COO 3459-13
CONF-770613--3

Contract No. EY-76-S-02-3459.*000

THE INFLUENCE OF HYDROGEN ON HIGH CYCLE FATIGUE OF POLYCRYSTALLINE VANADIUM

D. W. Chung, K. S. Lee and N. S. Stoloff
Rensselaer Polytechnic Institute
Troy, New York 12181

February 1977

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

6-11 / VI / 1977

H2
PARIS - FRANCE

DEUXIEME CONGRES INTERNATIONAL
L' HYDROGENE DANS LES METAUX
SECOND INTERNATIONAL CONGRESS
ON HYDROGEN IN METALS

RESERVE

Titre
Title

THE INFLUENCE OF HYDROGEN ON HIGH CYCLE FATIGUE OF POLYCRYSTALLINE VANADIUM.

Auteur (s)
Author (s)
CHUNG, D. W., LEE, K. S., STOLOFF, N. S.

Ville
Town
TROY, NY

Société
Company
RENSSELAER POLYTECHNIC INSTITUTE

Pays
Country
USA

RESUME: On decrit la fatigue de polycrystaux de V-H_2 a l'ambiente. L'Hydrogene augmente la duresse de vanadium non-etaillé mais reduit la duresse pour les échantillous entaillé. Les resultats d'étude d'augmentation de fissures sont mis en point de la contrainte d'ecoulement et la durcissement cyclique.

SUMMARY: The room temperature fatigue behavior of several polycrystalline V-H_2 alloys is described. Hydrogen extends the life of unnotched vanadium but has a deleterious effect in notched materials. Crack propagation data are correlated with tensile yield stress and cyclic strain hardening data.

① ② ③

I. INTRODUCTION

Considerable attention has been directed to the low temperature tensile properties of the group Va refractory metals in the presence of hydrogen, and an extensive recent review is available [1]. Little work, however, has been reported on possible effects of hydrogen on cyclic behavior of these metals, with the exception of a paper by Wilcox [2], who showed that hydrogen, either in solution or as hydrides, reduces the fatigue life of wrought, stress relieved tantalum.

Recent work in our laboratory [3] has revealed that the influence of hydrogen on fatigue of unnotched polycrystalline annealed vanadium depends upon the mode of testing: stress-controlled (high cycle) tests at a frequency of 20 Hz revealed an improvement in fatigue life with vanadium hydrides present, while strain-controlled (low cycle) tests at frequencies 0.2 - 1 Hz demonstrated severe reductions in fatigue life in the presence of hydrides. Hydrogen in solution had little effect on either high cycle or low cycle behavior. The purpose of the present paper is to report some further observations of high cycle fatigue behavior of vanadium.

II. EXPERIMENTAL PROCEDURE

Vanadium was obtained in two forms from Wah Chang Corp.: cold worked rod and annealed sheet; chemical analyses are listed in Table 1. The rod was annealed for 1 hour at 1050 - 1075°C in vacuum, then furnace cooled, followed by an anneal at 665°C in vacuum for 2 hours to produce an equiaxed grain size of 85 - 90 μ. Hydrogen was added at 600 - 660°C for 2 hours by thermally decomposing ZrH_2 in a closed system. Samples were then furnace cooled. Chemical analyses and hydride sizes are listed in Table 1, together with similar data from the previous work. Note that there is considerable uncertainty as to the solubility limit; previously we noted small (< 10 μ) hydride particles in a 400 ± 40 ppm H_2 alloy; in the present investigation an alloy prepared by the identical method exhibited no hydrides. Moreover, an alloy with 420 ppm (analyzed) also revealed no hydrides. Since the solubility limit of hydrogen in vanadium at room temperature is generally considered to be about 500 ppm [4,5], the original analysis of 400 ppm H_2 [3] may have been in error. The increased oxygen content which accompanied higher hydrogen levels appears to play a minor role in fatigue experiments on binary $V-O_2$ alloys [6].

