HYDROGEN EMBRITTLEMENT AND ITS CONTROL IN HYDROGEN-FUELED ENGINE SYSTEMS*

W. T. Chandler

Rockwell International/Rocketdyne Division

INTRODUCTION

It has been found that hydrogen environments, particularly high-pressure hydrogen environments, seriously degrade the mechanical properties of many metals, including several of those considered for use in advanced propulsion systems (ref. 1). Thus, the design, fabrication, and operation of such systems require a thorough understanding and consideration of all aspects of hydrogen embrittlement.

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SSME PROPELLANT FLOW SCHEMATIC

(Figure 1)

An example of an advanced, hydrogen-fueled engine is the Space Shuttle Main Engine (SSME), the rocket engine that will be used for the propulsion of the Space Shuttle vehicle. These engines, currently under construction at Rocketdyne Division/Rockwell International, are high-performance rocket engines that use oxygen and hydrogen propellants, and the hydrogen pressures in the SSME are higher than encountered in previous production engines. As shown in the flow schematic in the figure, liquid hydrogen is pumped first through a low-pressure turbopump and then a high-pressure turbopump to a pressure above 41.4 MN/m^2 (6000 psi). The high-pressure hydrogen is used to cool various structures such as the rocket nozzle and the hot-gas manifold and to drive the low-pressure pump turbine and, when reacted with oxygen, the high-pressure pump turbine before it is further reacted with oxygen and exhausted out the rocket nozzle to provide the thrust. Thus, in the SSME, metals are in contact with hydrogen at pressures from 0.21 MN/m^2 (30 psi) to over 41.4 MN/m^2 (6000 psi) and at temperatures from 20 K (-423 F) to over 922 K (1200 F).

In this paper, the nature of hydrogen embrittlement by high-pressure gaseous hydrogen will be described and methods of designing the SSME gaseous hydrogen systems, including techniques of hydrogen embrittlement prevention, will be discussed. Other than the possible effects of the cryogenic temperature, a liquid hydrogen environment does not have a deleterious effect on the properties of metals. Thus, the paper will be limited to discussing the effects of gaseous hydrogen environments. Extensive investigations of the effects of gaseous hydrogen environments on metals have been conducted at Rocketdyne under the SSME program and other NASA programs, all monitored by Marshall Space Flight Center. Results from these programs will be presented.

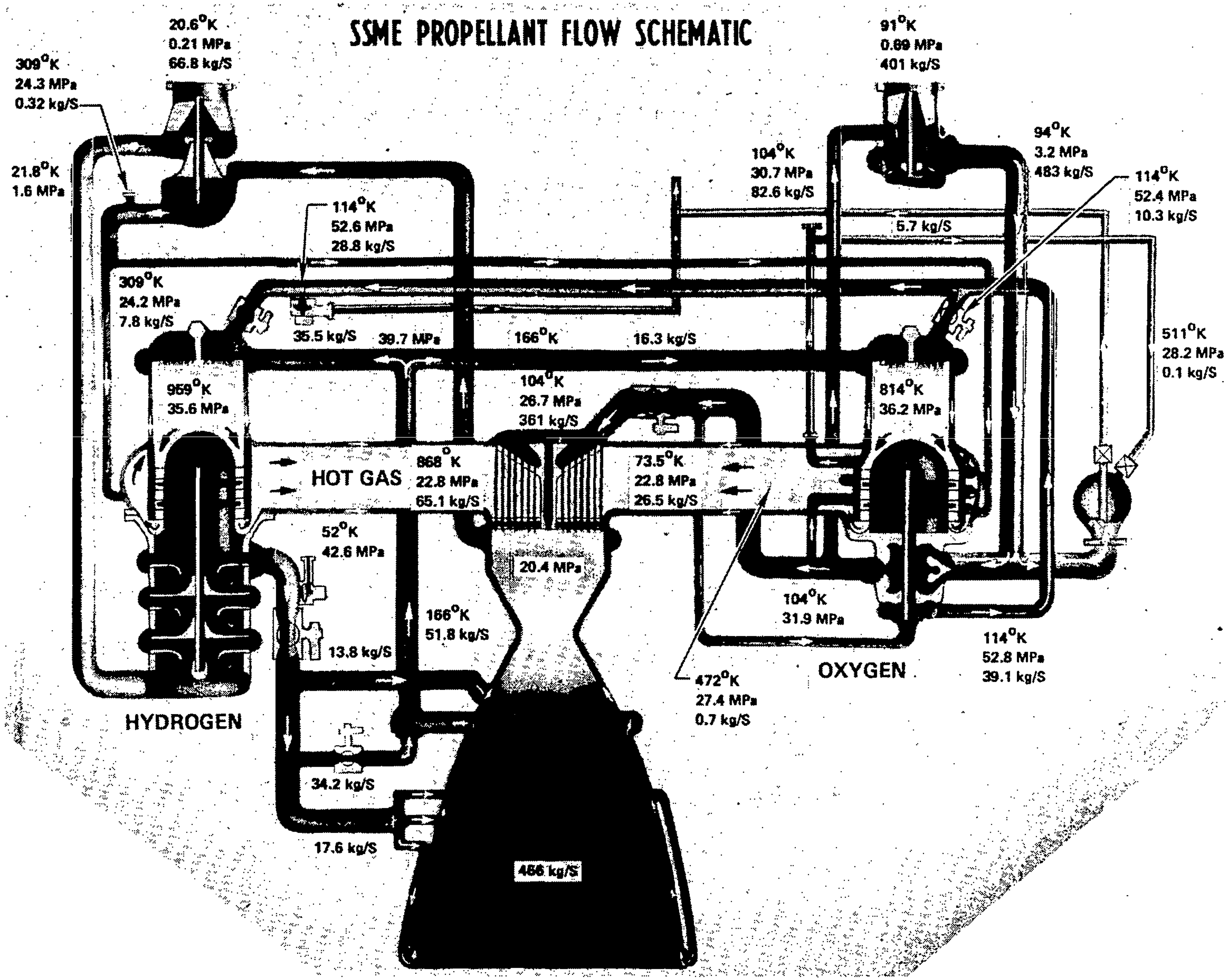

SSME PROPELLANT FLOW SCHEMATIC
20.6°K
0.21 MPa
66.8 kg/S
309°K
24.3 MPa
0.32 kg/S
21.8°K
1.6 MPa
91°K
0.69 MPa
401 kg/S
94°K
3.2 MPa
483 kg/S
104°K
30.7 MPa
82.6 kg/S
114°K
52.4 MPa
10.3 kg/S
5.7 kg/S
114°K
52.6 MPa
28.8 kg/S
309°K
24.2 MPa
7.8 kg/S
35.5 kg/S
39.7 MPa
166°K
16.3 kg/S
511°K
28.2 MPa
0.1 kg/S
959°K
35.6 MPa
104°K
26.7 MPa
361 kg/S
814°K
36.2 MPa
HOT GAS
868°K
22.8 MPa
65.1 kg/S
73.5°K
22.8 MPa
26.5 kg/S
52°K
42.6 MPa
20.4 MPa
104°K
31.9 MPa
166°K
51.8 kg/S
13.8 kg/S
114°K
52.8 MPa
39.1 kg/S
472°K
27.4 MPa
0.7 kg/S
OXYGEN
HYDROGEN
34.2 kg/S
17.6 kg/S
466 kg/S

Figure 1

TYPES OF HYDROGEN EMBRITTLEMENT

(Figure 2)

It is important to recognize that there are different types of hydrogen embrittlement that may be interrelated but have different embrittlement characteristics.

Hydrogen embrittlement may be classified into: (1) hydrogen reaction embrittlement, (2) internal-hydrogen embrittlement, and (3) hydrogen-environment embrittlement (ref. 1). Hydrogen-reaction embrittlement results when a chemical reaction occurs between hydrogen and the metal or some constituent in the metal to form an embrittling phase. For example, metals such as titanium, zirconium, columbium, and tantalum (present either as the base metal or as an alloying element) can react with hydrogen to form embrittling hydrides. Other long recognized examples of hydrogen-reaction embrittlement are the reaction of hydrogen with oxygen in copper to form water vapor or with carbon in steels to form methane. In either case, the resultant gas settles into voids or cracks at very high pressures, thus embrittling the metal by tending to force the crack apart and extending it. Also, the decarburization of a steel will reduce its strength. Hydrogen-reaction embrittlement is essentially a permanent, nonreversible embrittlement and increased temperatures and hydrogen pressures increase the rates of reaction and thus increase the tendency toward this type of embrittlement.

Internal-hydrogen embrittlement is that due to hydrogen which has been absorbed and permeated into the metal. The most widely recognized example of this embrittlement is the delayed failure of hydrogen-charged, high-strength steels. The absorption of hydrogen from a gas will be increased by increased temperature and gas pressure; however, for a given concentration of absorbed hydrogen, internal-hydrogen embrittlement is most severe in the vicinity of room temperature. Internal-hydrogen embrittlement is reversible in that, if cracks have not been formed, and if the hydrogen is removed from the metal, there is no embrittlement.

The term hydrogen-environment embrittlement (HEE) is used to signify the degradation of mechanical properties of a metal that occurs while the metal is exposed to a hydrogen environment as compared to an inert environment.

TYPES OF H_2 EMBRITTLEMENT

- HYDRIDE FORMATION - Ti, Zr, Cb, Ta
- HYDROGEN REACTION - C IN STEEL $\rightarrow$ CH_4

  O_2 IN Cu $\rightarrow$ H_2O
- INTERNAL HYDROGEN EMBRITTLEMENT - STEELS
- HYDROGEN-ENVIRONMENT EMBRITTLEMENT

Figure 2

CHARACTERISTICS OF HEE

(Figure 3)

Susceptible metals are embrittled by hydrogen environments in the sense that: (1) the ductility of the metal is lower in hydrogen than in other environments, (2) tensile plastic deformation in hydrogen results in surface cracking, (3) subcritical crack growth occurs in hydrogen, and (4) crack growth rates for given cyclic or sustained stress intensities are faster in hydrogen than in inert environments (ref. 1).

CHARACTERISTICS OF HEE

- NOTCH STRENGTH IS LOWER IN GH_2
- DUCTILITY IS LOWER IN GH_2
- TENSILE PLASTIC DEFORMATION IN GH_2 RESULTS IN SURFACE CRACKING
- THRESHOLD STRESS INTENSITIES FOR CRACK GROWTH ARE LOWER IN GH_2
- CRACK GROWTH RATES ARE FASTER IN GH_2

Figure 3

TENSILE TEST

(Figure 4)

The elastic properties and tensile yield strengths of metals are the same in hydrogen as in air or inert environments, as shown in the idealized stress/strain curve for a tensile test in hydrogen in the figure. The most significant effects of high-pressure hydrogen environments are on tensile ductility, notch tensile strength, and crack behavior. More precisely, the effect of the hydrogen environment is to embrittle the surface. The embrittled "surface" may be the immediate surface or a surface layer of some finite but limited thickness. The metal surface cannot undergo plastic deformation in tension to the same degree in hydrogen as it can in air or inert environments. When a susceptible metal is stressed in tension in hydrogen to some critical amount of plastic deformation, the surface fractures (i.e., a surface crack forms).

From the time that surface cracking begins, the test is no longer a normal tensile test but is a rather complex test of a crack specimen; this must be considered in assessing the meaning and usefulness of the strength and ductility data obtained from these tests.

