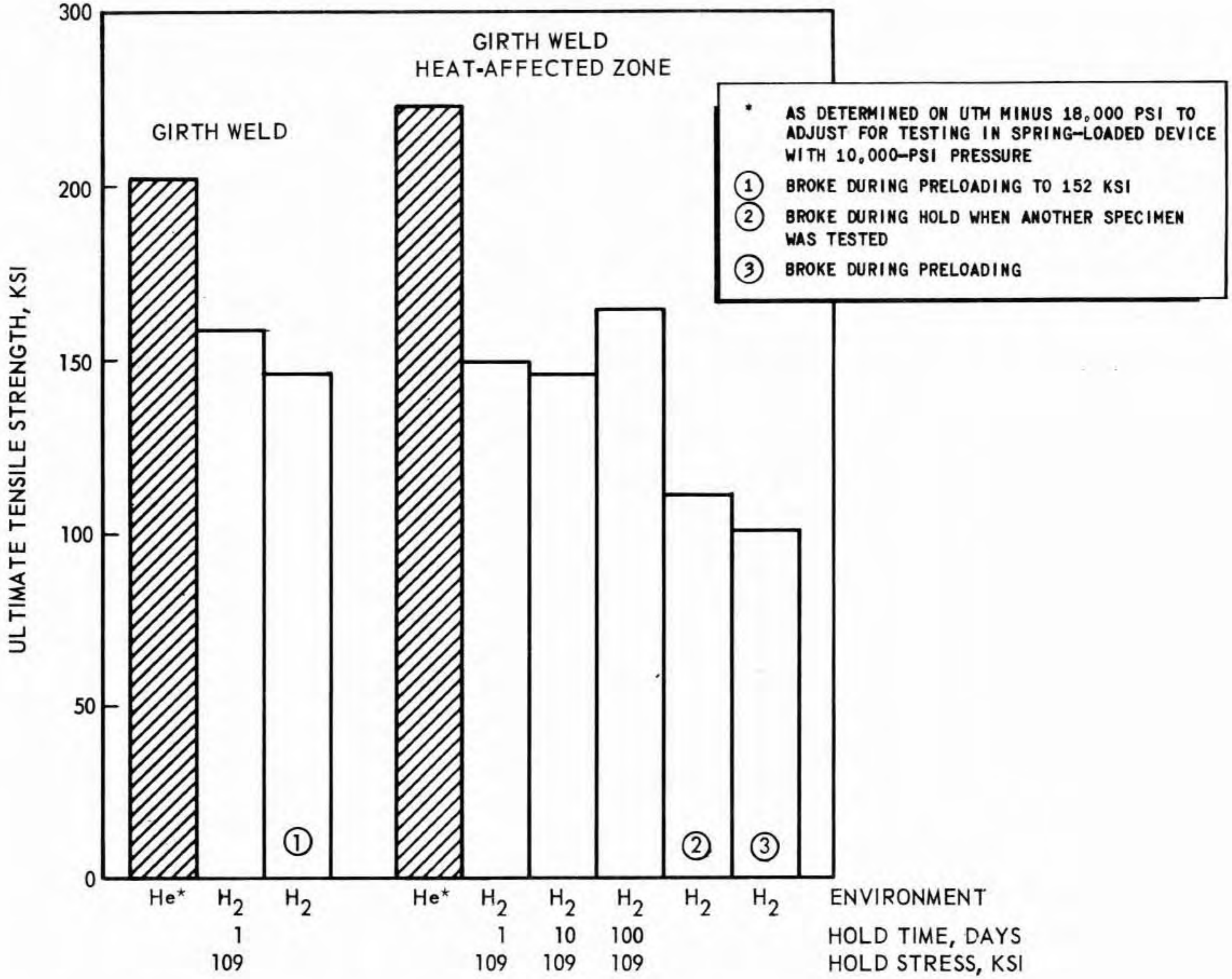


Figure 13. Ultimate Tensile Strength of A-302-56 Gr. B Modified With Nickel Notched Weld and Heat-Affected Zone Specimens in 10,000-psi Hydrogen and Helium

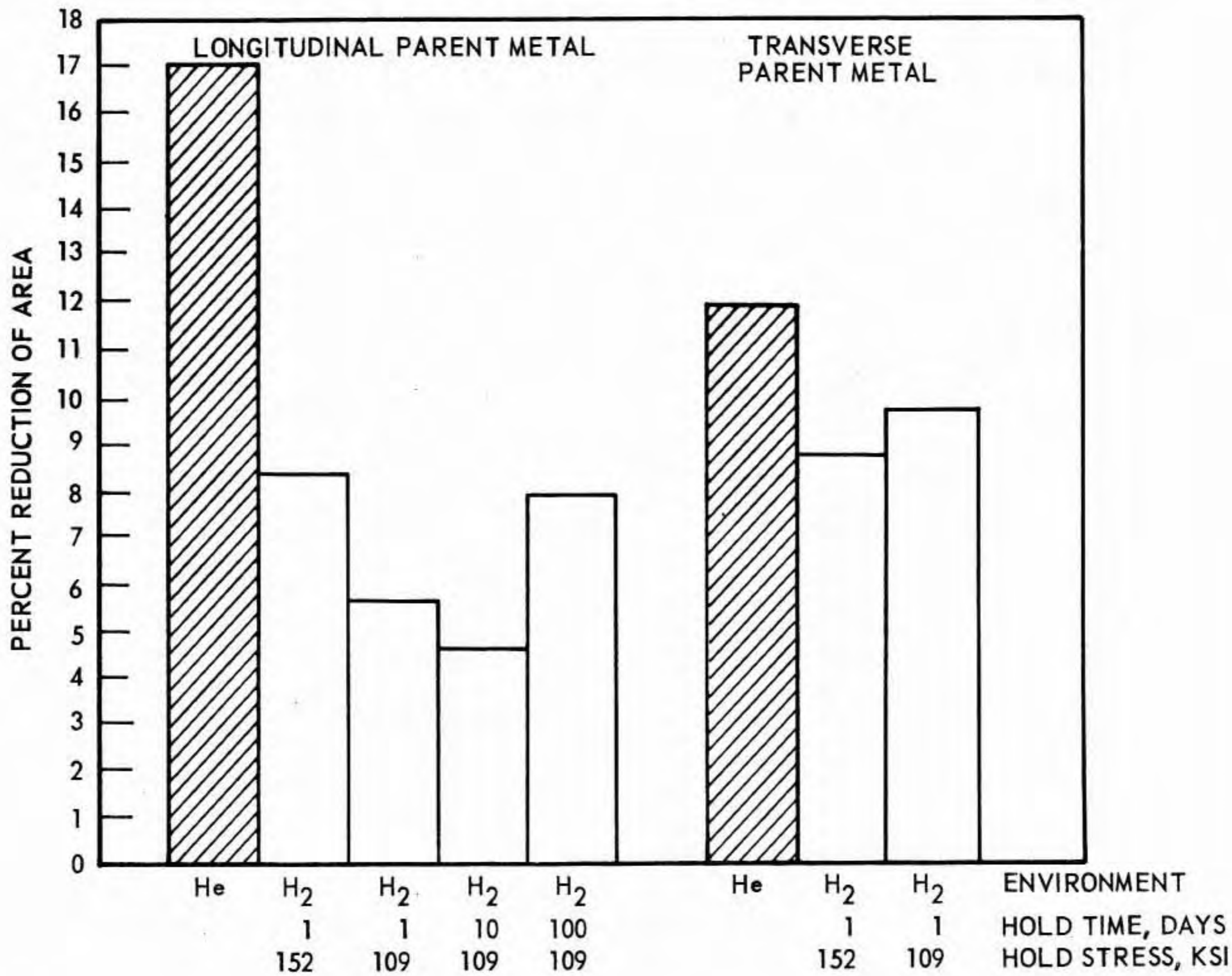
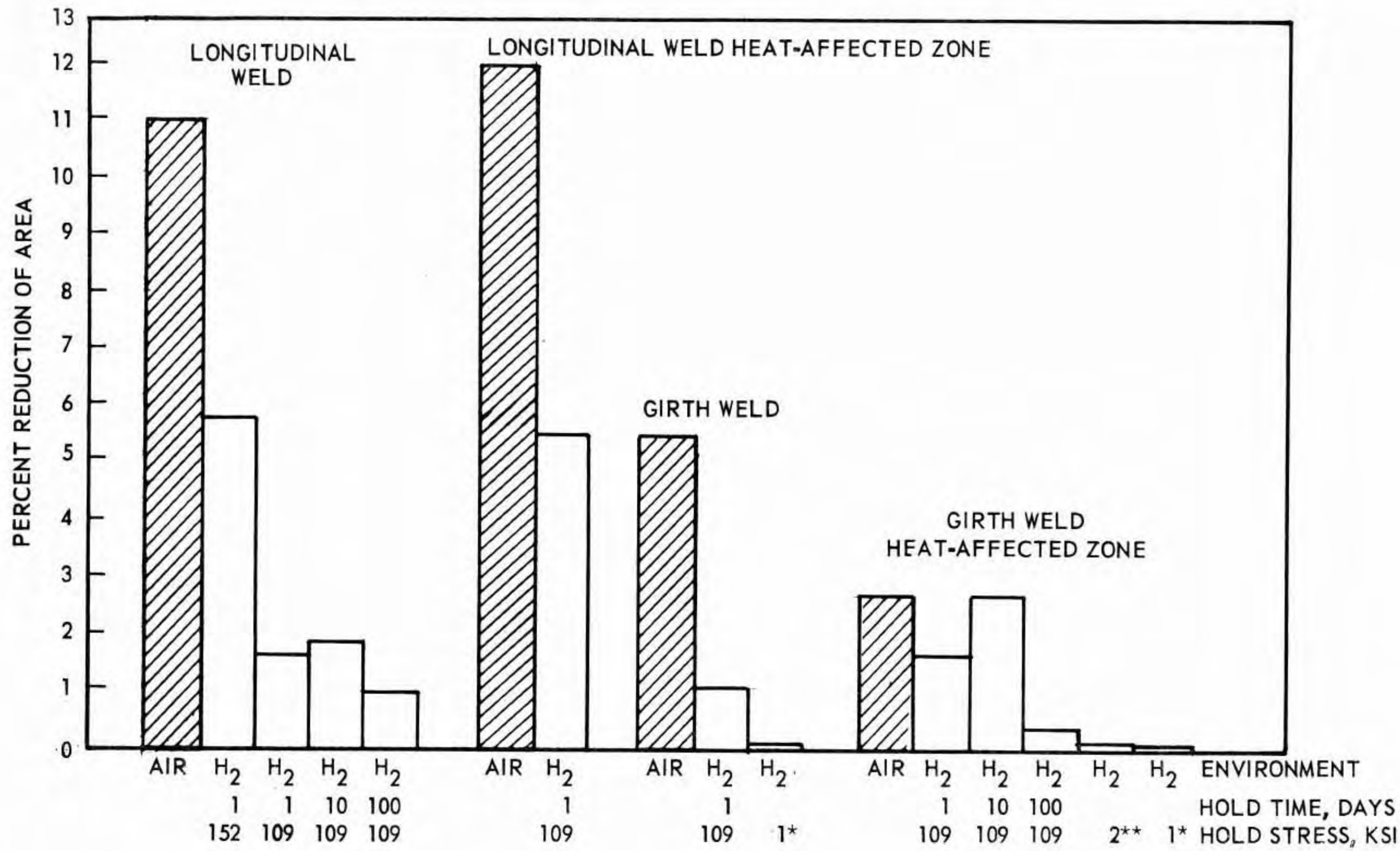