Two types of experiments were carried out on a closed-loop electrohydraulic machine at room temperature in air, utilizing stress control: a) effects of introducing a notch into rod, tested at 20 Hz in fully reversed tension-compression, and b) crack propagation studies on single edge notched sheet, tested at 20 Hz in tension-tension mode at various stress ranges. During the latter tests, measurements of crack length were made by means of plastic replicas taken from the crack tip; accuracy was estimated to be 2×10^{-4} cm. The stress intensity range was determined from a K calibration [7]:

$$\Delta K = \Delta\sigma \sqrt{a}\; f(a/w) \qquad (1)$$

where $f(a/w) = 1.99 - 0.41(a/w) + 18.70(a/w)^2 - 38.48(a/w)^3 + 53.85(a/w)^4$ with $\Delta\sigma$ the gross applied stress, a the effective half crack length and w the specimen width (1.43 cm).

Thin foils for transmission electron microscopy were prepared by jet electropolishing in 20% H_2SO_4 in methanol, and rinsed in ethanol.

III. EXPERIMENTAL RESULTS

III.1. Effects of Hydrogen on Unnotched Samples

Fig. 1 shows the influence of several levels of hydrogen on the unnotched fatigue life of vanadium at a test frequency of 20 Hz [3]. The lives of solid solution V-132 ppm samples are somewhat higher than for annealed vanadium, but the most striking results are observed for the hydride-containing 400 ppm and 1000 ppm H_2 alloys. The improvements in fatigue lives are far in excess of those to be expected from the differences in yield stresses (Table 2) and ultimate tensile stresses among the various alloys.

While a well-developed dislocation substructure is observed in annealed vanadium, Fig. 2a), and to a lesser extent in the solid solution alloy, hydrides effectively inhibit the development of a fatigue substructure, see Fig. 2b). In annealed material tested at $\sigma = \pm 144.9$ MN/m^2, intense dislocation tangling was noted at only 10% of total fatigue life.

In order to identify crack initiation sites and the mechanism of crack growth, interrupted tests were conducted on annealed vanadium and V-1000 ppm H_2 at 25°C. Slip lines were observed in annealed vanadium cycled at ± 144.9 MN/m^2 after the first cycle but grew hardly at all until about 30% of the life, where cracks developed at the slip bands and at grain boundary triple points. Nucleation of new cracks and intensification of cracks already formed occurred through the period to 80% of life. The major crack leading to final failure initiated at slip bands lying approximately at right angles to the stress axis, and followed a transgranular path.

Typical development of cracks in V-1000 ppm H_2 was different. Slip bands in the matrix remained at almost the same level of intensity up to fracture, while those in the hydride plates intensified with increasing number of cycles. At 20% of life, slip bands in the plates developed into microcracks, but remained within the plates until 60% of the life when microcracks started to propagate into the matrix. Microcracks in the plates grew deeper into the matrix and lead to final fracture, Fig. 3. Unlike the annealed condition, no linking-up of cracks was observed in hydrided material; therefore, the size of the initial crack was much smaller than in annealed specimens.

III.2. Effects of Hydrogen on Notched Samples

Both hydrogen in solution (132 and 400 ppm) and in the form of hydrides (1000 ppm) now produce a marked loss in notched fatigue life relative to annealed vanadium, see Fig. 4. The endurance limit of notched bars drops steadily with hydrogen content, while the fatigue notch sensitivity factor,

$$q = \frac{K_{f-1}}{K_{t-1}} \quad (2)$$

where K_f = fatigue limit unnotched/fatigue limit notched, and K_t, the stress concentration due to the notch = 10.2, varies from 0.156 for unalloyed vanadium to 0.255 for V-132 ppm H_2, 0.45 for V-400 ppm H_2 and 0.65 for V-1000 ppm H_2.

Fracture modes in notched samples were similar to those observed in unnotched bars [3]. Wavy striations were noted in vanadium and a solid solution 132 ppm H_2 alloy, but were interspersed with regions of cleavage in a solid solution 400 ppm H_2 alloy; V-1000 ppm H_2 showed only cleavage facets.