TENSILE TEST

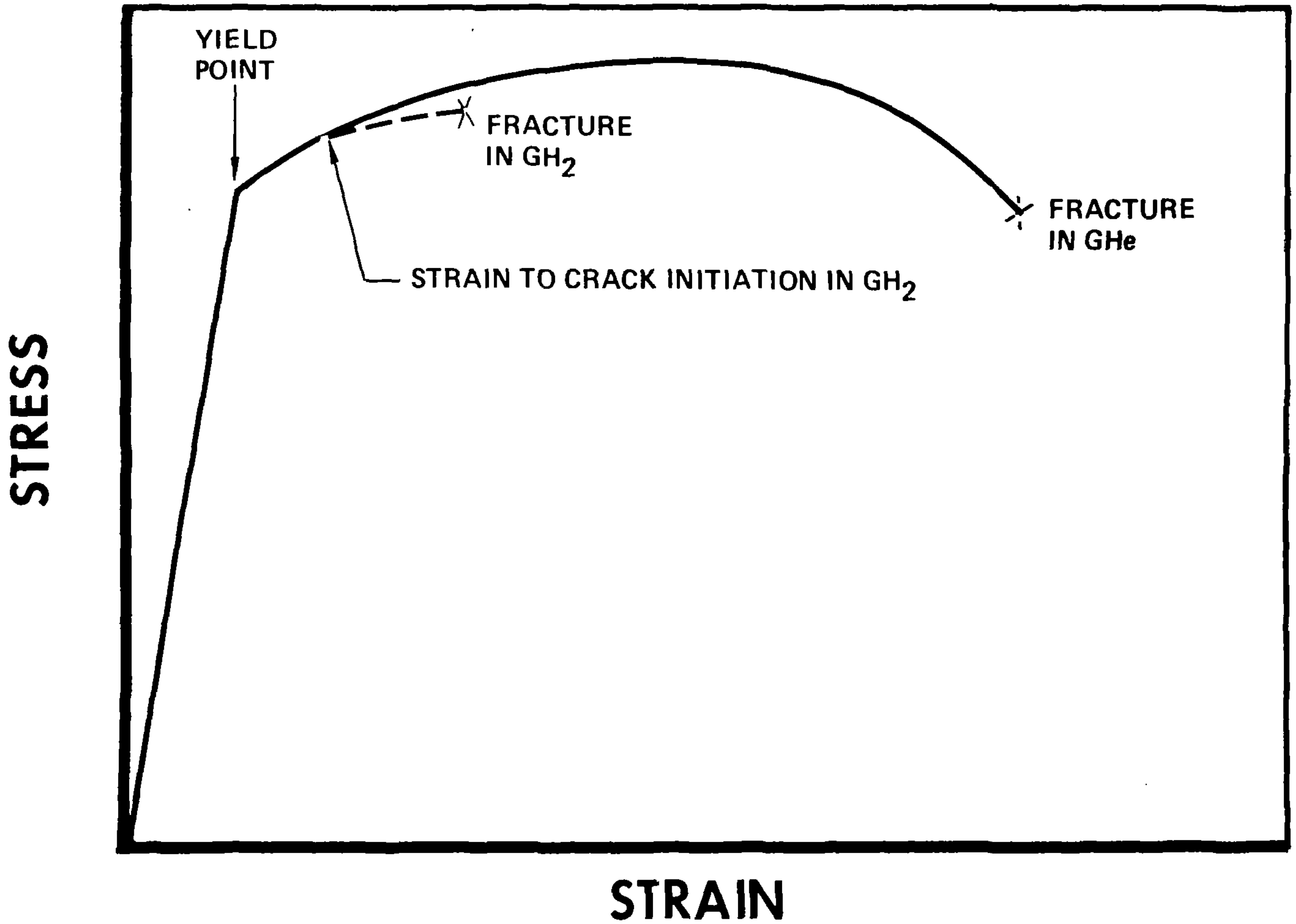


Figure 4

SURFACE CRACKING IN ASTM A-533-B STEEL IN H_2 AT RT

(Figure 5)

Surface cracks, examples of which are shown in the figure, provide some of the most dramatic visual evidence of hydrogen-environment embrittlement. The figure presents photomacrographs (10X) of ASTM A-533-B steel specimens that have been tensile tested in helium and in hydrogen at two pressures, all at room temperature (RT). The ASTM A-533-B steel is a low alloy steel that has been used extensively in large vessels for the storage of gases, including hydrogen, at high pressures.

For a susceptible metal, an existing crack or one formed in the hydrogen environment will propagate at a lower stress intensity and at a more rapid rate for a given stress intensity in hydrogen than in air or inert environments.

SURFACE CRACKING IN ASTM A-533-B STEEL IN H_2 AT RT

HELIUM
68.9 MN/m^2 (10,000 PSI)

HYDROGEN
6.89 MN/m^2 (1000 PSI)

HYDROGEN
68.9 MN/m^2 (10,000 PSI)

Figure 5

HEE OF EDNi VERSUS HYDROGEN PRESSURE H_{P_2}

(Figure 6)

Hydrogen-environment embrittlement is an environmental effect and no hold time in the hydrogen environment is required to establish the embrittlement. However, hydrogen-environment embrittlement is very sensitive to test rate, that is, strain rate or crack propagation rate. At high strain or crack propagation rates, the effect of the hydrogen environment will be reduced or eliminated. This is evidenced by the fact that the final failure in a tensile specimen pulled in hydrogen is a ductile, overload failure that is unaffected by the hydrogen environment. The effect of test rate is related to the rates of the processes by which hydrogen moves from the environment onto or into the metal. Thus, environmental parameters are of great importance.

For example, the degradation of tensile properties by hydrogen environments increases with increasing hydrogen pressure as shown in the figure for electrodeposited nickel, EDNi (N_{H_2} and N_{air} are the tensile strengths of notched specimens in hydrogen and air, respectively). It should be noted that significant effects of hydrogen environments on properties can occur at pressures of 1 atmosphere or lower.

The effect of hydrogen pressure on the degree of hydrogen-environment embrittlement probably pertains to any property involving a test rate, for example, strain rate or crack growth rate, and is related to the effect of hydrogen pressure on the rate of transfer of hydrogen from the environment onto or into the metal as noted above.

HEE OF EDNi vs P_{H_2}

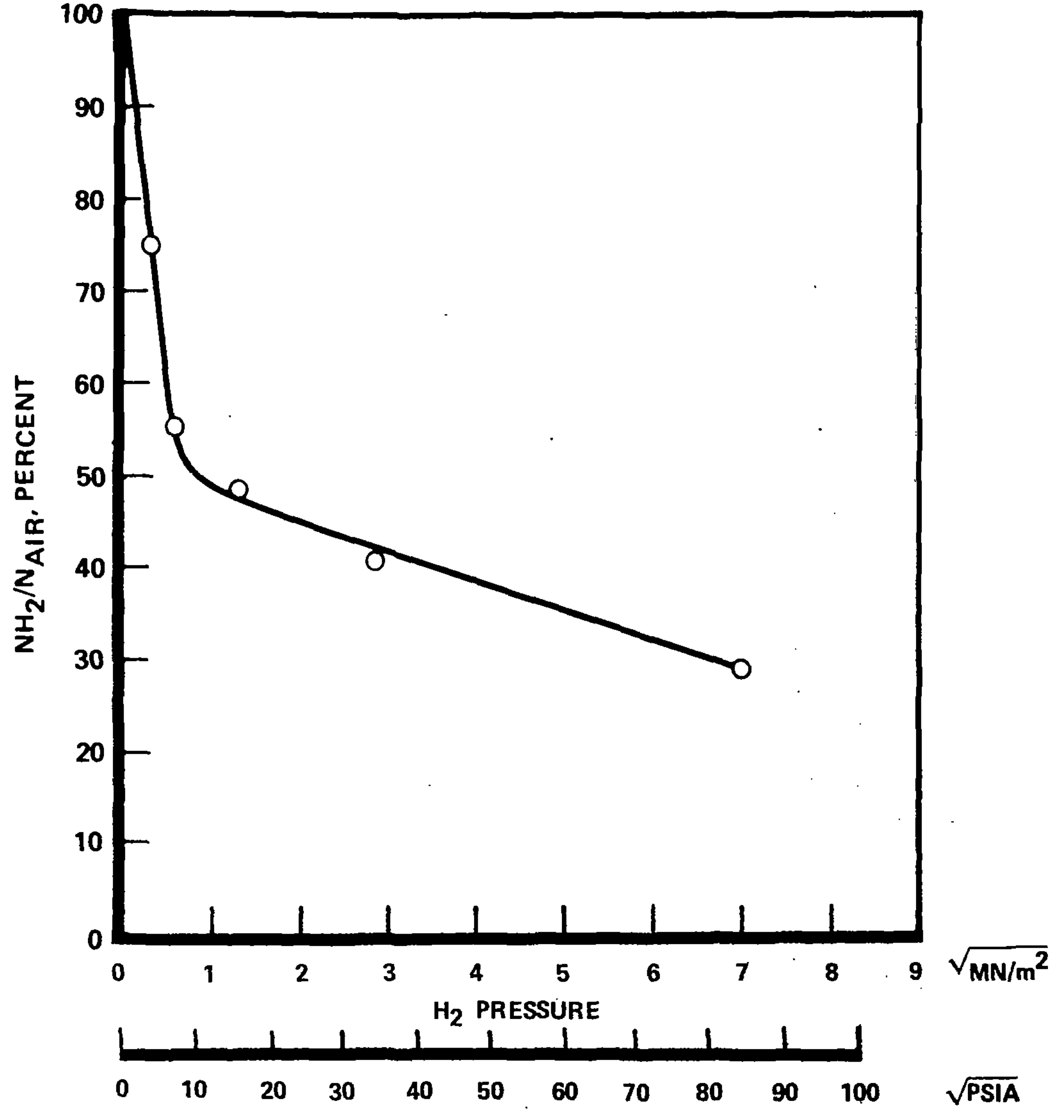


Figure 6

EFFECT OF TEMPERATURE ON HEE OF EDNi IN 8.3 MN/m^2 (1200 PSI) H_2

(Figure 7)

Hydrogen-environment embrittlement occurs over a wide range of temperatures from cryogenic (ref. 2) to at least 1144 K (1600 F), reference 3, but is most severe in the vicinity of (but not necessarily exactly at) room temperature. The variation in embrittlement with temperature may be quite rapid in the vicinity of room temperature as is shown in the figure for EDNi.

It should be remembered that at the higher temperatures there is the potential for hydrogen-reaction embrittlement or for the absorption of sufficient hydrogen to result in internal hydrogen embrittlement, particularly on subsequent cool down.

The interest at Rocketdyne in the hydrogen-environment embrittlement of electrodeposited nickel (EDNi) stems from the fact that the regeneratively cooled SSME combustion chamber is constructed of a copper-alloy liner in which slots are machined and closed out with EDNi to form the channels for the coolant hydrogen.