Figure 14. Ductility of A-302-56 Gr. B Modified With Nickel Notched Parent Metal Specimens



* BROKE ON PRELOADING

** BROKE DURING HOLD WHEN ANOTHER SPECIMEN BROKE

Figure 15. Ductility of A-302-56 Gr. B Modified With Nickel Notched Weld and Heat-Affected Zone for Tests in 10,000 psi Hydrogen

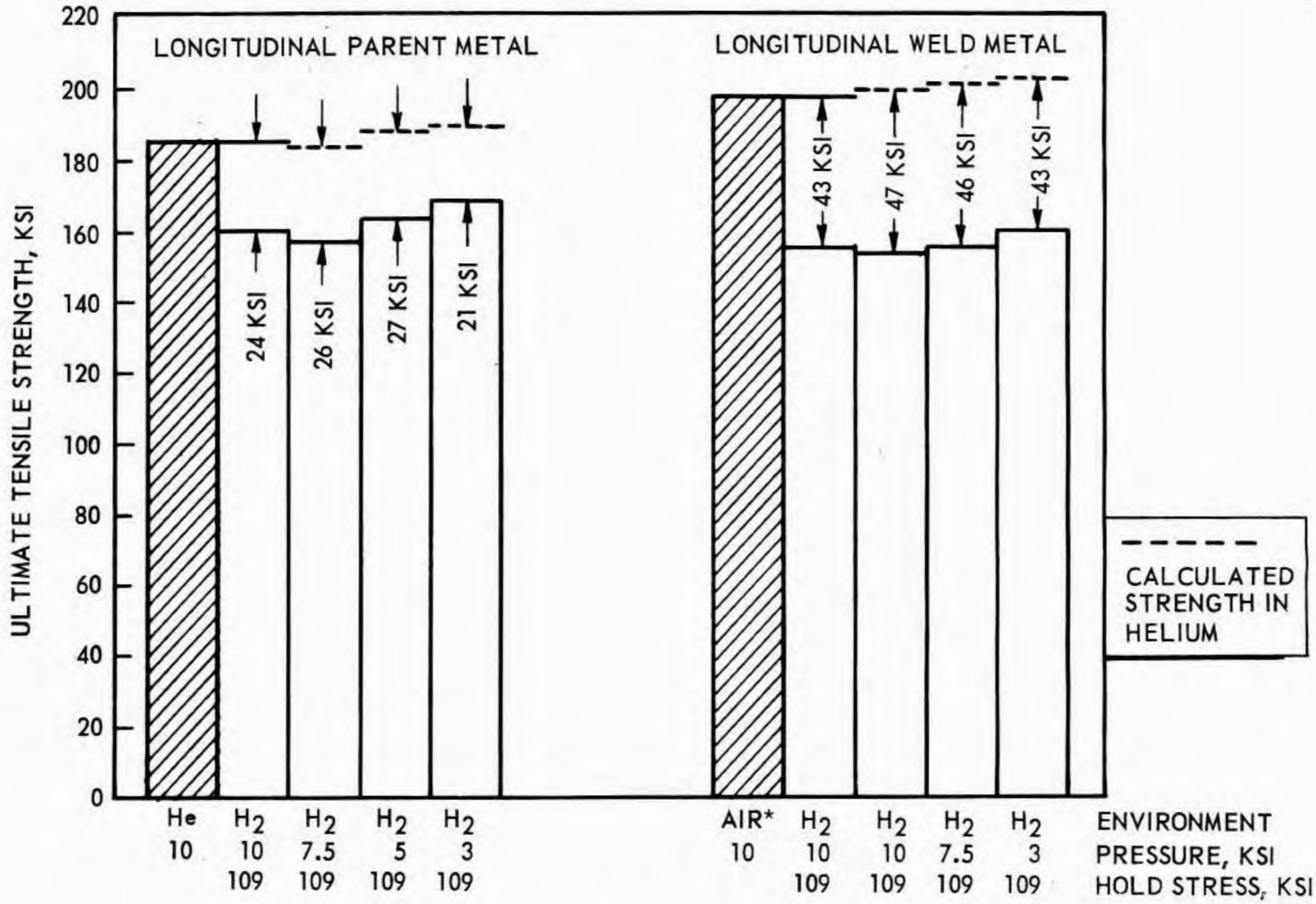
in Fig. 16 and 17 for the ultimate strength and reduction of area, respectively. The results indicate that, for A-302, the effect of the hydrogen environment on the ultimate strength was not very different for the different pressures. The decrease in ductility of A-302 cause(by the hydrogen environment also was not very different for the differε hydrogen pressures. Evidently, there must exist a sharp discontinuity in the degree of embrittlement of A-302 somewhere between 0 and 3000 ps hydrogen pressure.

An A-302 unnotched longitudinal parent metal specimen was tested in 1 atmosphere hydrogen pressure. The results indicated no degradation of the mechanical properties or surface cracking. The fracture had a well-formed shear lip.

Electron fractographs of A-302 indicate that exposure to 10,000 psi hydrogen affected the fracture mode in the following ways:

1. Exposure to high-pressure hydrogen considerably increases the proportion of the fracture surface which appears brittle.
2. There is evidence that high-pressure hydrogen causes cracking in the fracture surface and the amount of cracking increases with duration of exposure to hydrogen. Figure 18 shows intergranular cracks and Fig. 19 shows transgranular cracks on the fracture surface of a notched A-302 specimen.
3. Exposure to high-pressure hydrogen results in a brittle fracture mode at the fracture surface-machined surface interface of notched specimens (Fig. 20). In contrast, this interface in notched specimens tested in air or 10,000 psi helium was quite ductile (Fig. 21). Also, this interface in notched, hydrogen-charged specimens is ductile, Fig. 22 (Ref. 27).

A-212. In general, the strength of the unnotched specimens was unaffected by the 10,000 psi hydrogen environment.