III.3. Crack Propagation Experiments

The results of crack propagation experiments in tension-tension cycling of single edge notched sheet samples are summarized in Figs. 5-7. Fig. 5 shows that the time to grow a crack from the initial notch root (a = 0.127 cm) to Δa = 0.0127 cm is relatively insensitive to hydrogen in solution; however, hydrides appreciably delay the initial crack growth. Also shown in Fig. 5 is the effect of hydrogen on 0.2% offset yield stress [3]. A rough correlation appears to exist between the two curves.

Fig. 6 is a summary of fatigue crack propagation rates, da/dN, plotted vs. stress intensity factor range, $\Delta K = \Delta\sigma \sqrt{a}$, at a ratio, R, of minimum to maximum stress = 0.40. There is little influence of 200 ppm H_2 in solution on da/dN, but at 420 ppm (just below the solubility limit) cracks grow at a much faster, albeit more irregular rate. However, upon formation of vanadium hydrides the crack growth rate, even more erratic, is now midway between that of annealed vanadium and V-420 ppm H_2. When the stress range was changed to R = 0.05, Fig. 7, a somewhat different picture emerged. Hydrides now appear to increase crack growth rate somewhat at the 520 and 1500 ppm H_2 level, but have no effect at the 830 ppm level, relative to a nearly saturated V-420 ppm H_2 alloy.

In order to determine whether stress-induced hydride formation can occur in hydrogenated vanadium a series of replicas was taken from crack-tip regions of the sheet samples, see Fig. 8. A mark A in Fig. 8b) indicates three new hydride particles which had not been observed when the crack was far away, Fig. 8a). The mark B near the crack tip illustrates the dissolution of a hydride while growth of the adjacent hydride at mark C was simultaneously occurring. No evidence of stress-induced hydrides was noted in any alloy in which hydrogen was originally in solution.

IV. DISCUSSION

It is necessary to draw upon several results from tension tests and strain-controlled fatigue experiments [3] to explain the observed high cycle fatigue behavior. Table 2 summarizes the effects of hydrogen on 0.2% yield stress, σ_y, and cyclic strain hardening rate, n', showing that σ_y increases and n' decreases with hydrogen. While increased tensile strength often is associated with improved fatigue resistance we believe that there is a more complex interplay between hydrogen content and fatigue behavior. Hydrides certainly delay crack initiation at the root of a notch, see Fig. 5, perhaps due to decreased plastic flow per cycle. Hydrides also promote cleavage of the matrix, and therefore are likely to increase notch sensitivity, as was found in notched bar tests, Fig. 4. Consequently, crack growth in hydrided alloys containing 830 and 1500 ppm H_2 should be more rapid than in lower hydrogen alloys. The data of Figs. 6 and 7 are somewhat contradictory to this point of view. While hydrides in V-1500 ppm H_2 (with R = 0.4) cause accelerated crack growth relative to annealed vanadium, crack growth is actually slower than in a solid solution 420 ppm H_2 alloy, Fig. 6. Fig. 7 shows that for R = 0.05 hydrides do not markedly accelerate crack growth relative to the 420 ppm alloy. A summary of crack growth parameters, Table 2, according to the Paris-Erdogan [8] equation:

$$\frac{da}{dN} = C\Delta K^{m} \tag{3}$$

(which was obeyed for hydrided alloys only over very narrow ranges of ΔK) shows that there is an inverse relation between values of m taken from straight line segments of Figs. 6 and 7 and n', the cyclic strain hardening rate. That is, hydrogen lowers n' and also increases m. An inverse relation between m and n' has also been suggested by Hickerson and Hertzberg [9]. A simple inverse relation is observed also between C and σ_y^2, as shown in Table 2. (C decreases with increasing hydrogen concentration.) By setting $C = \alpha/\sigma_y^2$, where α is a structural constant, two regions of widely differing average α values were found: $\alpha = 6.4 \times 10^{-5}$ for solid-solution alloys and 1.4×10^{-6} for hydrided alloys. Thus for hydrogen in solution:

$$\frac{da}{dN} \simeq 6.4 \times 10^{-5} \frac{\Delta K^{b/n'}}{\sigma_y^2} \tag{4}$$

and for hydrided alloys

$$\frac{da}{dN} \simeq 1.4 \times 10^{-6} \frac{\Delta K^{c/n'}}{\sigma_y^2} \tag{5}$$

where b and c are experimental constants which can only be approximated from the data of Table 2.