EFFECT OF TEMPERATURE ON HEE OF EDNi IN $8.3 MN/m^2$ (1200psi)H_2

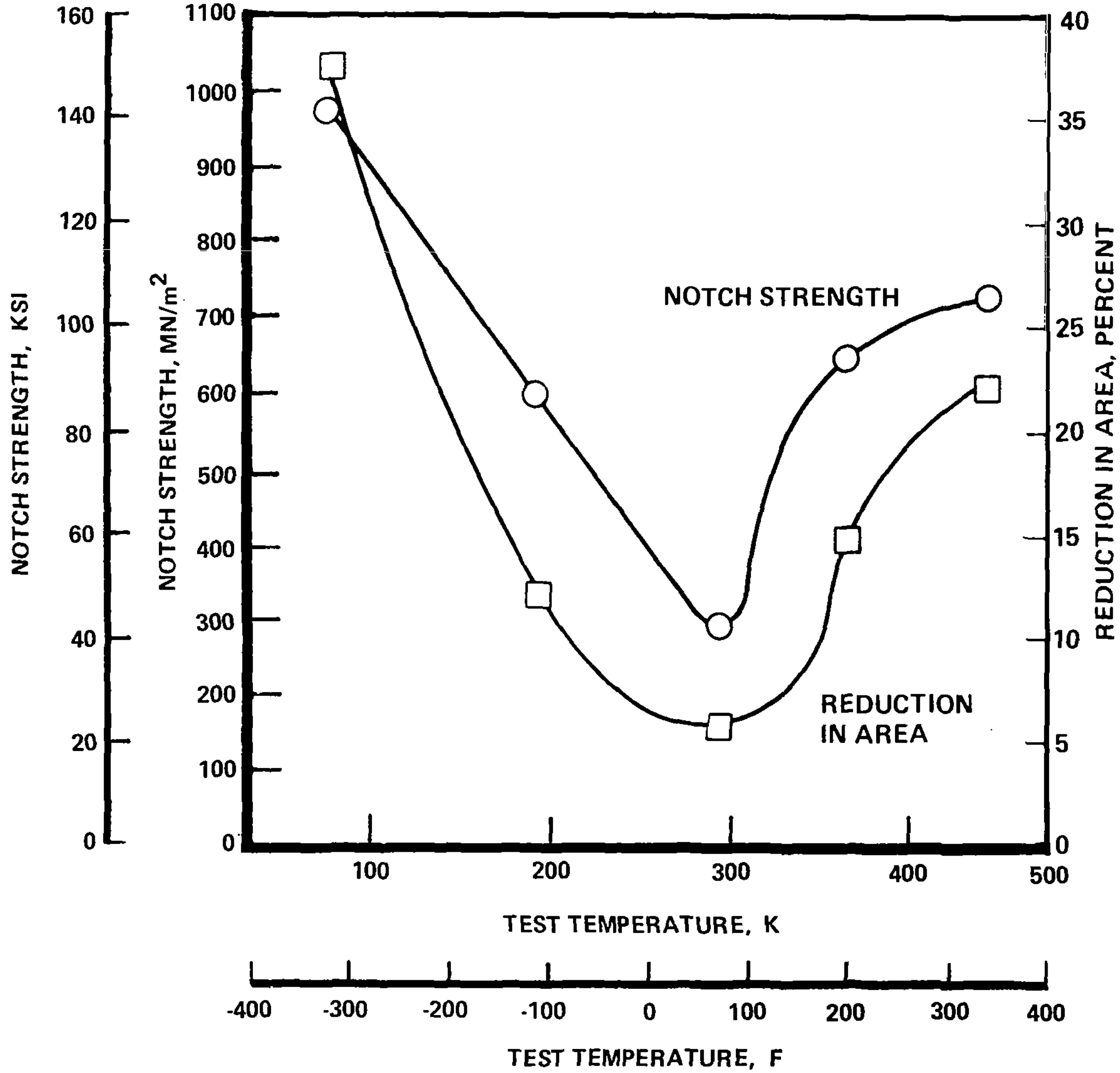


Figure 7

EFFECT OF O_2 IN GH_2 ON HEE AT RT
(Figure 8)

The purity of the hydrogen is important. For example, it has been found that even small amounts of oxygen in hydrogen inhibits hydrogen-environment embrittlement, as shown in the figure for a plain carbon (approximatley 0.20 percent carbon) steel (ref. 4). The embrittlement inhibiting effect of oxygen in 10.1 MN/m^2 (1500 psi) hydrogen becomes noticeable above 0.1 ppm oxygen.

The hydrogen gas to which the metals are exposed in the SSME is of very high purity. Thus, considerable effort has been expended at Rocketdyne in developing hydrogen purification and test system purging techniques to give a high purity hydrogen for property testing (ref. 5). Analyses of hydrogen samples taken at test location have yielded the following: < 0.2 ppm O_2, < 0.5 ppm Argon, 0.6 to 0.9 ppm N_2, < 0.5 ppm CH_4, < 0.5 ppm CO, < 0.5 ppm CO_2, and 208 K (-85°F) dewpoint (~1 ppm H_2O).

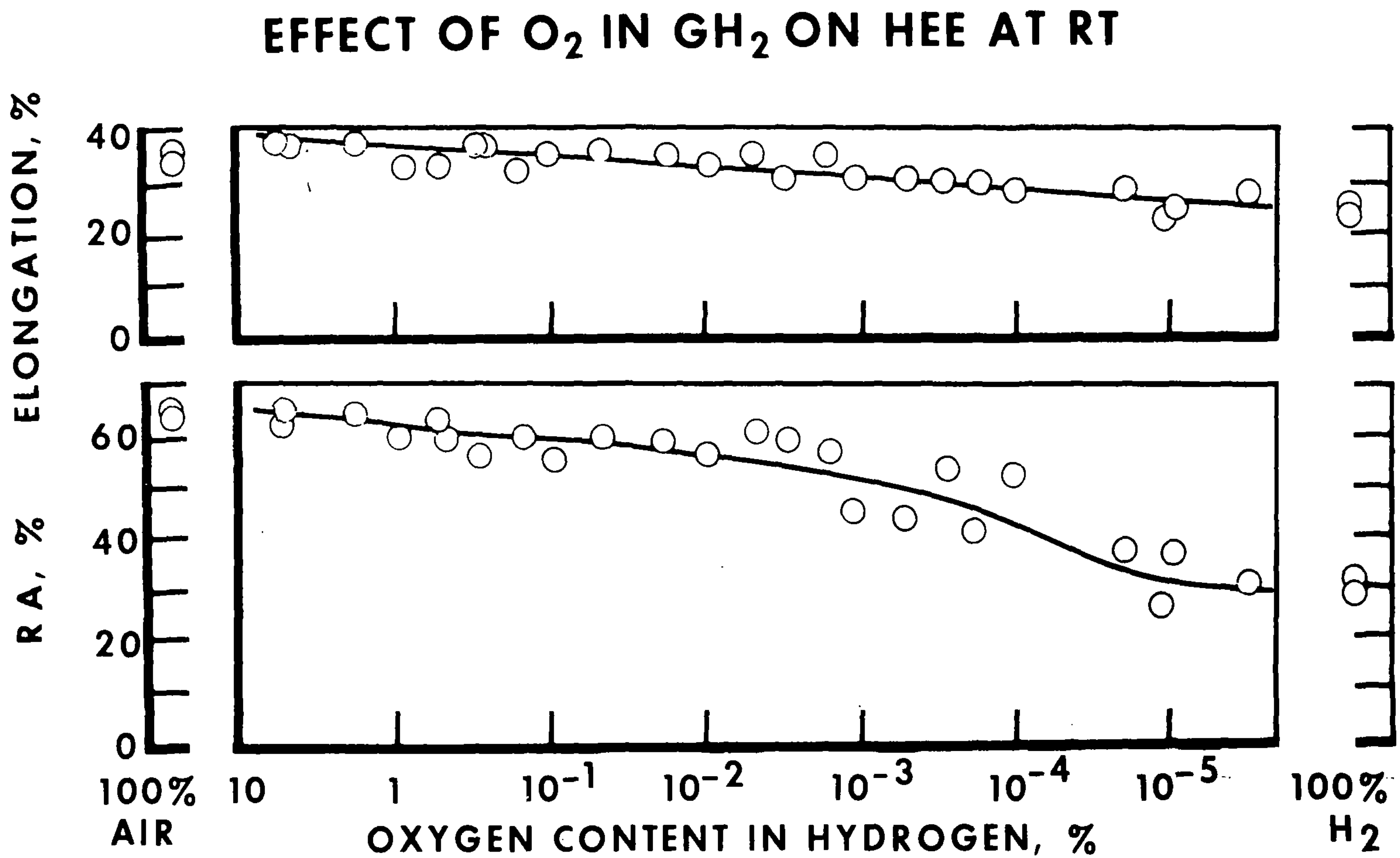

EFFECT OF O_2 IN GH_2 ON HEE AT RT
ELONGATION, %
RA, %
40
20
0
60
40
20
0
100%
AIR
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
100%
H_2
OXYGEN CONTENT IN HYDROGEN, %

Figure 8

DESIGNING FOR GH_2 SERVICE
(Figure 9)

The preceding summary of the characteristics of hydrogen-environment embrittlement suggests a number of approaches that can be employed in the design of hydrogen systems. The accompanying figure shows a simplified logic diagram for designing for hydrogen service. The remainder of the paper will be devoted to working through this diagram particularly as it has been applied to the SSME and with the presentation of supporting data.

First, of course, the service conditions should be carefully reviewed (considering all transient conditions) to determine if hydrogen-environment embrittlement is a potential problem.

DESIGNING FOR GH_2 SERVICE

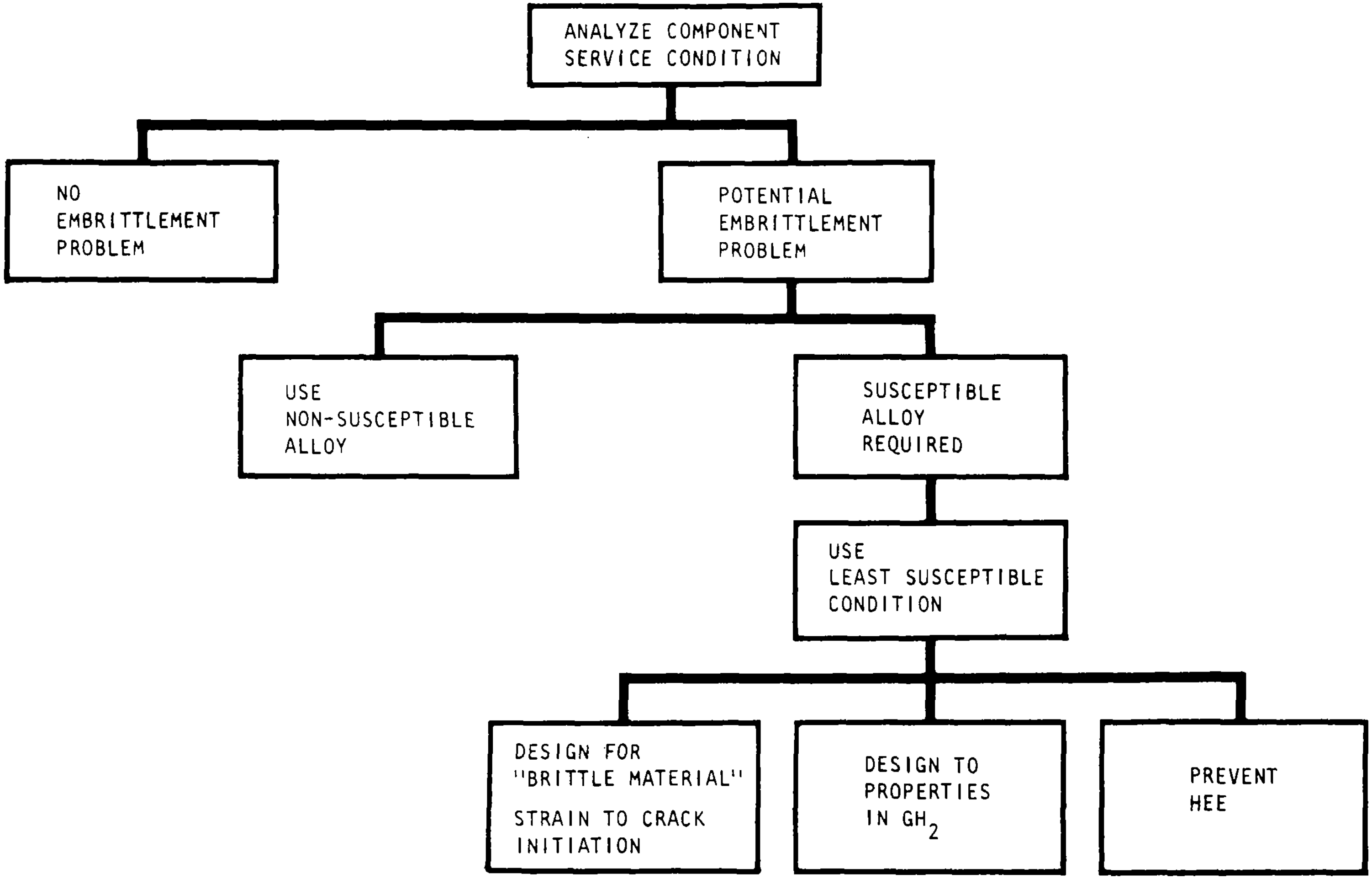


Figure 9

K_{IC} AND K_{TH} OF INCONEL 718 IN 34.5 MN/m^2 (5000 PSI) H_2 AND He
(Figure 10)

If the temperature of the metal part always remains well below room temperature, there may be no embrittlement caused by the hydrogen environment. For example, the figure presents low-temperature fracture mechanics data, K_{IC}, for Inconel 718, which is used extensively in the SSME. It can be seen from the sustained-load crack growth threshold stress intensity (K_{TH}) that there is a large effect of hydrogen at room temperature but a negligible effect at 144 K (-200 F).