* AS DETERMINED ON UTM MINUS 18,000 PSI TO ADJUST FOR TESTING IN SPRING-LOADED DEVICE WITH 10,000-PSI PRESSURE

Figure 16. Effect of Hydrogen Pressure on the Ultimate Tensile Strength of A-302-56 Gr. B Modified With Nickel Notched Longitudinal Parent Metal and Longitudinal Weld Metal Specimens; 1-Day Hold

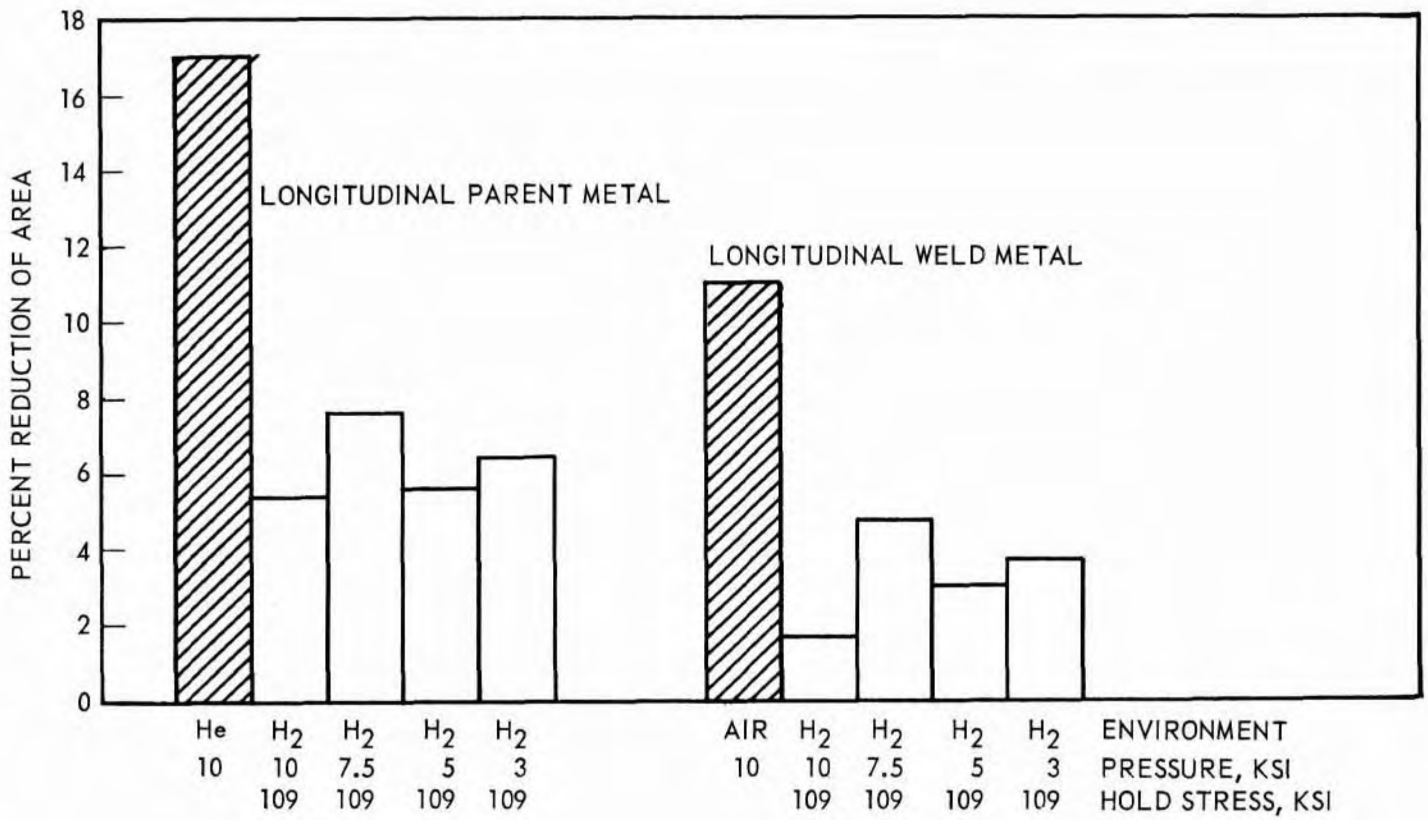
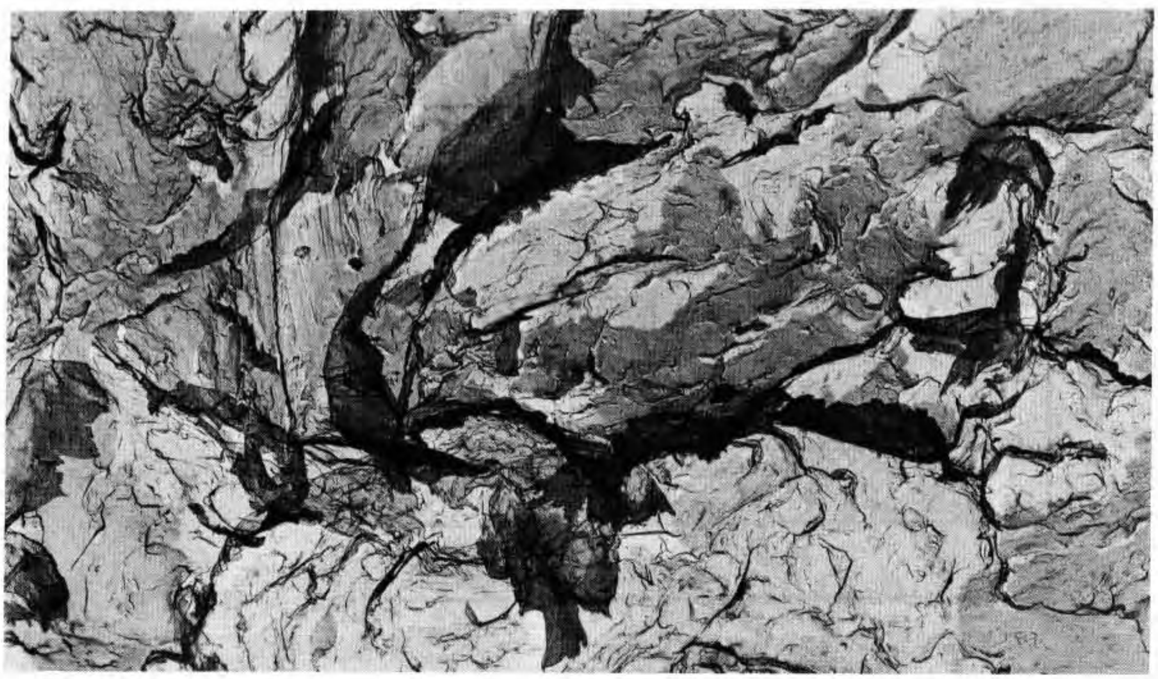


Figure 17. Effect of Hydrogen Pressure on the Reduction of Area of A-302-56 Gr. B Modified With Nickel Notched Longitudinal Parent Metal and Longitudinal Weld Metal Specimens; 1-Day Hold

493-B Electron Fractograph 7500X

Figure 18. A-302 Notched Longitudinal Weld Metal Specimen Tested in 10,000 psi Hydrogen; 1-Day Hold

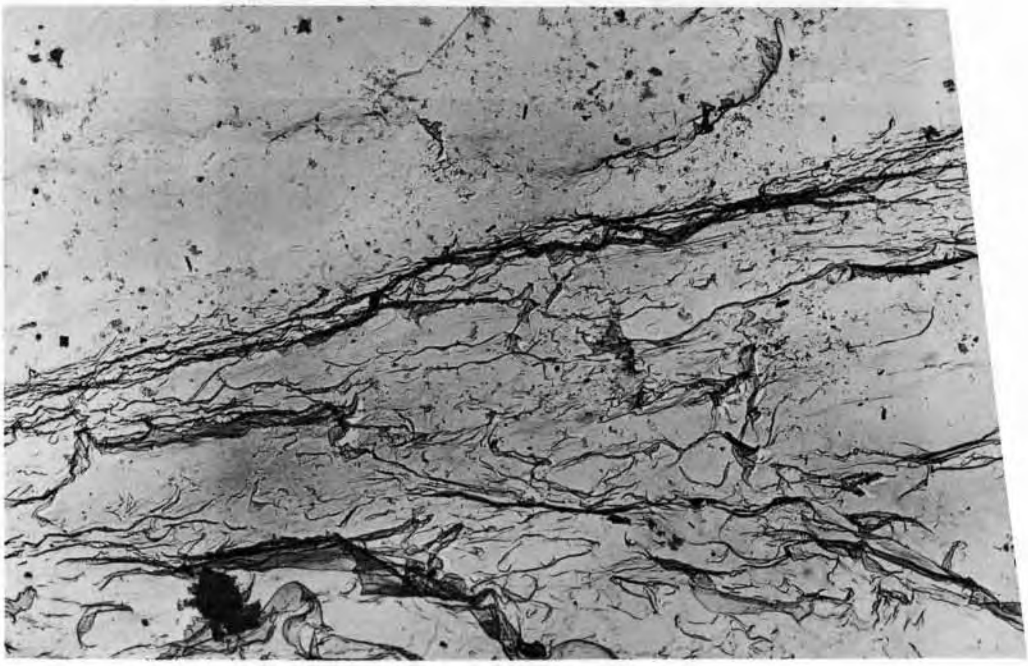


1132-A Electron Fractograph 7500X

Figure 19. A-302 Notched Girth Weld Heat-Affected Zone Specimen, Tested in 10,000 psi Hydrogen; 10-Day Hold