Stress-induced hydride formation, which occurs only in previously hydrided alloys, results in erratic crack growth, but does not seem to accelerate the growth rate relative to concentrated solid-solution alloys. There is no interfacial cracking of these hydrides, nor is there any evidence that they are particularly prone to brittle failure. On the other hand, pre-existing hydrides have been shown to crack, see Fig. 3. The hydrides produced at a crack tip during the fatigue test are oriented parallel to the crack axis (90° to applied stress), while pre-existing hydrides are randomly oriented. This factor also would tend to favor hydride cracking during cyclic loading if, for example, impinging slip bands were responsible for hydride cleavage. It is possible that pre-existing hydrides contain structural defects which render them more brittle than the stress-induced hydrides, or that the chemical composition of the two types of hydride differ.

V. SUMMARY AND CONCLUSIONS

Hydrogen increases the high cycle fatigue life of unnotched polycrystalline vanadium, but decreases fatigue life of notched bars. Hydrogen reduces the propensity for dislocation substructure formation. Crack initiation from notch roots is delayed in the presence of hydrides; crack propagation is slowed relative to a concentrated solid solution of H_2 in vanadium. The coefficients C and m of the Paris-Erdogan [8] equation depend upon σ_y^{-2} and n'^{-1}, respectively. Fracture morphology changes from a striated mode in vanadium and dilute alloys with hydrogen to cleavage in hydrided alloys.

VI. ACKNOWLEDGEMENTS

The authors are grateful to the U. S. Energy Research and Development Administration for financial support under Contract EY-76-S-02-3459.*000.

Table 1

Summary of Alloys and Microstructures

Alloy	H_2 ppm	O_2 ppm	Test Type**	Microstructure
Annealed V	5	90	UB,NB	single phase
Annealed V	6 ± 1	65 ± 8	NS	single phase
V-132 H_2	132 ± 10	125 ± 10	UB,NB	single phase
V-200 H_2	200		NS	single phase
V-400 H_2	--	--	NB	single phase
V-420 H_2	420 ± 40	170 ± 10	NS	single phase
V-400 H_2	400 ± 40	210 ± 20	UB	$10\mu_m$ hydride
V-520 H_2	520 ± 40	130	NS	$10\mu_m$ hydride
V-830 H_2	830 ± 80	190	NS	$40\mu_m$ hydride
V-1000 H_2	1000 ± 100	300 ± 30	UB,NB	$60\mu_m$ hydride
V-1500 H_2	1500 ± 100	480 ± 40	NS	$70\mu_m$ hydride

* Alloys given same hydrogen treatment; 10μ long hydrides observed in material used for unnotched tests, no visible hydrides in material used for notched bar tests.

** UB - unnotched bar; NB - notched bar; NS - notched sheet

Table 2

Effects of Hydrogen on Constants from Paris-Erdogan Crack Growth Equation

Alloy	R	C cm/cycle	σ_y MN/m^2	α		m	n'
Annealed V	0.4	3.67×10^{-9}	136.5	6.8×10^{-5}	*	2.63	0.33
V-200 H_2	0.4	3.05×10^{-9}	146.1	6.5×10^{-5}		3.00	∿ 0.25***
V-420 H_2	0.4	1.97×10^{-9}	173.3	5.9×10^{-5}		6.5	--
V-520 H_2	0.05	5.18×10^{-11}	181.7	1.7×10^{-6}	**	7.15	∿ 0.14***
V-830 H_2	0.05	3.68×10^{-11}	189.3	1.3×10^{-6}		6.7	∿ 0.085***
V-1500 H_2	0.4	2.79×10^{-11}	203.7	1.2×10^{-6}		7.7	--