K_{IC} AND K_{TH} OF INCONEL 718

IN 34.5 MN/m^2(5000 psi) H_2 AND He

HEAT TREATMENT	TEMPERATURE		HELIUM				HYDROGEN	
			K_{IC}		K_{TH}		K_{TH}	
	K	F	$MN/m^{3/2}$	KSI$\sqrt{IN.}$	$MN/m^{3/2}$	KSI$\sqrt{IN.}$	$MN/m^{3/2}$	KSI$\sqrt{IN.}$
1214, 991-894K (1725, 1325-1150F)	294 144	70 -200	78 98	71 89	58 81	53 74	14 73	13 66
1325, 1033-922K (1925, 1400-1200F)	294 200 144	70 -100 -200	119 160 122	108* 146* 111	112 160 138	102 146* 126	42 <46 123	38 <42 112

*NOT VALID PLANE STRAIN FRACTURE TOUGHNESS

Figure 10

MATERIALS EXTREMELY EMBRITTLED

(Figure 11)

If it is established that the conditions of hydrogen exposure are conducive to hydrogen-environment embrittlement, then, obviously, the first approach is to select metals not susceptible to hydrogen-environment embrittlement.

A large number of alloys have been investigated at Rocketdyne, and on the basis of tensile tests on unnotched and notched (stress intensity factor, K_t, = 8.4) specimens in 68.9 MN/m^2 (10,000 psi) hydrogen at room temperature, the alloys have been classified into four categories, viz., extreme, severe, slight, and negligible embrittlement. Unfortunately, as can be seen from this figure, most of the high-strength iron- and nickel-base alloys are extremely embrittled.

Embrittlement of alloys in this category is characterized by a large decrease of notch strength and ductility and some decrease of unnotched strength. Large reductions of ductility are found for all three common measures of ductility (elongation and reduction of area of unnotched specimens and reduction of area of notched specimens). Surface cracks are not usually found in failed specimens because the first crack to form quickly proceeds to failure before another crack can form.

MATERIALS EXTREMELY EMBRITTLED

68.9 MN/m² (10,000 psi) GH_2, RT

MATERIAL	STRENGTH RATIO, H_2/He		UNNOTCHED DUCTILITY			
			ELONGATION, PERCENT		RA,** PERCENT	
	NOTCHED (K_t = 8.4)	UNNOTCHED	He	H_2	He	H_2
18 Ni-250 MAR	0.12	0.68	8.2	0.2	55	2.5
410 SS	0.22	0.79	15	1.3	60	12
1042 QT	0.22	--	--	--	--	--
17-7 PH SS	0.23	0.92	17	1.7	45	2.5
Fe-9Ni-4Co-0.20C	0.24	0.86	15	0.5	67	15
H-11	0.25	0.57	8.8	0	30	0
RENE 41	0.27	0.84	21	4.3	29	11
ELECTROFORMED Ni*	0.31	--	--	--	--	--
4140	0.40	0.96	14	2.6	48	9
INCONEL 718	0.46	0.93	17	1.5	26	1
440 C	0.50	0.40	--	--	3.2	0

*TESTED IN 48.3 MN/m² (7000-PSI) H_2

**RA = REDUCTION IN AREA

Figure 11

MATERIALS SEVERELY EMBRITTLED

(Figure 12)

Metals that are severely embrittled by high-pressure hydrogen include ductile, lower strength steels, Armco iron, pure wrought nickel, and the titanium-base alloys. Embrittlement is characterized by a considerable reduction of notch strength and ductility, but no reduction of unnotched strength. The measure of ductility most affected by the high-pressure hydrogen environment is the reduction of area of notched specimens. A large number of deep surface cracks are found in failed specimens.

MATERIALS SEVERELY EMBRITTLED

68.9 MN/m² (10,000 psi) GH_2, RT

MATERIAL	NOTCH STRENGTH RATIO, H_2/He (K_t = 8.4)	UNNOTCHED DUCTILITY			
		ELONGATION, PERCENT		RA*, PERCENT	
		He	H_2	He	H_2
Ti-6Al-4V (STA)	0.58	--	--	--	--
430 F	0.68	22	14	64	37
NICKEL 270	0.70	56	52	89	67
A-515	0.73	42	29	67	35
HY-100	0.73	20	18	76	63
A-372 CLASS IV	0.74	20	10	53	18
1042 NORMALIZED	0.75			59	27
A-533-B	0.78			66	33
Ti-6Al-4V (ANNEALED)	0.79	--	--	--	--
AISI 1020	0.79			68	45
HY-80	0.80			70	60
Ti-5Al-2.5Sn ELI	0.81			45	39
ARMCO IRON	0.86			83	50

*RA = REDUCTION IN AREA

Figure 12

MATERIALS SLIGHTLY EMBRITTLED

(Figure 13)

The alloys shown in this figure were found to be only slightly embrittled by high pressure hydrogen with the embrittlement characterized by some decrease of strength of notched specimens, a negligible decrease in ductility of unnotched specimens, and the formation of only a few shallow surface cracks.

It should be noted that others have found 304 stainless steel to be more severely embrittled than is indicated in the figure. A more extensive discussion of the effects of high-pressure hydrogen on stainless steels can be found in reference 6.

Also, although pure titanium was found to be relatively unembrittled under these conditions of tensile testing in high-pressure hydrogen at room temperature, titanium and titanium alloys are subject to serious embrittlement by hydride formation at higher temperatures.

MATERIALS SLIGHTLY EMBRITTLED

68.9 MN/m^2 (10,000 psi) GH_2, RT

MATERIAL	NOTCH STRENGTH RATIO, H_2/He ($K_t = 8.4$)	UNNOTCHED DUCTILITY (R A, PERCENT) *	
		He	H_2
304 ELC SS	0.87	78	71
305 SS	0.89	78	75
Be-Cu ALLOY 25	0.93	72	71
TITANIUM	0.95	61	61

*R A = REDUCTION IN AREA

Figure 13

MATERIALS NEGLIGIBLY EMBRITTLED

(Figure 14)

The alloys essentially unaffected by high-pressure hydrogen in tensile tests at room temperature are shown in this figure. Thus, if one were to select a metal not susceptible to hydrogen-environment embrittlement for use in a hydrogen system, it would come from this group. It is immediately apparent that the range of properties available from this group of alloys is limited and, in many instances, will not meet other requirements.

Before one of these alloys could be considered for incorporation in a system on the basis of non-susceptibility to hydrogen-environment embrittlement, it would be necessary to confirm that the alloy is not embrittled by hydrogen under the particular hydrogen exposure and part stressing conditions pertinent to the system. Alloys found not to be embrittled by hydrogen in tensile tests have been found to be embrittled by hydrogen in other tests, as will be discussed.

MATERIALS NEGLIGIBLY EMBRITTLED

68.9 MN/m^2(10,000)GH_2, RT

MATERIAL	NOTCH STRENGTH RATIO H_2/He (K_t =8.4)	UNNOTCHED DUCTILITY (R A, PERCENT)**	
		He	H_2
310 SS	0.93	64	62
A-286	0.97	44	43
7075-T73 Al ALLOY	0.98	37	35
INCOLOY 903***	1.00	50	47
316 SS	1.00	72	75
OFHC COPPER	1.00	94	94
NARloy-Z*	1.10	24	22
6061-T6 Al ALLOY	1.10	61	66
1100-0 Al	1.40	93	93

*ROCKWELL INTERNATIONAL CORPORATION TRADEMARK; TESTED IN 40 MN/m^2 (5800-psi) H_2

**RA = REDUCTION IN AREA

***TESTED IN 48.3 MN/m^2 (7000-psi) H_2

Figure 14

HEE OF INCO 718 IN VARIOUS CONDITIONS

(Figure 15)

In many cases, metals susceptible in some degree to hydrogen-environment embrittlement will have to be used in a hydrogen system. In such cases, the selected metal should be used in the condition least embrittled by the hydrogen environment.

It has been found that the condition of an alloy can have a profound effect on the degree of hydrogen-environment embrittlement of the alloy. Inconel 718 is an example. The first Inconel 718 to be tested in high-pressure hydrogen was that listed in Figure 11, which had been given a 1214, 991-894 K (1725, 1325-1150 F) heat treatment. Subsequently, much less embrittlement was found for Inconel 718 specimens that had been given a 1325, 1033-922 K (1925, 1400-1200 F) heat treatment. This led to a more comprehensive investigation (ref. 7) in which tensile tests were performed on notched specimens in 34.5 MN/m^2 (5000 psi) hydrogen at ambient temperature on Inconel 718 in three forms and three heat treatment conditions.

The results are given in the accompanying figure. The microstructures resulting from the different forming operation/heat treatment conditions could be related to the degree of hydrogen-environment embrittlement. Unfortunately, identification of the condition least embrittled by hydrogen environments is, as yet, limited to a very few metals, examples are Udimet 700/Astroloy (ref. 5) and electrodeposited nickel (ref. 8), for which the effects of deposition current density and post-deposition annealing temperatures on hydrogen-environment embrittlement have been investigated.

HEE OF INCO 718 IN VARIOUS CONDITIONS

34.5 MN/m^2 (5,000 psi), RT

HEAT TREATMENT	MATERIAL	ENVIRONMENT	NOTCHED PROPERTIES		
			STRENGTH, MN/m^2	NH_2/NHe	RA, PERCENT
1214, 991-894 K (1725, 1325-1150 F) (A)	ROLLED BAR	HELIUM	1950	--	2.9
		HYDROGEN	1050	0.54	0.9
	FORGING	HELIUM	2000	--	3.0
		HYDROGEN	1170	0.59	1.1
	PLATE	HELIUM	1980	--	3.0
		HYDROGEN	1700	0.86	2.0
1214, 1089-922 K (1725, 1500-1200 F) (B)	ROLLED BAR	HELIUM	1650	--	2.9
		HYDROGEN	1160	0.70	1.8
	FORGING	HELIUM	1740	--	2.2
		HYDROGEN	990	0.57	1.2
	PLATE	HELIUM	1730	--	2.7
		HYDROGEN	1500	0.86	2.1
1325, 1033-922 K (1925, 1400-1200 F) (C)	ROLLED BAR	HELIUM	2220	--	5.0
		HYDROGEN	1590	0.71	1.7
	FORGING	HELIUM	2340	--	4.6
		HYDROGEN	1780	0.76	1.8
	PLATE	HELIUM	2210	--	3.7
		HYDROGEN	1700	0.77	2.3

Figure 15

STRAIN AT CRACK INITIATION OF INCONEL 718 EXPOSED TO
48.3 MN/m^2 (7000 PSI) H_2 AT RT

(Figure 16)

In some instances, when the design permits, a susceptible metal may be designed into a hydrogen system by utilizing a "brittle material" design approach. Generally, such an approach would be limited to nonwelded structures. The conditions under which a brittle material design approach is appropriate are difficult to define precisely and must be based on engineering judgment; however, the following characteristics are essential. The structure must not contain sharp notches and the finish and accessibility to inspection of the surface in contact with hydrogen must be such that the absence of surface cracks can be ensured. The stress and strains must be predictable with a high degree of confidence based on accurately known loads and configuration simplicity. Most importantly, the peak or localized stresses and strains must be less than the "available" stress and strain for the material in hydrogen, i.e., the stress and strain at crack initiation in hydrogen under the appropriate conditions.