Machined Surface

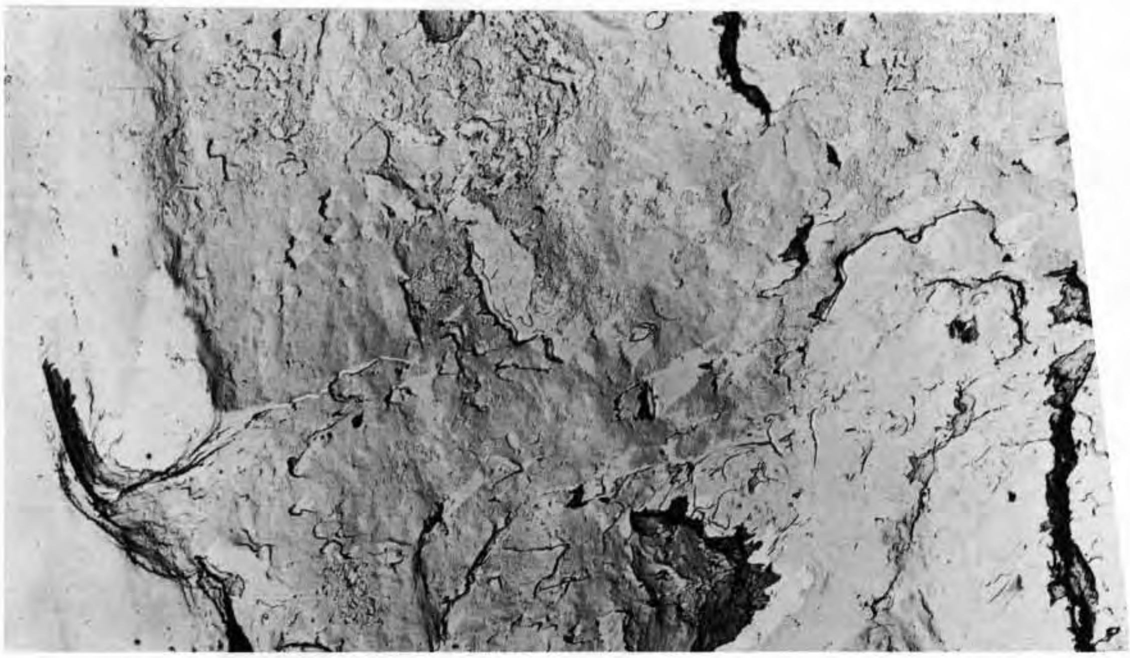
Fracture



1475-2A Electron Fractograph

Figure 20. A-302 Notched Longitudinal Weld Specimen Tested in psi Hydrogen; 10-Day Hold

Machined Surface Fracture



1524-2B Electron Fractograph 7500

Figure 21. A-302 Notched Transverse Parent Metal Specimen Tested in 10,000 psi Helium

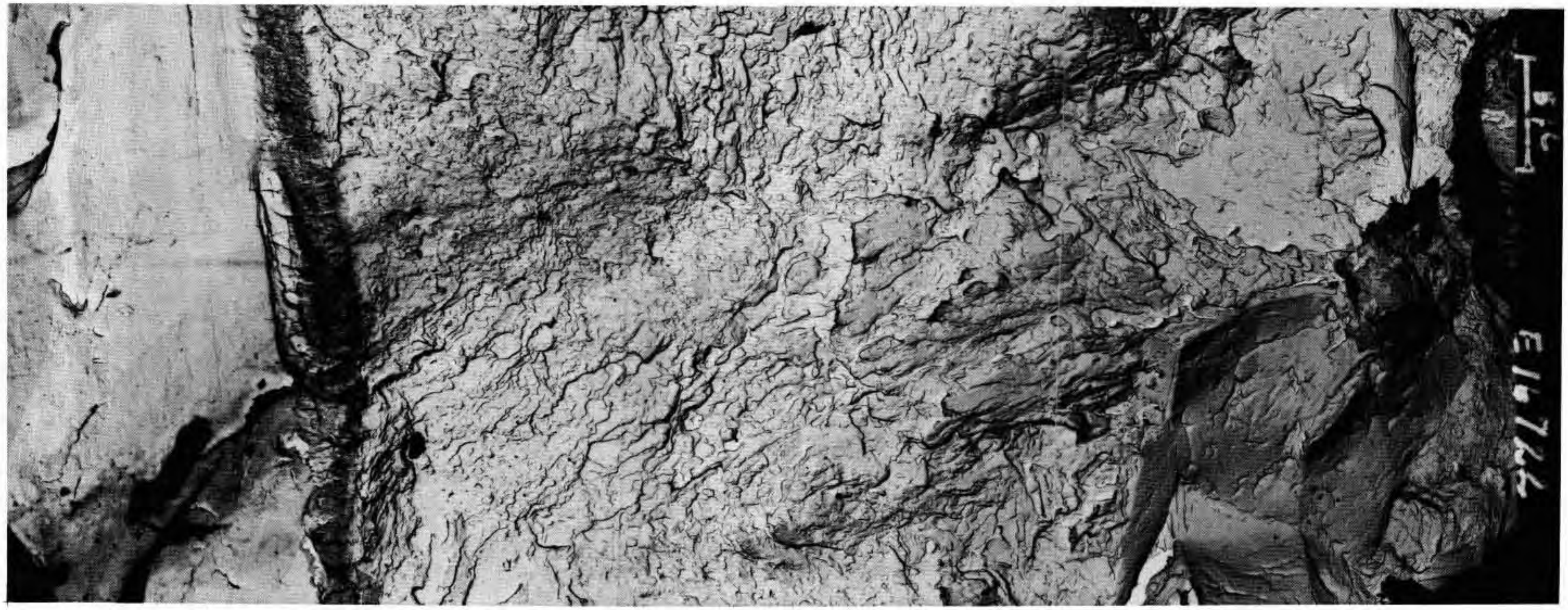


Figure 22. Notched 300M Specimen, Cd Plated and Baked Failed After 75 Minutes at 124 ksi (50 Percent of Yield)

However, the exposure to 10,000 psi hydrogen resulted in a significant reduction of ductility as measured by both reduction of area and elongation (Fig. 23). The greatest ductility decrease, which was nearly 50 percent as measured by both area and length change, occurred after the 10-day exposure.

The notched longitudinal parent metal specimens had the greatest reduction of strength of any of the specimens taken from the A-212 welded plate. The strength of these specimens is plotted in Fig. 24. Two specimens failed during preloading while attempting to load to a hold stress of 77,000 psi, which corresponds to 75 percent of the yield strength. The failures occurred at stresses of 73,000 and 76,000 psi. The hold stress was then reduced to 70,000 psi, but one specimen failed at this hold stress after only 1-1/2 to 2 hours. A second specimen did not fail during the 1-day hold period at the 70,000 psi hold stress, and the ultimate strength at the end of the test period was 80,000 psi. Holding at 65,000 resulted in failure of one specimen in the eighth day of the 10-day tests, and a second specimen in the forty-fourth day of the 100-day tests. Failure at 65,000 psi corresponded to a 41 percent reduction of notched strength. For those specimens that did not break on preloading or during the hold period, there was a general increase of strength with increasing duration of exposure.

The ductility of the notched parent metal A-212 specimens is shown in Fig. 25. The reduction of area was between 0.1 to 6.3 percent in 10,000 psi hydrogen and 13 percent in 10,000 psi helium.

The results of the tests conducted at various hydrogen pressures on the notched longitudinal parent metal and longitudinal weld metal specimens of A-212 are plotted in Fig. 26 and 27 for the ultimate strength and ductility, respectively. It can be seen for both types of specimens that when the test pressure was reduced from 7500 to 5000 psi, there was a sharp decrease in the effect of the hydrogen environment on strength.