* Average ≃ 6.4×10^{-5}

** Average ≃ 1.4×10^{-6}

*** Estimated from strain control tests on similar compositions and microstructures [3].

VII. REFERENCES

[1] BIRNBAUM, H. K. - GROSSBECK, M. - GAHR, S., The effects of hydrogen on the mechanical properties and fracture of Zr and refractory metals", in Hydrogen in Metals (Bernstein, I. M. - Thompson, A. W., eds.), Am. Soc. Met., Metals Park, Ohio (1974), 303-323.

[2] WILCOX, B. A., Fatigue behavior of hydrogen-charged tantalum, Trans. Met. Soc. AIME 230 (1964), 1199-1200.

[3] LEE, K. S. - STOLOFF, N. S., Fatigue of vanadium-hydrogen alloys, in Effect of Hydrogen on Behavior of Materials (Thompson, A. W. - Bernstein, I. M., eds.), AIME, New York, N.Y. (1976), 404-414.

[4] OWEN, C. V. - SHERMAN, D. H. - SCOTT, T. E., On the relation of the terminal solubility of hydrogen to the ductility drop in vanadium, Trans. Met. Soc. AIME 239 (1967), 1666-1667.

[5] WESTLAKE, D. G., A resistometric study of phase equilibria at low temperatures in the vanadium-hydrogen system, Trans. Met. Soc. AIME 239 (1967), 1341-1344.

[6] LEE, K. S., Fatigue of vanadium-hydrogen alloys, Ph.D. Thesis, Rensselaer Polytechnic Institute, August (1976).

[7] BROWN, W. F., JR. - SRAWLEY, J. E., Plane strain crack toughness testing of high strength metallic materials, ASTM STP 410, Am. Soc. Test. Mat., Philadelphia, Pa. (1969).

[8] PARIS, P. - ERDOGAN, F., A critical analysis of crack propagation laws, Trans. ASME 85, J. Basic Eng., Series D (1963), 528-534.

[9] HICKERSON, J. P. - HERTZBERG, R. W., The role of mechanical properties in low-stress fatigue crack propagation, Met. Trans. 3 (1972), 179-189.

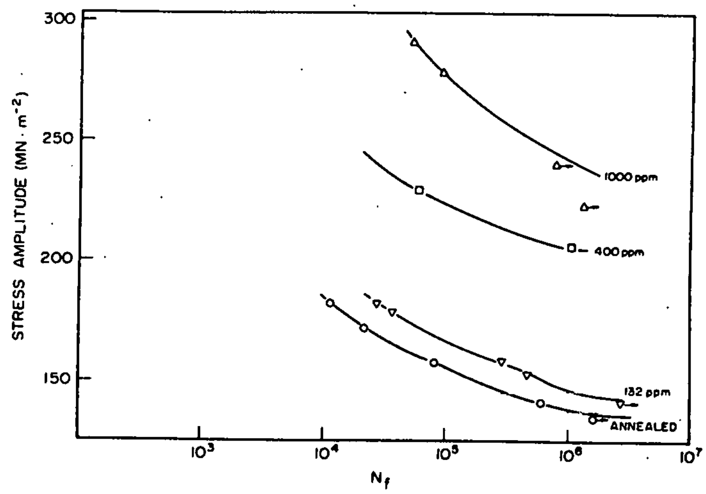
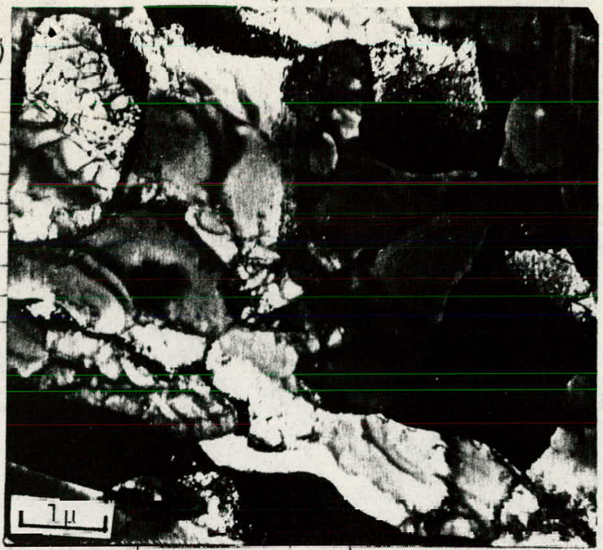
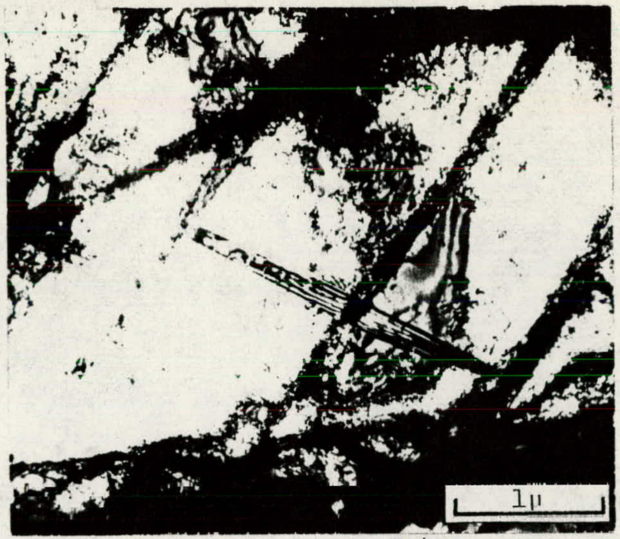