Results of tensile tests to determine strain at crack initiation for Inconel 718 are presented in the figure. Although the two heat treatment conditions listed in the figure experienced very different degrees of degradation of notch strength as shown in Figure 15, the strain at crack initiation was essentially the same. However, the strain at failure was quite different, indicating that the major effect of hydrogen environments on tensile specimens is on crack growth rates.

STRAIN AT CRACK INITIATION OF INCONEL 718
EXPOSED TO 48.3 MN/m^2(7,000psi) H_2 AT RT

HEAT TREATMENT	PERCENT ELONGATION	
	AT CRACK INITIATION	AT FAILURE
1214, 991-894K (1725, 1325-1150F)	3	3 TO 5
1325, 1033-922K (1925, 1400-1200F)	3 TO 5	21

Figure 16

INCONEL 718 LOW-CYCLE FATIGUE DATA

(Figure 17)

When metals that are susceptible to hydrogen embrittlement are to be used in hydrogen systems, the design must be based on properties of the metal determined in the hydrogen environment under conditions simulating service conditions.

Notch tensile strength is one of the properties most sensitive to hydrogen environments because of the large plastic strains that occur at the tip of the notch. When designs of hydrogen components are based on tensile properties, it appears feasible to use the reduction of notch tensile strength in hydrogen under appropriate conditions combined with good engineering judgment to set additional safety factors to compensate for the effect of the hydrogen environment.

In many cases, properties other than tensile properties must be considered in designing components of hydrogen systems. Then, the appropriate property determined in hydrogen under appropriate conditions must be used in designing the part.

The most severe property degradation in high-pressure hydrogen of specimens that do not initially contain cracks occurs in tests involving plastic strain. Thus, considerable reductions of stress-rupture strengths and cycles to failure in low-cycle fatigue (strain cycling) tests in hydrogen are to be expected. The figure shows the decrease of low-cycle fatigue life of Inconel 718 (Heat Treatment C, Fig. 15) during exposure to 41.4 MN/m^2 (6000 psi) hydrogen at ambient temperature. A substantial portion of low-cycle fatigue life occurs after crack initiation. The cyclic-crack growth rate in aggressive environments is strongly dependent upon the cyclic rate. Thus, low-cycle fatigue testing should be performed at strain cycling rates which simulate the hardware application.

INCONEL 718 LOW CYCLE FATIGUE DATA

41.4 MN/m^2 (6000 PSI), RT, Hz = 0.5

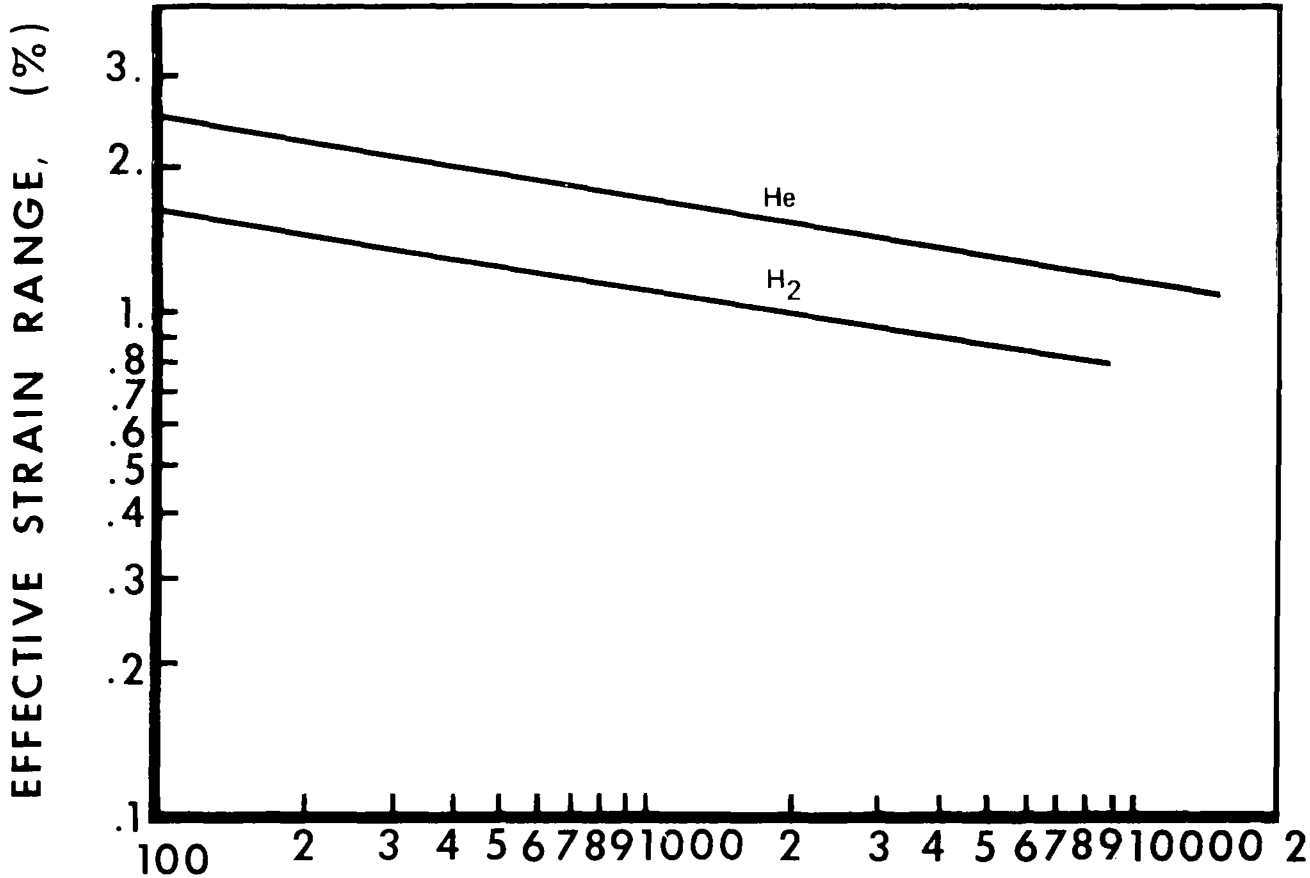


Figure 17

CREEP OF A-286

(Figure 18)

Harris and Van Wanderham (ref. 3) found degradation of the stress-rupture life by hydrogen environments for a number of nickel- and iron-base alloys. Their test results for A-286 stainless steel tested in 34.5 MN/m^2 (5000 psi) hydrogen and helium environments at 950 K (1250 F) are shown in the figure and the large effect of the hydrogen environment on the creep rate and stress-rupture life is very evident. It is interesting to note that the ambient temperature tensile properties of A-286 stainless steel are not reduced by exposure to high-pressure hydrogen environments (Fig. 14). This shows the importance of performing the test (or tests) appropriate to a given application in hydrogen and that it is not possible to draw conclusions as to the effect of hydrogen on one property from the effect of hydrogen on different properties.

CREEP OF A-286

34.5 MN/m$_2$ (5,000 psi), 950K(1250F)

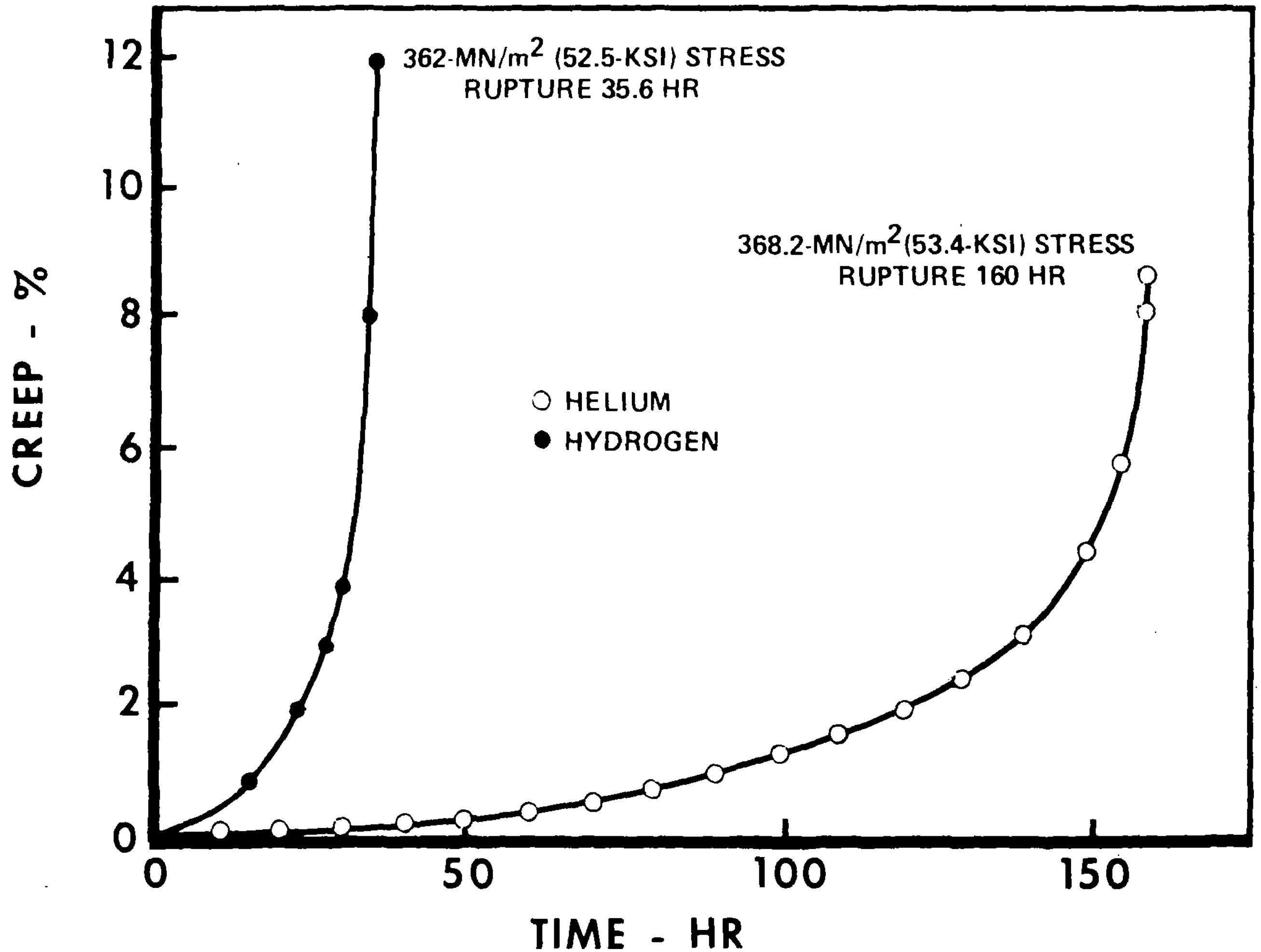


Figure 18

da/dN AS A FUNCTION OF CYCLE DURATION

(Figure 19)

The most significant effect of hydrogen environments on metals is on crack initiation and propagation. Therefore, fracture mechanics, which is the study of crack behavior, is a valuable approach to be applied, where feasible, to life verification of components of hydrogen systems. Such an analysis requires data on threshold stress intensity (K_{TH}) and cyclic-load crack growth rates (da/dN) in hydrogen under appropriate conditions. From this data, the acceptable initial crack size, i.e., the crack size that will not propagate to failure during service, can be established. Then, nondestructive inspection or proof tests are used to confirm that any cracks present are smaller than the acceptable size.