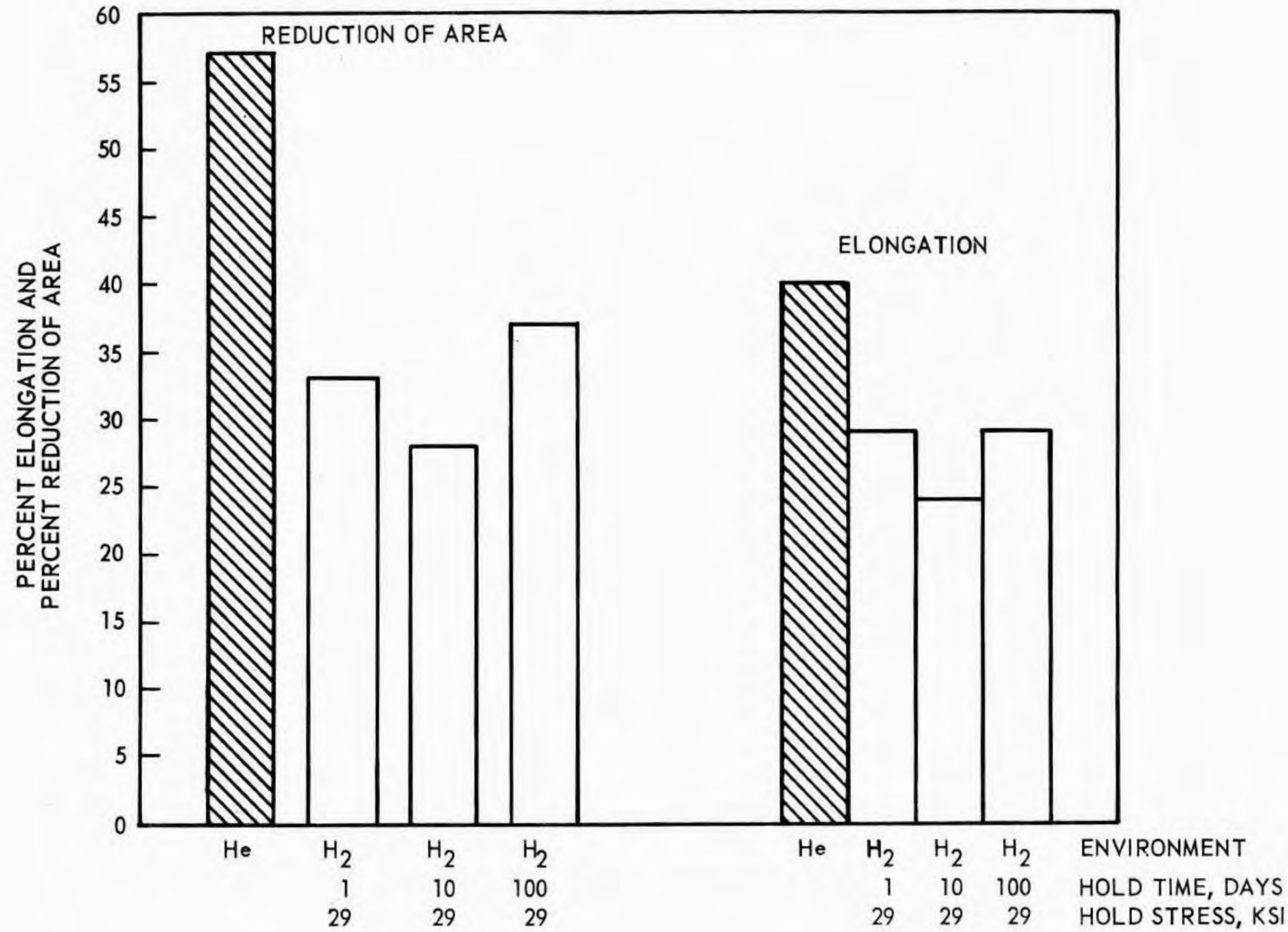


Figure 23. Reduction of Area and Elongation in 10,000 psi Hydrogen and Helium of A-212-61T Gr. B-FB Unnotched Parent Metal Longitudinal Specimens

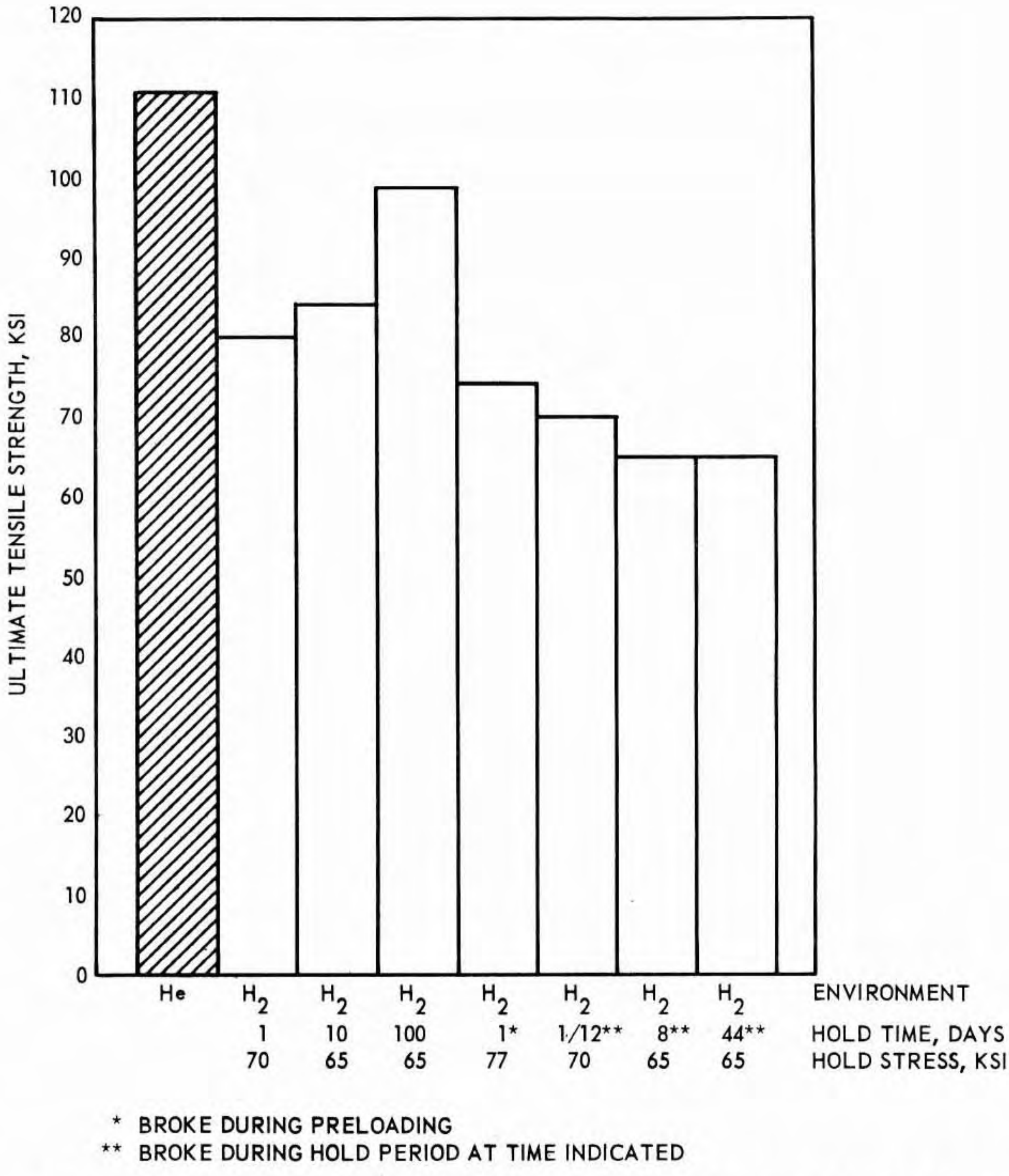


Figure 24. Ultimate Tensile Strength in 10,000 psi Hydrogen and Helium of A-212-61T Gr. B-FB Notched Parent Metal Specimens

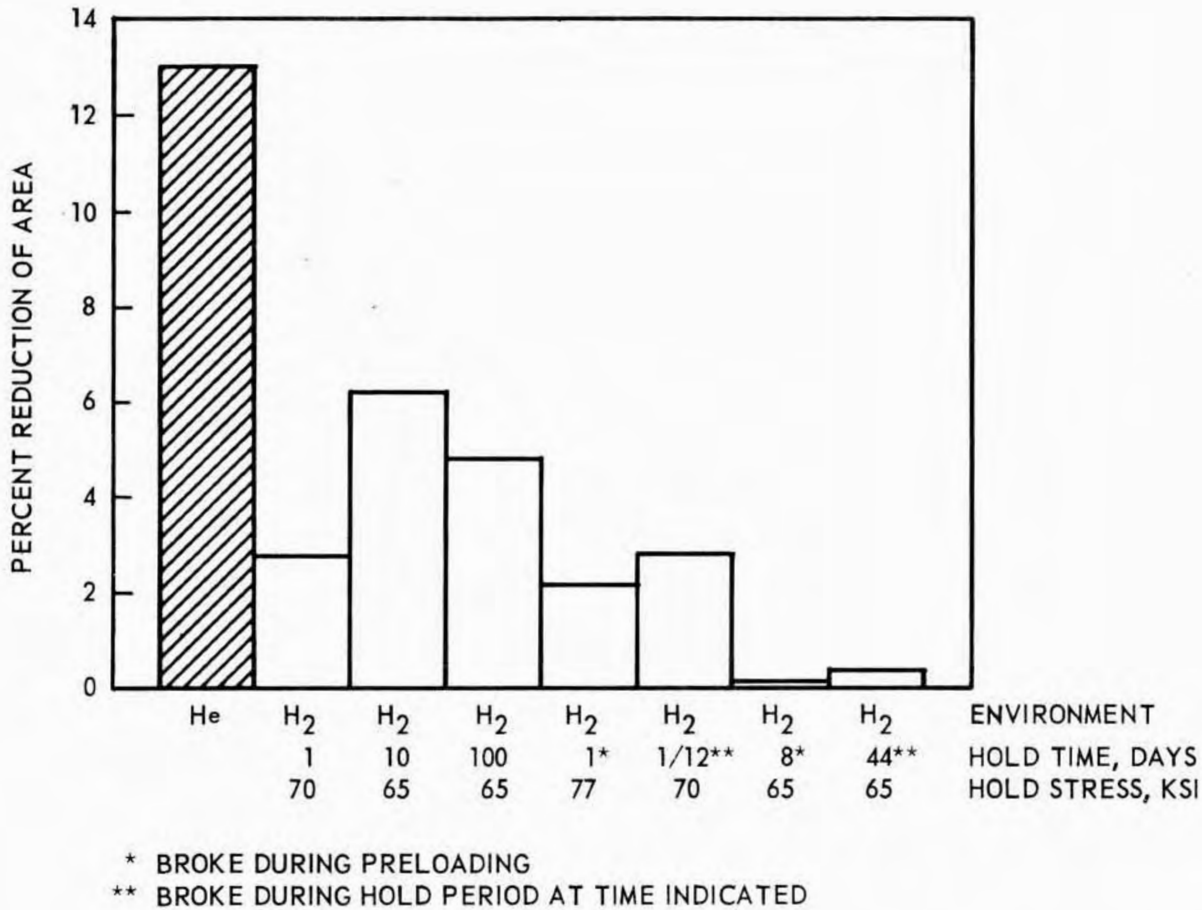
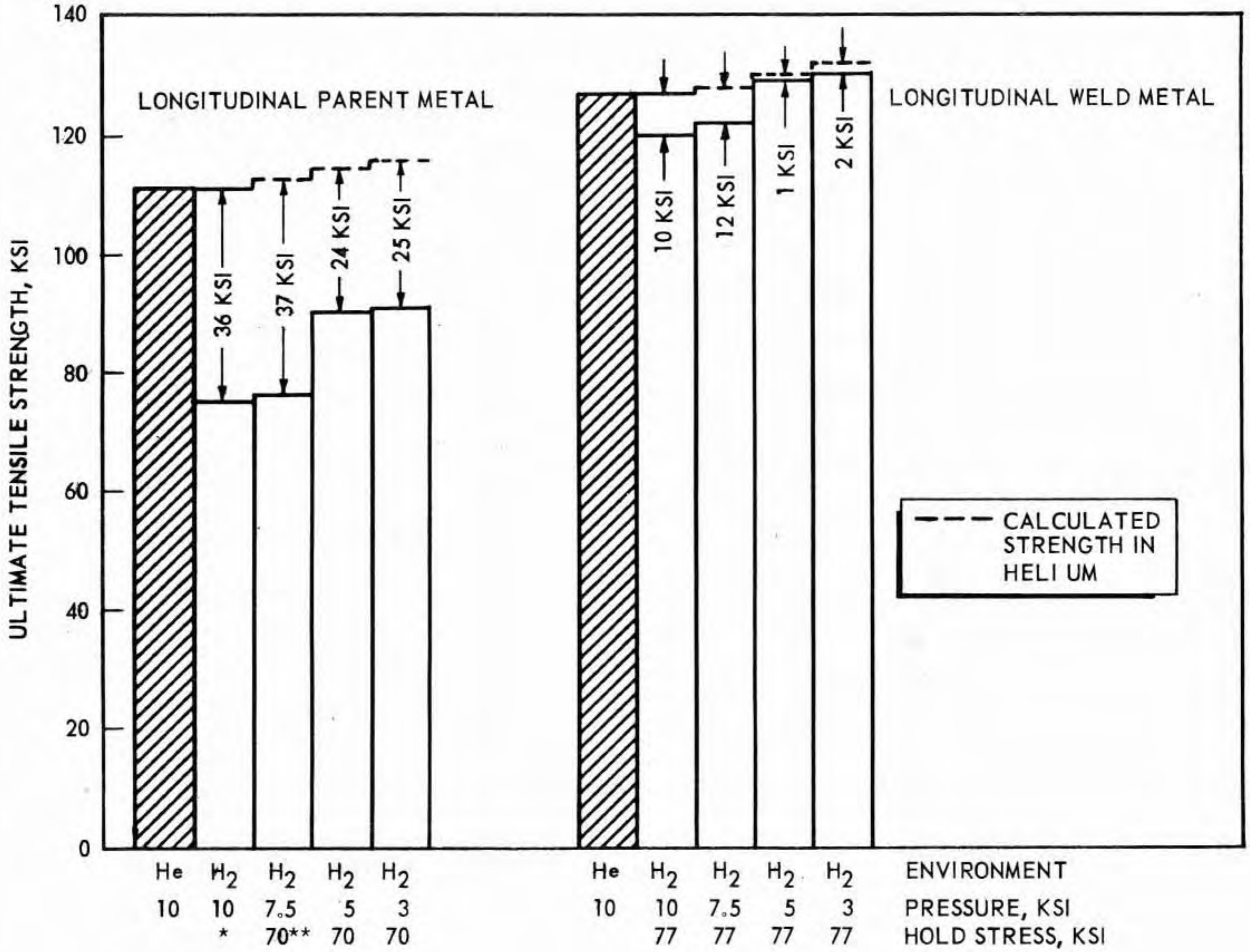