Fig. 1. σ-N behavior of unnotched V-H_2 alloys [3]; 400 and 1000 ppm H_2 alloys contain hydrides.



2a)



2b)

Fig. 2. Effect of hydrogen on dislocation structures a) annealed vanadium, $N_f = 2.3 \times 10^4$ b) V-1000 ppm H_2, $N_f = 9.1 \times 10^4$.

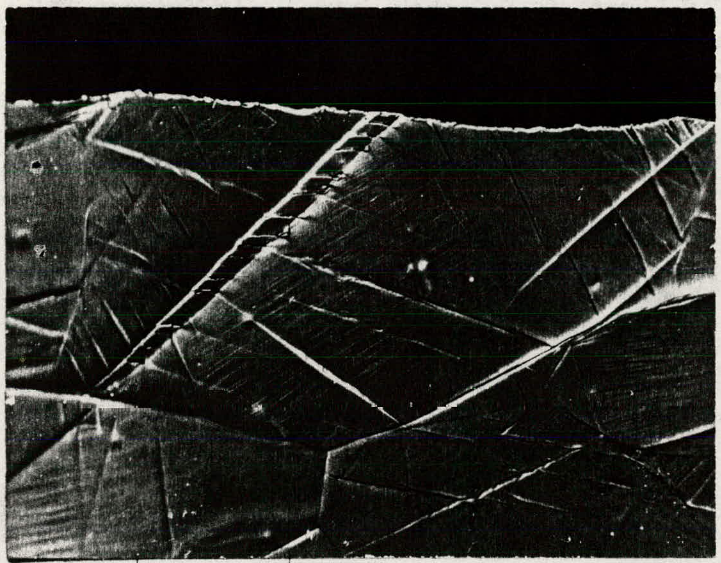


Fig. 3. Fatigue crack through hydride in V-1000 H_2, unnotched, $\sigma = \pm\ 276\ MN/m^2$, $N_f = 5 \times 10^4$, X200.