The da/dN is greatly influenced by the nature of the loading cycle applied to a metal and this is particularly true for da/dN in hydrogen for metals susceptible to hydrogen-environment embrittlement. A program was conducted at Rocketdyne to determine the effect of high-pressure hydrogen on da/dN in ASME SA-105 Grade II steel, a plain carbon steel (ref. 9). This steel was in use in a compressor used to pressurize hydrogen for rocket engine testing. As a part of the program, the effect of cycle duration on da/dN in hydrogen was determined. The results are shown in the figure for two stress intensity ranges (ΔK). It can be seen that for shorter time cycles there is a large effect of cycle duration on da/dN but the effect appears to "saturate" at longer times. Thus, da/dN in hydrogen to be used in fracture mechanics analysis must be determined with a loading cycle in hydrogen which simulates as closely as possible service loading conditions or a program must be conducted for each of the metals of interest to establish simpler, for example, shorter, cycles which adequately simulate services conditions.

da/dN AS A FUNCTION OF CYCLE DURATION

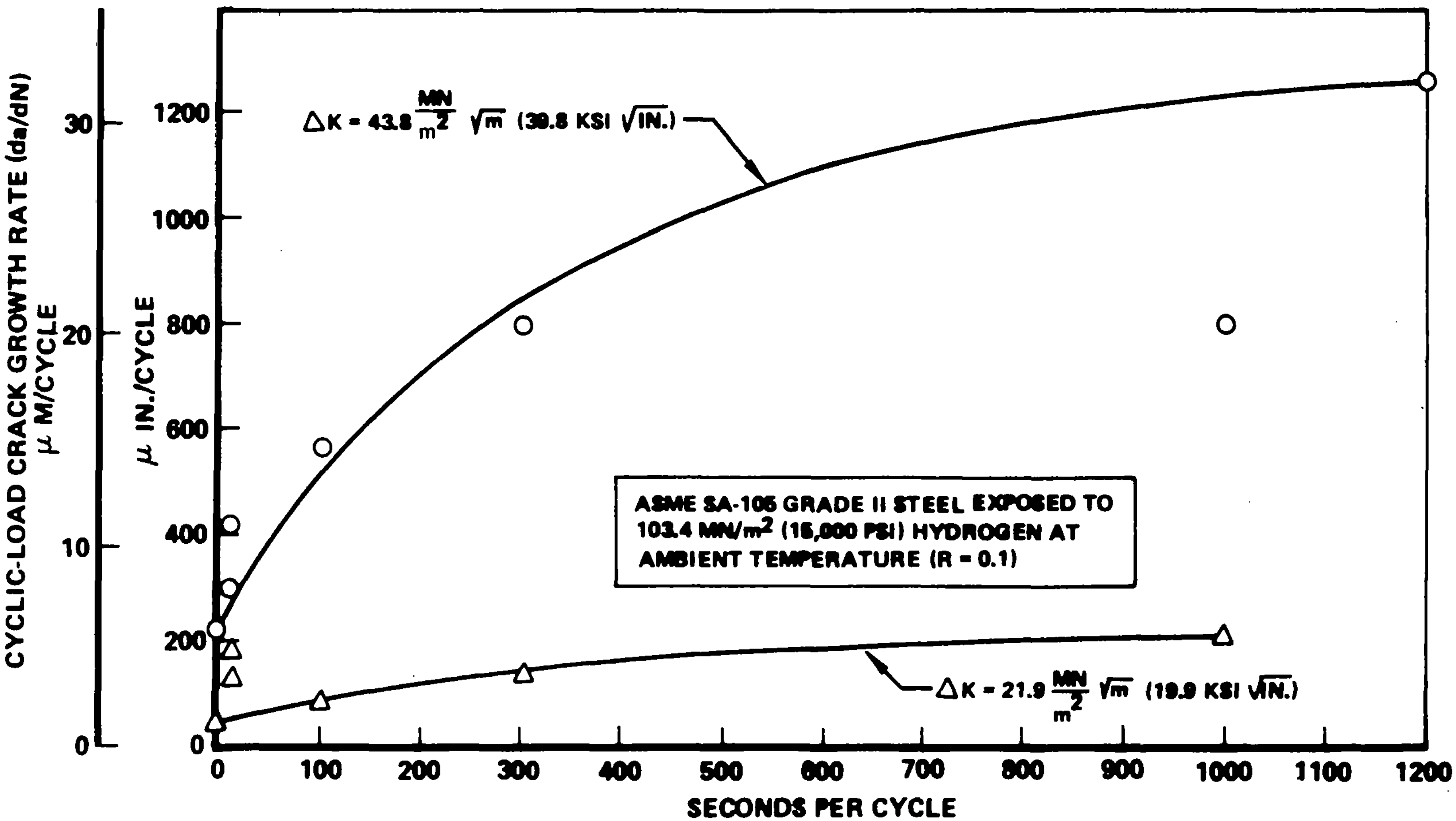


Figure 19

SIMULATED SSME LOAD-TIME CYCLE

(Figure 20)

Under the SSME program, cyclic-load crack growth rate (da/dN) tests are being conducted in support of fracture life verification analyses of all fracture critical parts, most of which are operating in contact with high-pressure hydrogen. The da/dN tests are being performed utilizing a cycle, nearly 9 minutes long, that simulates the SSME operating cycle. The load-time profile is shown in the figure. The long cycle time required to simulate the SSME engine cycle results in very long test times.

SIMULATED SSME LOAD—TIME CYCLE

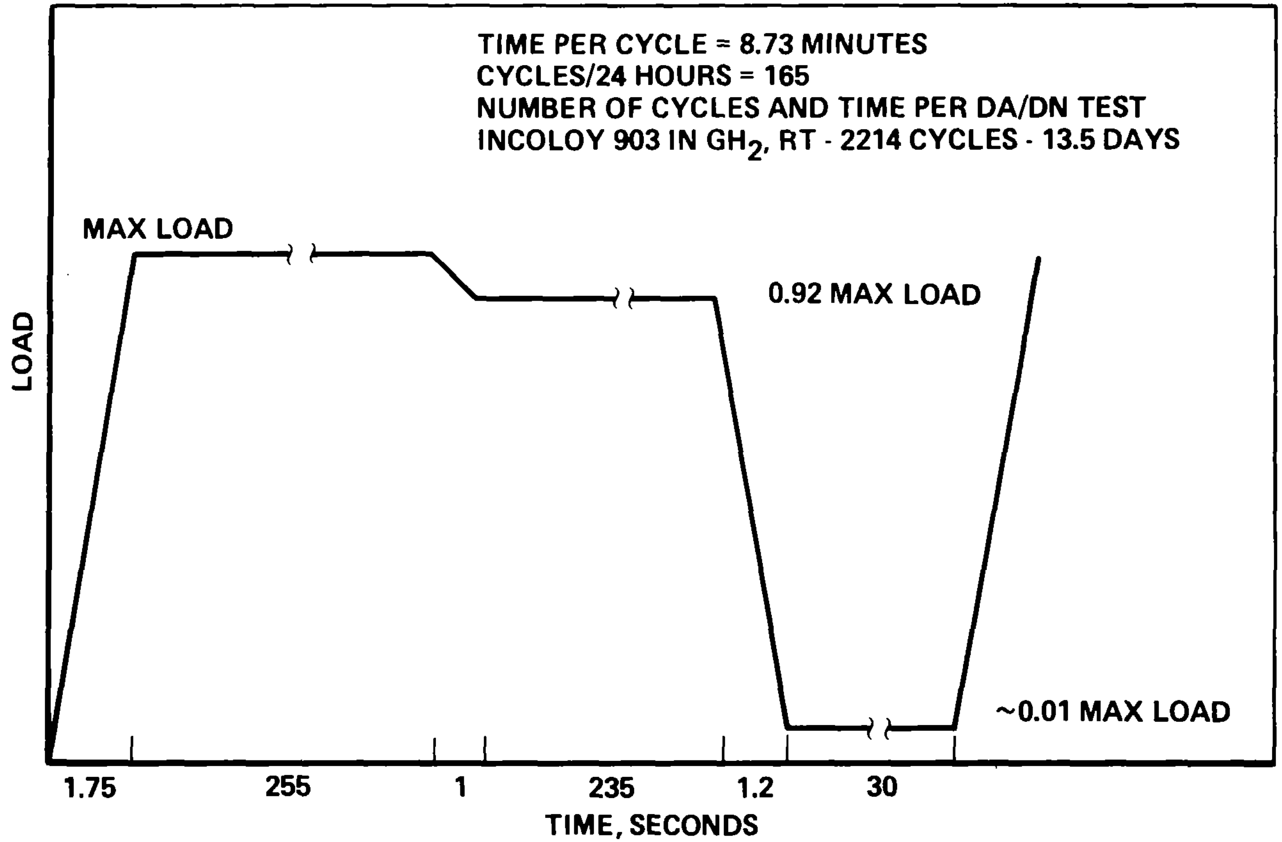


Figure 20

EFFECT OF 34.5 MN/m^2 (5000 PSI) H_2 ON da/dN IN INCONEL 718
(Figure 21)

The most extensive investigations of da/dN in hydrogen for the SSME were conducted on Inconel 718. The da/dN in Inconel 718 was determined for forged, cast, and welded material with da/dN being determined for cracks in the weld metal and in the heat-affected zone (HAZ) for both as-welded and heat treated welds. Some of the results are presented in the figure. The weld and HAZ results are for heat-treated welds. The large effect of hydrogen on da/dN in Inconel 718 is evident. Somewhat unexpectedly, da/dN in hydrogen was slower in the weld metal and HAZ than in the forged base material.