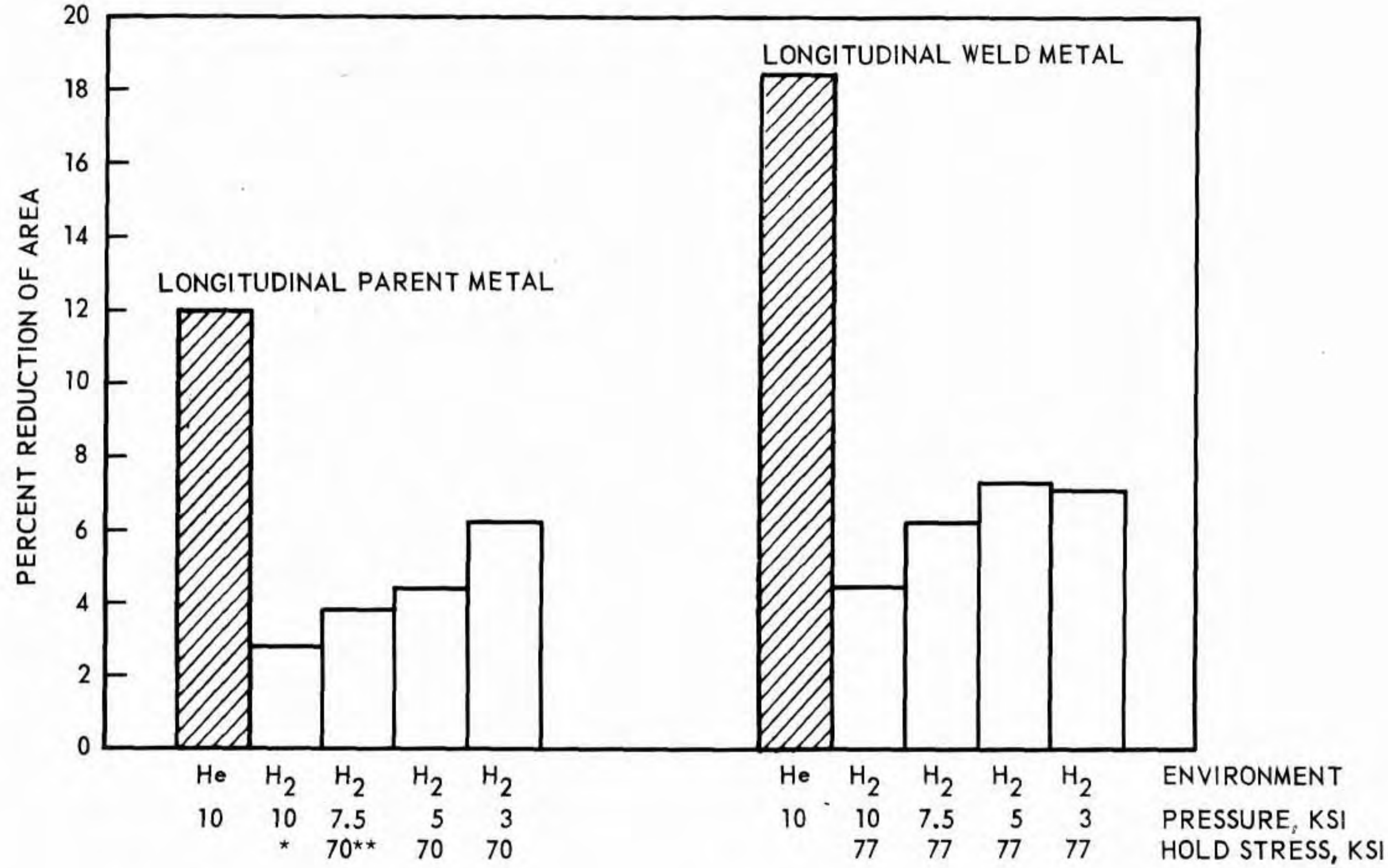
Figure 25. Reduction of Area in 10,000 psi Hydrogen and Helium of A-212-61T Gr. B-FB Notched Parent Metal Specimens



* BROKE ON PRELOADING

** ONE OF THE TWO SPECIMENS BROKE AFTER 4 1/2 HOURS OF HOLD PERIOD

Figure 26. Effect of Hydrogen Pressure on the Ultimate Tensile Strength of A-212-61T Gr. B-FB Notched Longitudinal Parent Metal and Longitudinal Weld Metal Specimens; 1-Day Hold



* BROKE ON PRELOADING

** ONE OF THE TWO SPECIMENS BROKE AFTER 4 1/2 HOURS OF HOLD PERIOD

Figure 27. Effect of Hydrogen Pressure on Reduction of Area of A-212-61T Gr. B-FB Notched Longitudinal Parent Metal and Longitudinal Weld Metal Specimens; 1-Day Hold

For hydrogen pressures of 3000 and 5000 psi, the strength of the weld metal specimens was about the same as the calculated strengths in helium at the same pressures, i.e., there was no decrease of strength due to exposure to hydrogen for pressures of 3000 and 5000 psi. However, there was an appreciable decrease of strength of the parent metal specimens at 3000 and 5000 psi hydrogen pressure. At 3000 psi, there is about an 18 percent reduction of strength from that in 10,000 psi helium and about 22 percent reduction of strength from the calculated strength in 3000 psi helium.

The ductility of both the parent metal and weld metal specimens definitely increased with decreasing pressure.

Visual examination of the fracture of the two A-212 parent metal specimens which fractured after 8 and 44 days under load revealed an unusual appearance. There was an outer brittle region containing crack-like facets extending from the edge toward the center of the fracture. The central region of both fractures had a more ductile appearance and did not contain the crack-like flaws.