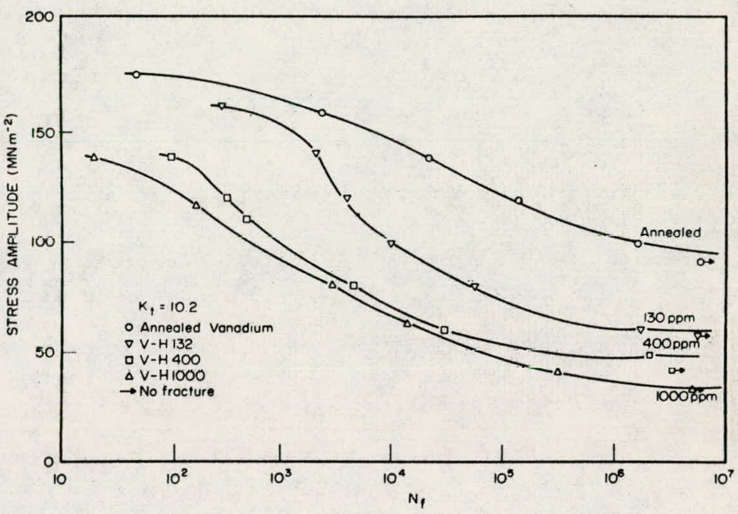


Fig. 4. σ-N behavior of notched V-H_2 alloys (400 ppm alloy has no visible hydrides).

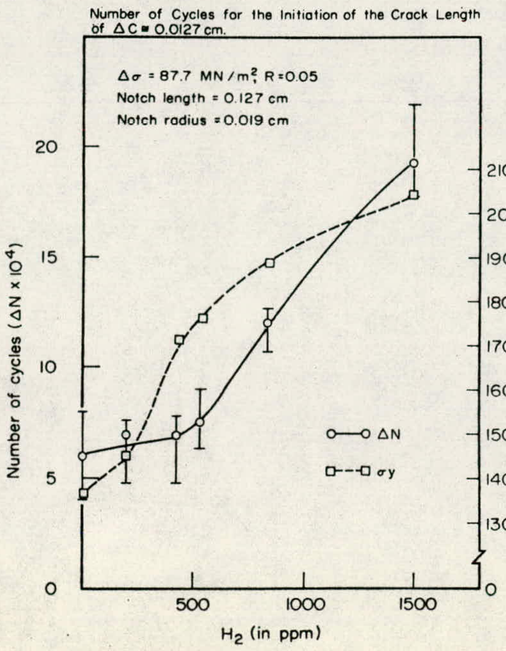
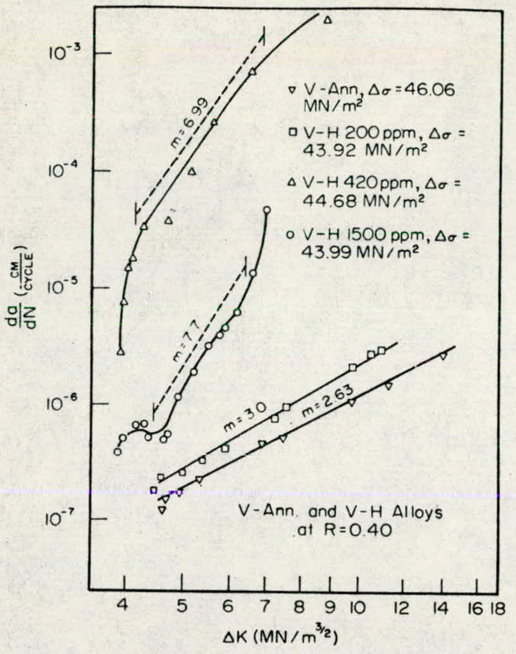


Fig. 5. Number of cycles, ΔN_i, to initiate a crack length of 0.0127 cm in notched sheets; $\Delta\sigma = 87.7\ MN/m^2$.