EFFECT OF 34.5MN/m² (5000psi) H_2 ON da/dN IN INCONEL 718

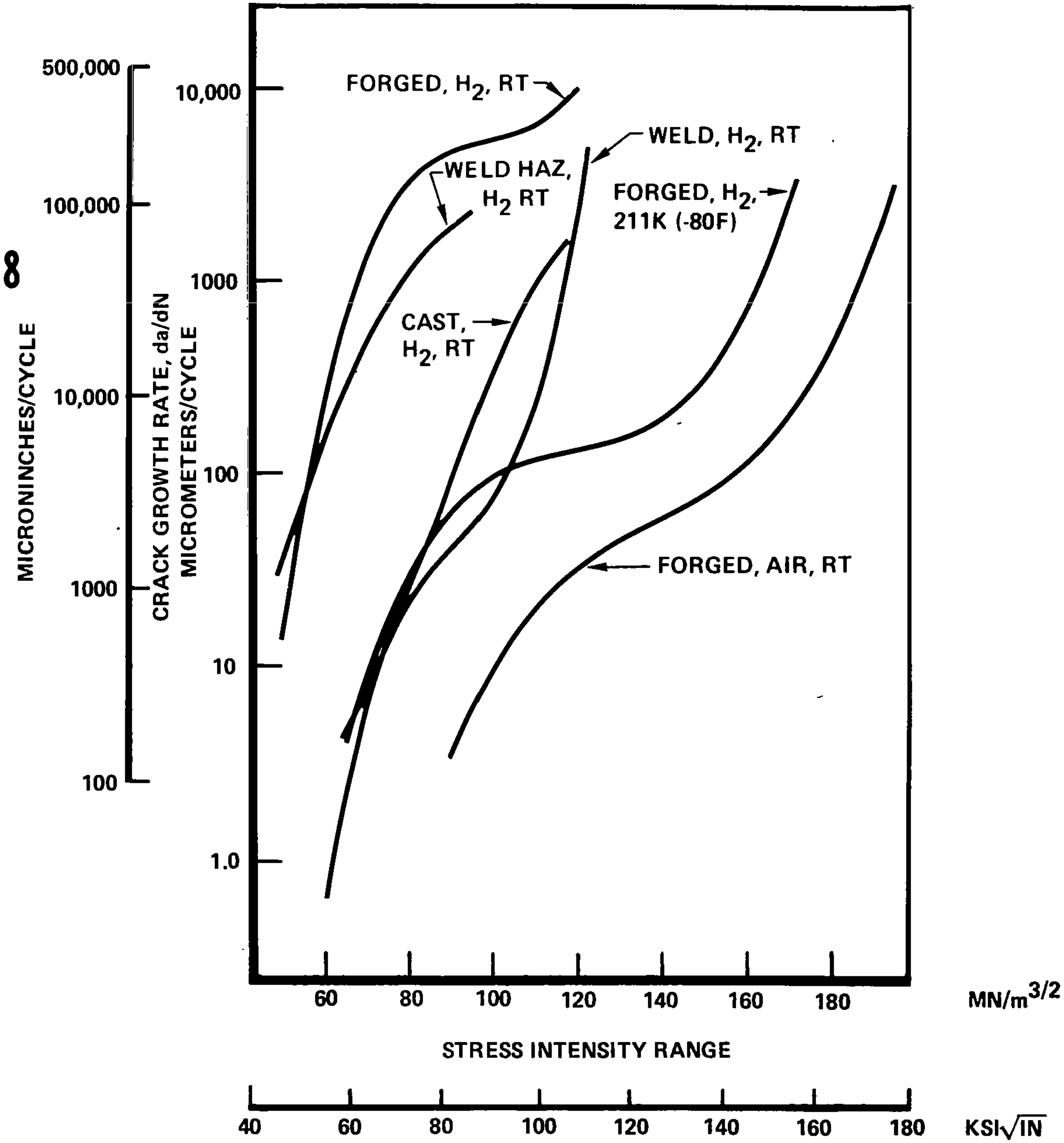


Figure 21

PREVENTION OF HEE

(Figure 22)

Situations can be expected to arise in designing hydrogen components in which a metal has such an attractive combination of properties for a certain application as to dictate its use, but it is quite susceptible to hydrogen-environment embrittlement. The most effective approach may then be to use that metal and take steps to prevent its embrittlement.

There are two basic methods by which hydrogen-environment embrittlement of susceptible metals can be prevented. One involves the use of additives to the hydrogen to inhibit its embrittling effect and the second involves the use of a barrier or coating so that the hydrogen environment cannot contact the susceptible metal. A successful technique for large, high-pressure hydrogen storage vessels has been the use of a vented liner of a nonsusceptible metal (austenitic stainless steel) to protect the load-carrying structural steel which is susceptible to hydrogen-environment embrittlement. Small holes drilled through the structural steel vent out to the atmosphere any hydrogen that diffuses through the liner. Thus, 11 large vessels made of ASTM A-533-B steel (see Figs. 5 and 12)were lined with stainless steel for the storage of hydrogen at 96.5 MN/m^2 (14,000 psi) for SSME testing at Rocketdyne.

PREVENTION OF HEE

- INHIBITION
- VENTED LINER
- COATINGS AND OVERLAYS

Figure 22

da/dN IN HP 9-4-20 STEEL IN VARIOUS ENVIRONMENTS AT ROOM TEMPERATURE

(Figure 23)

As yet, no use of inhibition to prevent hydrogen-environment embrittlement in a system has been reported. The inhibiting effects of oxygen were shown in Figure 8. Studies of the inhibiting effects of other gas species have been limited. Results from one such investigation conducted at the Rockwell International Science Center are shown in the figure (ref. 10). In these tests, the hydrogen pressure was low, 13 KN/m^2 (1.9 psi), and the partial pressure of the inhibiting gas was the same.

Liu, et al. (ref. 11) investigated the influence of inhibitors on the effect of 1 atmosphere pressure hydrogen on crack growth in SAE 4340 steel and found that the introduction of 0.5% SO_2 into the hydrogen would stop a running crack. However, in tensile tests on notched specimens of SAE 4340 steel in 48.3 MN/m^2 (7000 psi) hydrogen at Rocketdyne (ref. 12), it was found that the inhibiting effect of essentially the same concentration of SO_2 was small, the N_{H_2}/N_{He} ratio was 0.23 in hydrogen and 0.33 in the hydrogen containing SO_2. Thus, again, if one wishes to consider prevention of hydrogen-environment by inhibition, it will be necessary to conduct tests on the effect of the inhibitor using temperature, hydrogen pressure, and stressing conditions that properly simulate service conditions.

da/dN IN HP 9-4-20 STEEL IN VARIOUS ENVIRONMENTS AT ROOM TEMPERATURE

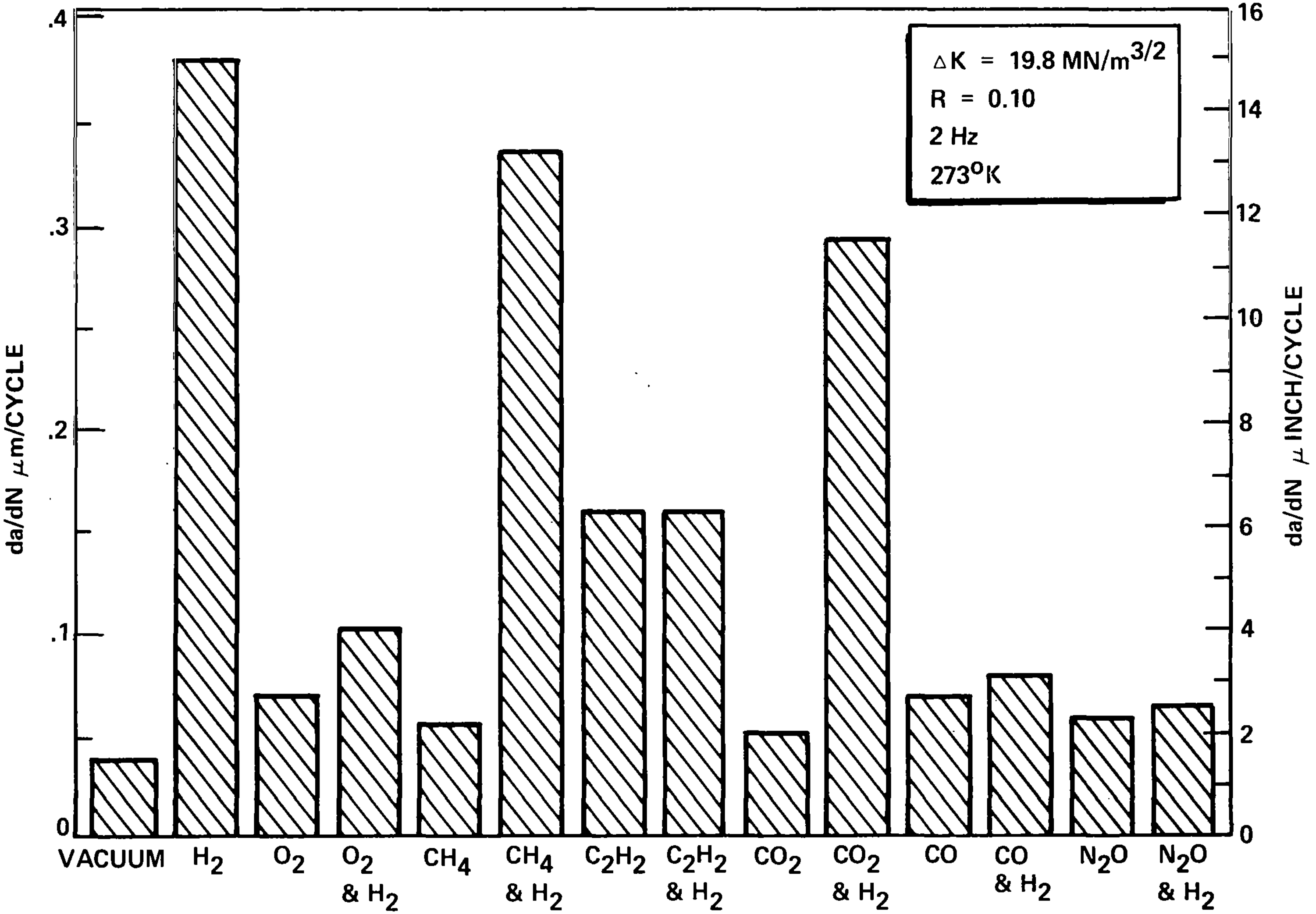


Figure 23

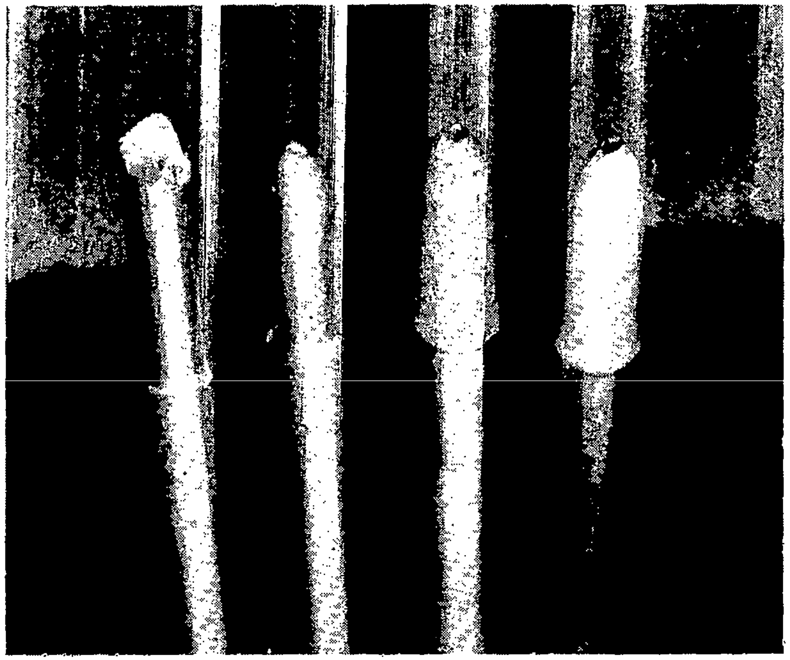
MACROGRAPHS OF EDNi

(Figure 24)

Extensive investigations have been conducted at Rocketdyne on the use of coatings to prevent or reduce hydrogen-environment embrittlement. It has been noted that hydrogen-environment embrittlement occurs only when the metal is plastically deformed (including that at the tip of notches or cracks) in hydrogen. It follows that any coating for the prevention of this embrittlement must be effective during plastic deformation of the metal to be protected. Investigations at Rocketdyne have shown copper and gold coatings to be effective in preventing embrittlement of susceptible metals by high-pressure hydrogen as is evident from the macrographs shown in the figure. The uncoated EDNi specimen tensile tested in hydrogen has a very brittle appearing fracture while the two specimens coated with copper and gold have the same very ductile appearance as the specimen tested in helium.

Because EDNi is considerably affected by hydrogen (see Fig. 11), the EDNi in the SSME is protected from hydrogen by a layer of electrodeposited copper (EDCu). To confirm the effectiveness of EDCu to protect EDNi, a series of burst, sustained, and cyclic pressure tests were performed on slotted specimens designed to simulate the combustion chamber coolant passages. The results of these tests have been reported elsewhere (ref. 8).