T-1. The T-1 specimens most affected by exposure to hydrogen were longitudinal weld specimens notched in the weld. The ultimate strength of specimens notched in the weld and in the heat-affected zone of the longitudinal weld are plotted in Fig. 28. Two specimens notched in the weld broke between 1/2 and 2 hours in 10,000 psi hydrogen after being loaded to a hold stress of 137,000 psi, which corresponds to a 32 percent reduction of strength. A third specimen notched in the weld broke on preloading with a 43 percent strength reduction. The strength of those specimens that did not fail during the 1- and 10-day hold periods had very similar strength reductions of 14, 15, 16, and 17 percent.

The ductilities of the T-1 longitudinal weld specimens notched in the weld and the heat-affected zone are shown in Fig. 29. The ductility of the notched specimens was considerably less in hydrogen than in helium.

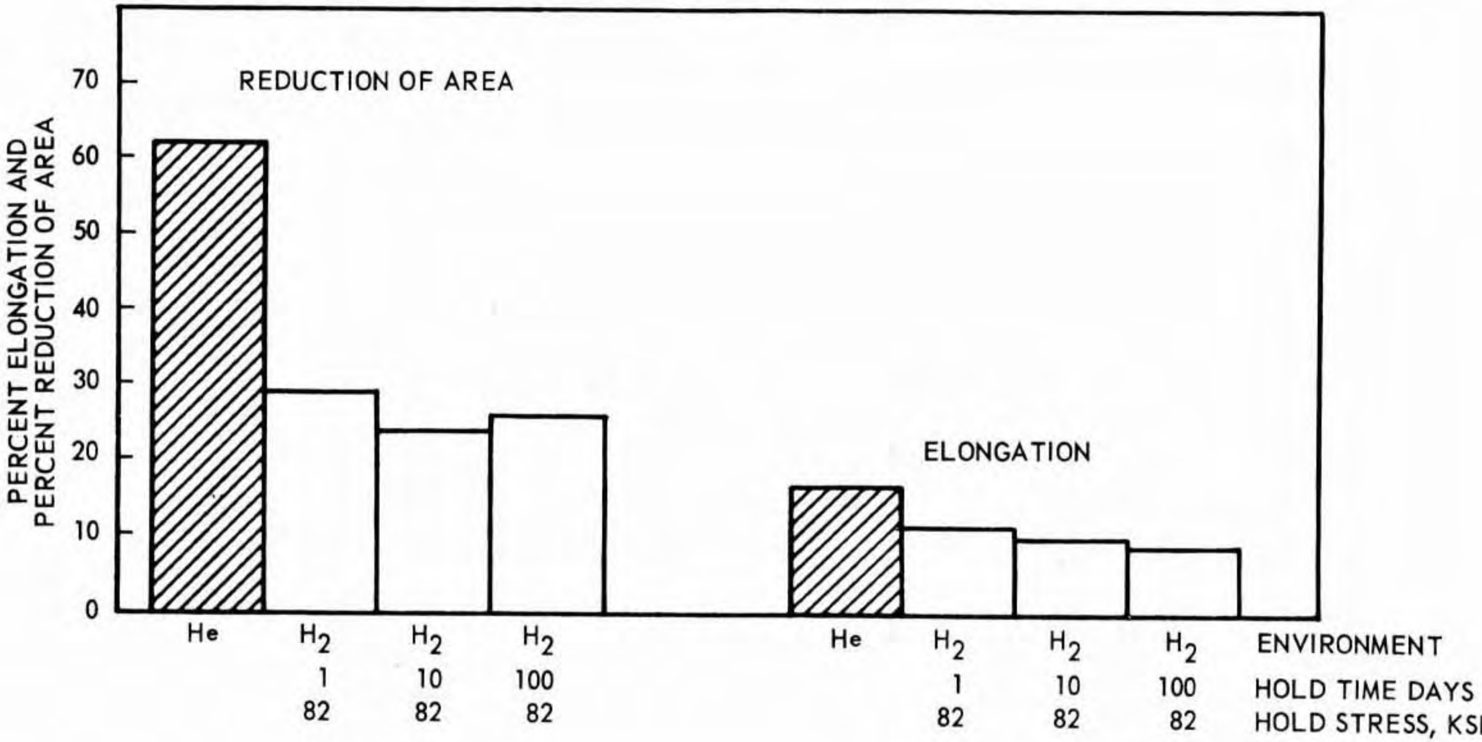


Figure 28. Elongation and Reduction of Area in 10,000 psi Hydrogen and Helium of A-517-64 Gr. F(T-1) Unnotched Longitudinal Weld Specimens

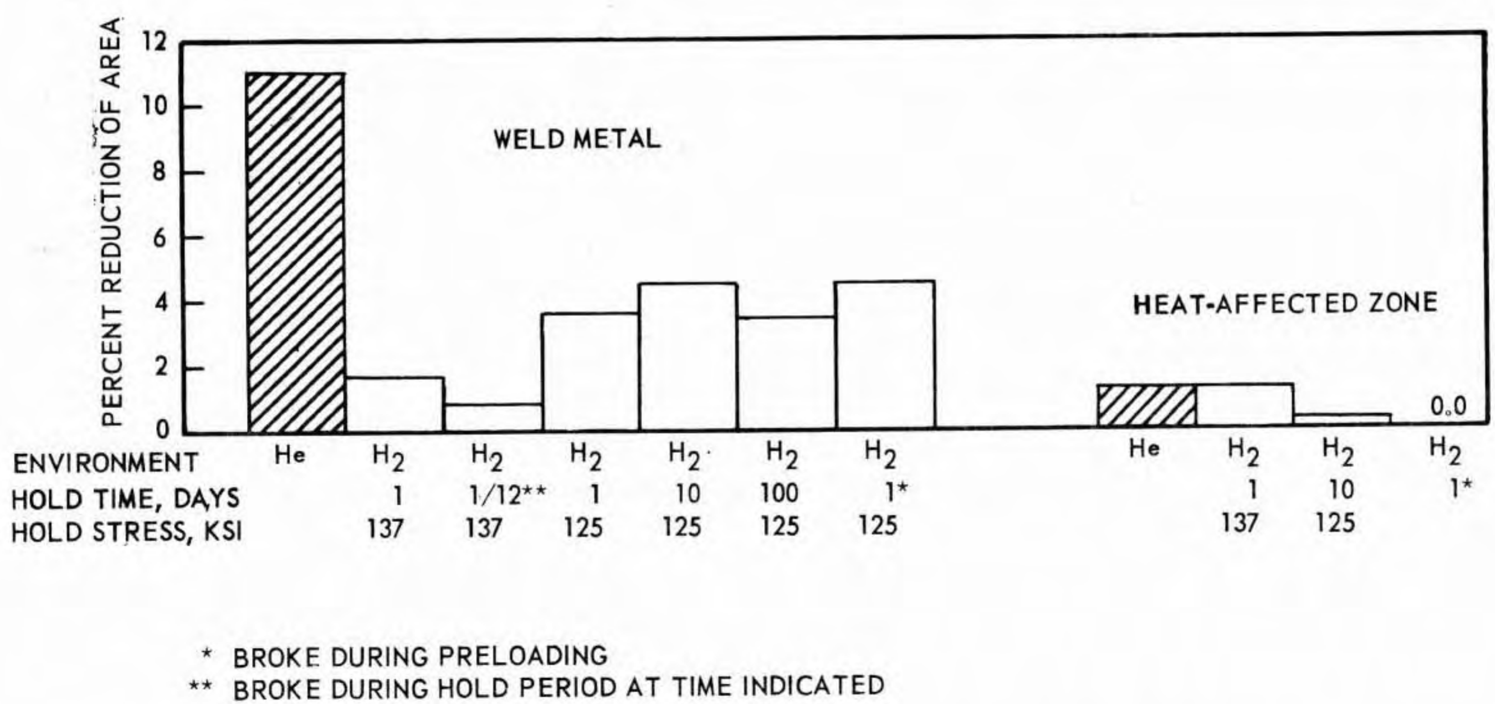


Figure 29. Reduction of Area in 10,000-psi Hydrogen and Helium of A-517-64 Gr. F(T-1) Specimens Notched in Longitudinal Weld and in Heat-Affected Zone

A series of T-1 longitudinal weld specimens notched in the weld which were tested in hydrogen were examined by electron fractography. The results of the examination showed that the fracture surfaces appeared essentially the same as the A-302 longitudinal weld metal fracture surfaces.

The fracture surface-machined surface interface in the T-1 specimen was quite brittle (Fig. 30).

The fracture surface of the T-1 specimens that fractured during the hold period had a brittle-appearing outer ring and a ductile-appearing inner portion. Thus, these fracture surfaces resembled those for the A-212 specimens that failed during the hold period.