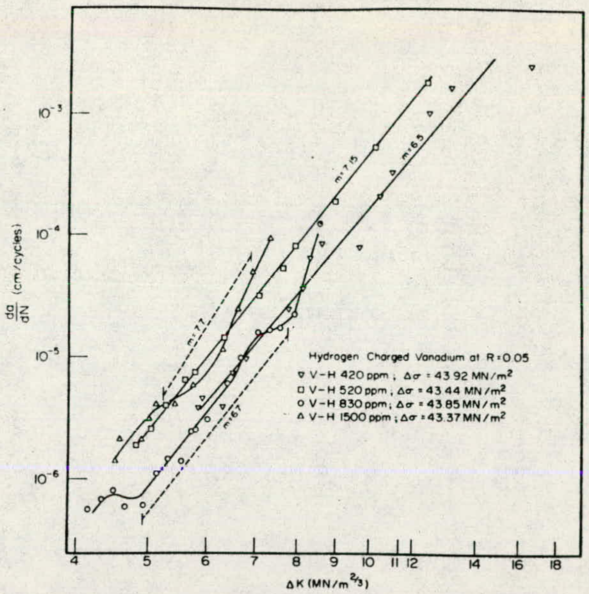
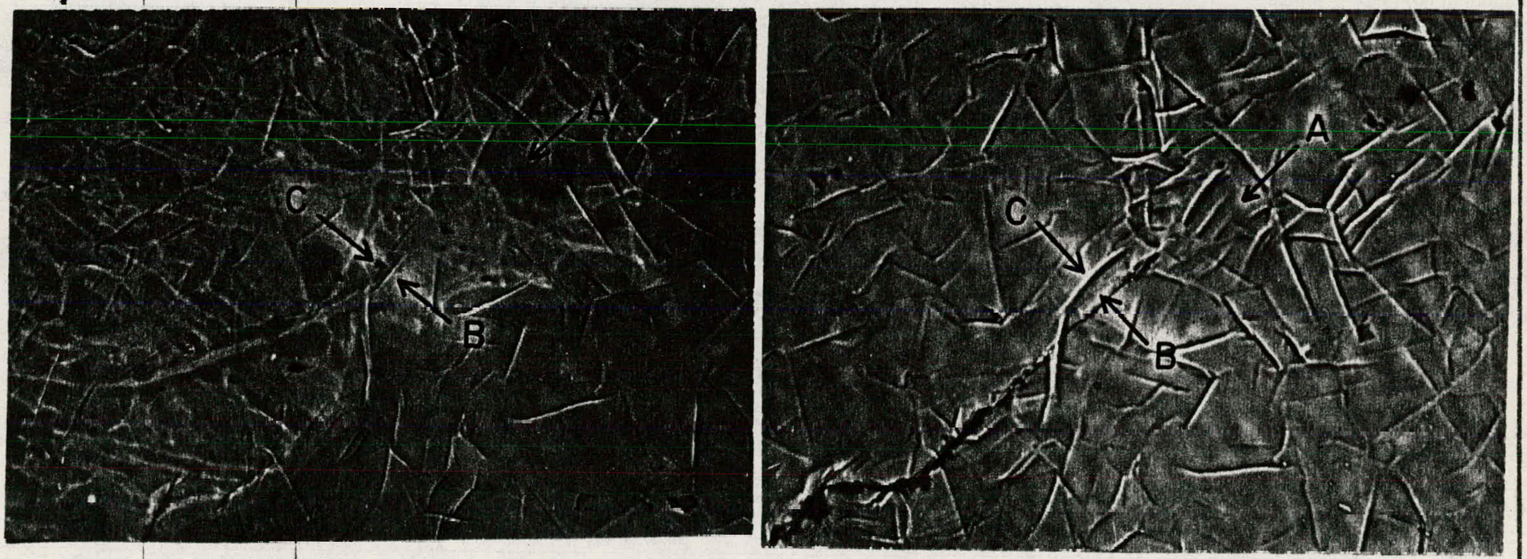


Fig. 6. da/dN vs. ΔK for various alloys, R = 0.4 (no visible hydrides in V-420 ppm H_2).

Fig. 7. da/dN vs. ΔK for various alloys, R = 0.05 (no visible hydrides in V-420 ppm H_2).



8a) 8b)

Fig. 8. Stress-induced hydride formation; V-830 ppm H_2, notched, $\Delta\sigma = 43.8$ MN/m^2, R = 0.05, X150 a) 10,000 cycles, b) 83,000 cycles.