MACROGRAPHS OF EDNi



1 2 3 4

1. AS DEPOSITED, TESTED IN 8.3 MN/m^2 (1200 PSI) HYDROGEN AT AMBIENT TEMPERATURE
2. AS DEPOSITED, TESTED IN 8.3 MN/m^2 (1200 PSI) HELIUM AT AMBIENT TEMPERATURE
3. COPPER PLATED, AS DEPOSITED, TESTED IN 8.3 MN/m^2 (1200 PSI) HYDROGEN AT AMBIENT TEMPERATURE
4. GOLD PLATED, AS DEPOSITED, TESTED IN 8.3 MN/m^2 (1200 PSI) HYDROGEN AT AMBIENT TEMPERATURE

Figure 24

LCF AT RT OF EDCu AND BARE- AND Cu-COATED INCONEL 718, STA (R = -1, Hz = 0.5)

(Figure 25)

In certain locations in the SSME, Inconel 718 is protected from the hydrogen environment by EDCu. Tensile tests on unnotched specimens showed that the copper-coated Inconel 718 specimens had the same ductility in hydrogen as in helium provided that the copper was at least 38 μm (0.0015 inch) thick for specimens given the Inconel 718 STA (solution treated and aged) heat treatment after copper plating or at least 76 μm (0.003 inch) thick for specimens heat treated before plating.

However, the protection afforded Inconel 718 in low-cycle fatigue (LCF) tests was found to depend on the strain range as shown in the figure. The copper coating appears to improve low cycle fatigue life only for strain ranges above 1 percent. This is because the copper basically has poorer low cycle fatigue properties than Inconel 718 at the lower strain ranges. That is, the copper fails first because of low-cycle fatigue thus exposing the Inconel 718 to hydrogen. Fortunately, copper does afford protection at the strain ranges above 1 percent, which are the strain ranges for which protection is required in the SSME. The cycle life requirement of the SSME is 60 cycles and to provide a factor of safety it is designed to a cyclic life of 240 cycles. But again, these results show the importance of conducting tests in hydrogen which simulate service conditions.

LCF AT RT OF ED Cu AND BARE AND Cu COATED INCONEL 718, STA (R=–1,Hz=0.5)

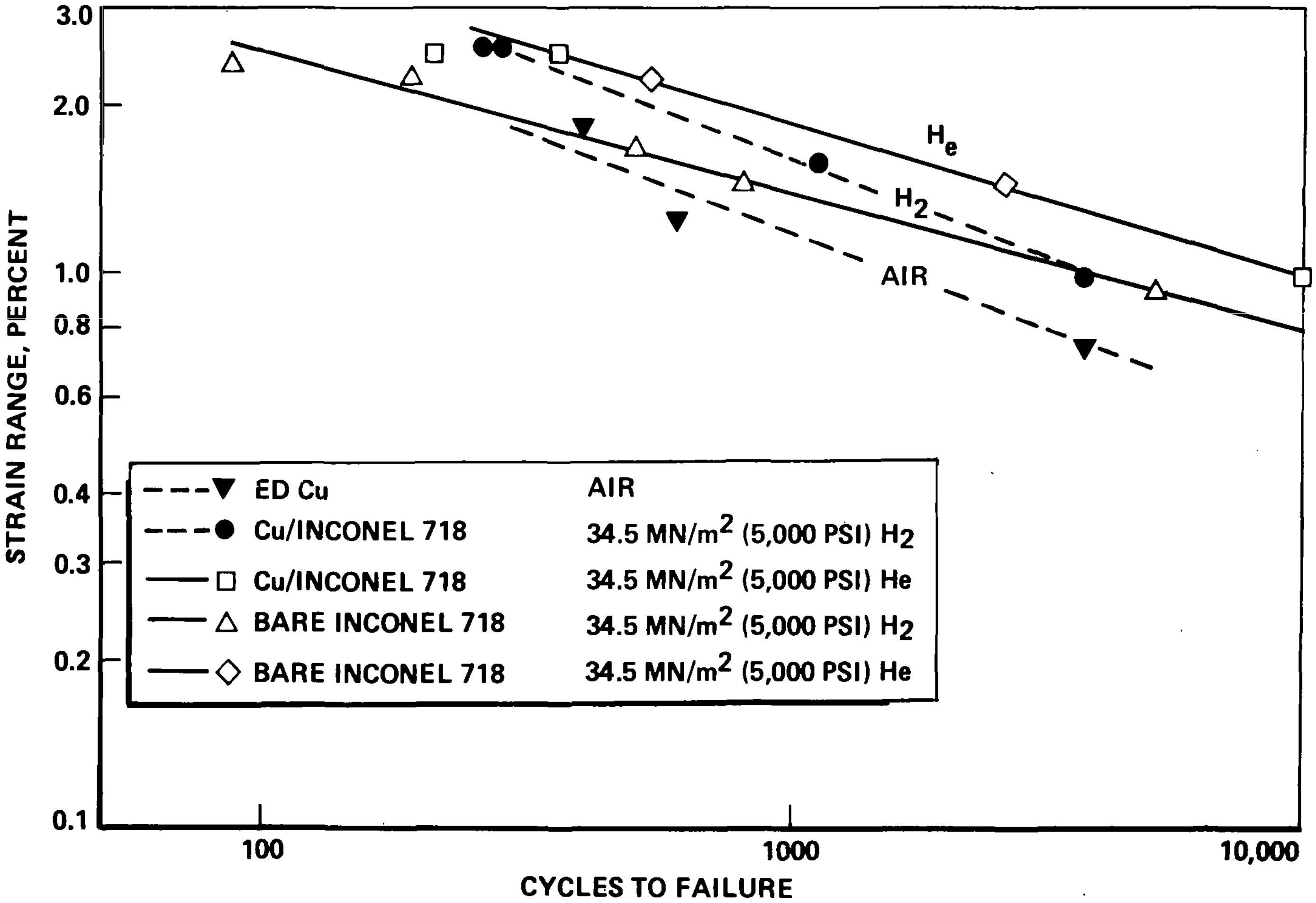


Figure 25

EFFECT OF H_2 ON da/dN IN INCONEL 718 WELDS AND ALLOY 903 OVERLAY AT RT

(Figure 26)

In the SSME, the Inconel 718 welds exposed to hydrogen are protected from the hydrogen. In some cases, the completed weld is copper plated but the majority of welds requiring protection are protected by using a weld overlay, with Alloy 903 (see Fig. 11) being the overlay alloy most often used. The surfaces that will be in contact with hydrogen on each of the two Inconel 718 pieces to be joined are covered with the weld overlay alloy for a distance of at least 1.27 cm (1/2 inch) from the joint surface. The overlayed pieces are then machined so that when fitted together the overlay material overlaps the Inconel 718 weld joint and the weld bottoms in the overlay material. Thus, in the weld area only the overlay material contacts the hydrogen. As required, the hydrogen exposed Inconel 718 is plated with copper up to the overlay material prior to welding.

To confirm that the weld overlay concept is effective, cyclic-load crack growth rate (da/dN) tests were conducted in hydrogen on specimens prepared to simulate the welds in Inconel 718 with the weld overlay. The results of such tests for weld overlay of Alloy 903 are shown in the figure. It can be seen that da/dN in the Alloy 903 overlay is much slower than in the Inconel 718 weld metal or heat-affected zone and approximately the same as for Inconel 718 tested in air.

EFFECT OF H_2 ON da/dn IN INCONEL 718 WELDS AND ALLOY 903 OVERLAY AT RT

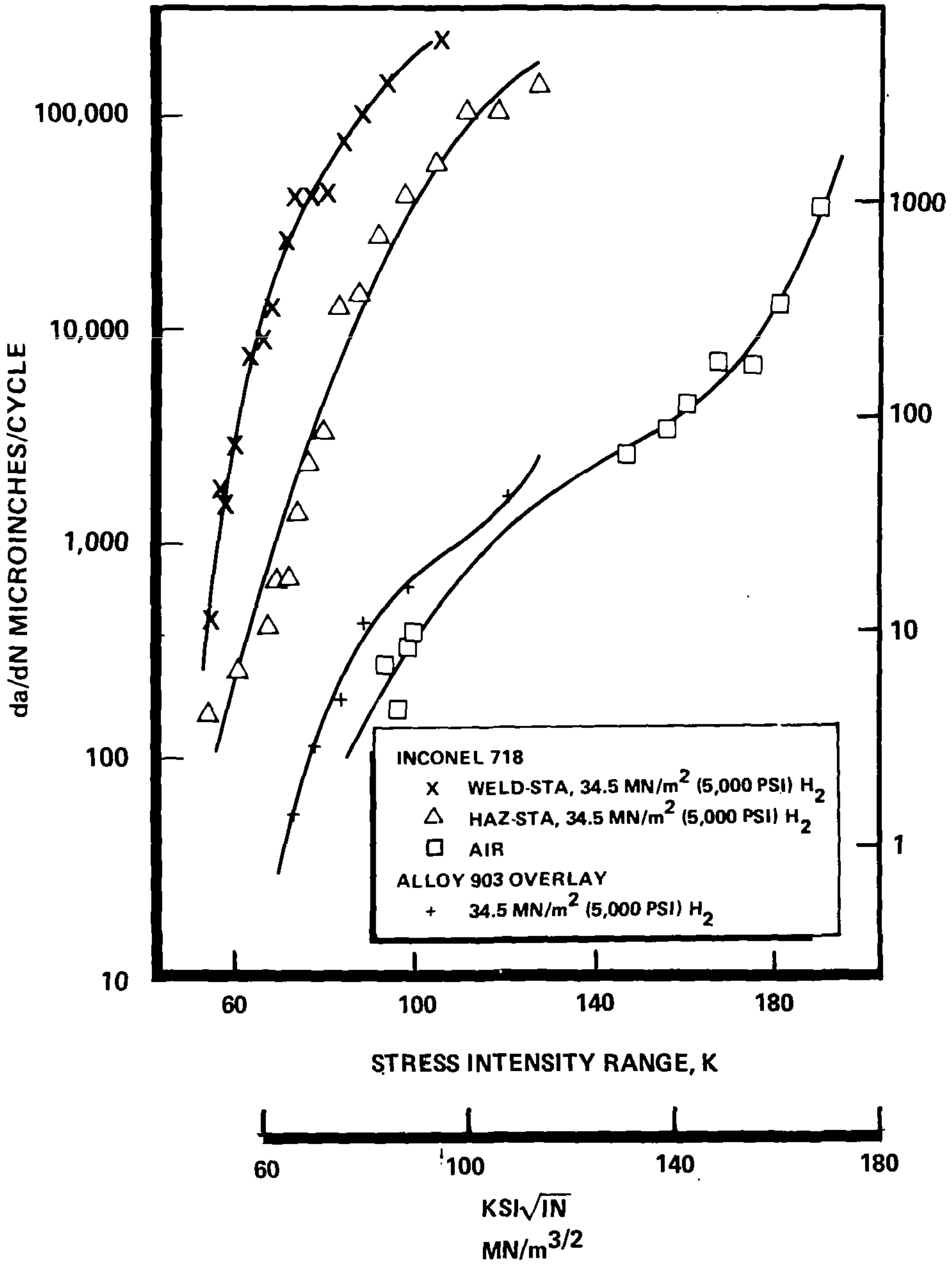


Figure 26

SUMMARY

To summarize, in designing components of hydrogen systems, the conditions of hydrogen exposure are analyzed to determine if hydrogen-environment embrittlement is a potential problem. If it is, then, if possible, metals not susceptible to hydrogen-environment embrittlement are used. If susceptible metals must be used, good design and production processes are especially important. Notches and stress concentrations are reduced and, if possible, eliminated and surface finishes are tightly controlled. The least susceptible condition of the metal is used. Where possible, parts are designed so that susceptible metals are not plastically deformed in hydrogen. Properties used in design are based on tests (e.g., tensile, fatigue, creep, and fracture mechanics) performed in hydrogen under conditions simulating service conditions. If required, liners or coatings are used to protect susceptible metals from the hydrogen environment.

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