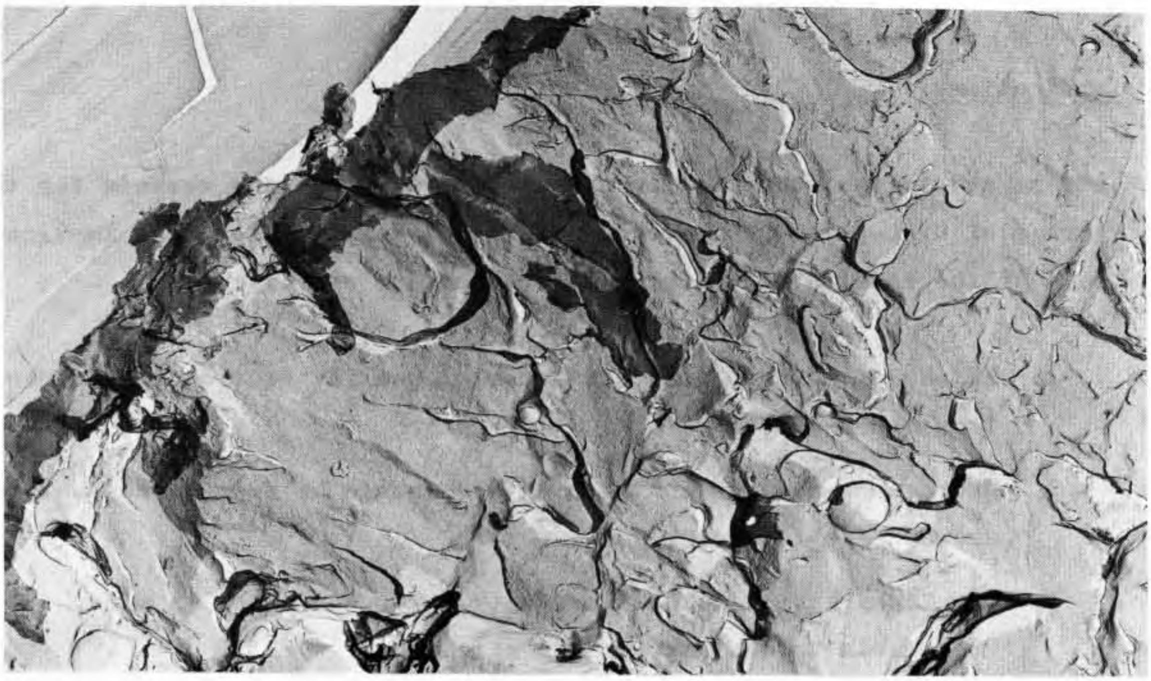
Summary

In summary, the important results of this program were as follows. The ultimate tensile strengths of notched specimens of the three steels tested were reduced considerably by high-pressure hydrogen environments. The magnitude of the strength reduction varied with the type of specimen and test conditions but ranged as high as 59 percent for A-302 specimens, 41 percent for A-212 specimens, and 51 percent for T-1 specimens. The reduction of notched strength was accompanied by a considerable decrease of the notched ductility. There was no appreciable effect of high-pressure hydrogen environments on the ultimate tensile strength of unnotched specimens, but there was a substantial decrease of ductility of these specimens. An important phenomenon encountered in unnotched specimens tested in high-pressure hydrogen environments was surface cracking in the necked-down region with the cracks oriented essentially normal to the direction of the applied load.

The major portion of the embrittling effect of the high-pressure hydrogen occurred immediately; i.e., as rapidly as a test could be run. There may be an effect of hold time, but it is smaller.

Machined
Surface

Fracture



7146-A   Electron Fractograph   7500X

Figure 30. A-517 Notched Longitudinal Weld Specimen Tested in 10,000-psi Hydrogen; 1-Day Hold

Of the parent metals, the lowest strength steel, the A-212, was the most affected by the high-pressure hydrogen. However, this was believed due to the fact that A-212 had the lowest yield strength-to-ultimate strength ratio of the three steels tested.

The brittle fracture mode at the machined surface-fracture surface interface of the notched specimens suggests that the effect of high-pressure hydrogen is a surface (environmental) effect.

Implications

With regard to the construction and use of large, welded vessels for the storage of high-pressure hydrogen at ambient temperatures, the implications of the results of the present program are as follows:

1. Effect of notches indicates special quality control and inspection necessary.
2. Hydrogen pressures in tanks in use should be reduced below those deemed safe for inert gas.
3. New tanks should be designed with lower strengths in mind. Preferable to design to yield strengths.
4. Safest procedure at this time appears to be the use of vented stainless steel liner.

The considerable effect of notches in specimens tested in high-pressure hydrogen in this and other programs indicates that special quality control measures and continuing inspection are of vital importance in high-pressure hydrogen vessels to ensure that no cracks or stress raisers are present on the interior surfaces of the vessels. It should be noted that the notch used in this program was a relatively mild one. The reductions of notched strength which have been found for steels tested in high-pressure hydrogen indicate that existing vessels should be operated at lower pressures than would be considered safe for the storage of, for example, nitrogen, argon, or helium. Future vessels should be designed with the lower strengths in mind.

The tests on the A-302 specimens indicate reductions of ultimate strength by 10,000 psi hydrogen as high as 59 percent, which was for girth weld specimens notched in the heat-affected zone. However, since the girth weld would be stressed only to approximately 50 percent of the hoop stress, which acts across the longitudinal weld, the low strength of the heat-affected zone of the girth weld would probably not be the determining factor. The critical problem area of the A-302 vessels would probably be the longitudinal weld metal which had a reduction of notched strength after 100-day exposure to 10,000 psi hydrogen of approximately 26 percent, the most embrittling exposure tested for this material. Therefore, for operation of an A-302 vessel at 10,000 psi, a 26 percent reduction of pressure from that believed safe for the storage of an inert gas appears reasonable.

For the T-1 steel, the longitudinal weld specimens notched in the weld or in the heat-affected zone were the most susceptible to embrittlement by high-pressure hydrogen. Testing in 10,000 psi hydrogen resulted in isolated failures on preloading at strength reductions of 42 percent for a specimen notched in the heat-affected zone. Delayed failures were observed at strengths 30 percent below the ultimate strength for specimens notched in the weld metal. There was essentially no improvement of strength of T-1 specimens because the hydrogen pressure at which the tests were conducted went from 10,000 to 3000 psi. Thus, in this pressure range, T-1 pressure vessels should be operated at a hydrogen pressure at least 30 percent, and possibly as high as 50 percent, below the pressure considered safe for the storage of an inert gas.

The A-212 parent metal specimens were more susceptible to embrittlement than the weld metal specimens. The tests conducted in 10,000 psi hydrogen indicate a 41 percent strength reduction. However, the tests conducted at 3000 and 5000 psi hydrogen pressure indicated that the loss of strength was approximately 32 percent less than in 10,000 psi hydrogen. Therefore, an A-212 vessel suitable for the storage of an inert gas at 5000 psi should not be used to store hydrogen at a pressure above approximately 3600 psi, i.e., 28 percent below 5000 psi.

The reductions of design strengths or operating pressures recommended above for the storage of high-pressure hydrogen should be considered as tentative, minimum reductions since many untested factors such as cyclical loading or sharper notches could combine with the high-pressure hydrogen environment to result in even greater reductions.

If it were possible, it would appear more reasonable to design high-pressure hydrogen storage vessels on the basis of yield strength rather than ultimate tensile strength.

The safest procedure at this time appears to be to use a vented austenitic stainless steel liner in the vessels. The stainless steel should be a highly stable one which does not appreciably transform to martensite on cold working, e.g., Types 310, 316, or 305. Recent work (Ref. 28) has shown that the ultimate tensile strength of 304L stainless steel was considerably (up to 19 percent) lower in 10,000 psi hydrogen than in 10,000 psi nitrogen. The same investigators found no effect of high-pressure hydrogen on 310 stainless steel.

PRESENT ROCKET PROGRAM

Presently, at Rocketdyne, a NASA-funded program is underway to investigate the effects of high-pressure hydrogen on a wide variety of materials (37) under various conditions. The program consists of the following phases:

- Phase I: Influence of Short Time Duration on the Degree of Embrittlement
- Phase II: Screening Tests to Determine the Effect of High-Pressure Hydrogen on a Variety of Alloys

Phase III:	Effect of Sustained Loads and Long Time Duration on the Degree of Embrittlement
Phase IV:	Influence of Gas Pressure on the Degree of Embrittlement
Phase V:	Influence of Notch Severity on the Degree of Embrittlement
Phase VI:	Influence of Hydrogen on Low Cycle Fatigue Properties
Phase VII:	Relation Between the Mechanical Properties of Steels and Susceptibility to Hydrogen Embrittlement
Phase VIII:	Protection from Hydrogen Embrittlement
Phase IX:	Effect of a Clean Surface on Embrittlement

Some preliminary results on A-302, Ti-6Al-4V, and 310 stainless steel are available. These tests were made in 10,000 psi hydrogen on unnotched and sharply notched (K_T = 8 to 9) specimens with no hold stresses and hold times of 0, 1, 8, and 24 hours for A-302 and 310 stainless steel and 0 and 24 hours for Ti-6Al-4V.

The length of the hold period had no effect. With unnotched A-302 specimens, the high-pressure hydrogen did not affect the ultimate tensile strength but the ductility as measured by reduction of area was reduced nearly 50 percent, which is higher than found for parent metal A-302 in the earlier program. For notched A-302 specimens, the strength was reduced by about 22 percent (as opposed to 14 percent in the earlier tests with K_T = 4.2) and the percent reduction of area was reduced from 11 percent (with helium) to 3.5 percent.

The ultimate tensile strength and ductility of the unnotched Ti-6Al-4V specimens were not affected by the high-pressure hydrogen but some surface cracking took place. Notched specimens, however, had reductions of strength as high as 35 percent but with no loss of ductility. The ductility of notched specimens in helium was very low, about 2 percent.

The ultimate tensile strength and ductility of unnotched 310 stainless steel specimens were not affected by the high-pressure hydrogen and no surface cracking was found. Notched specimens experienced small decrease in strength, about 5 percent, and ductility, from 20 percent in helium to 17.5 percent in hydrogen.

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