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Final Report

INFLUENCE OF HYDROGEN AND TEST TEMPERATURE ON MECHANICAL PROPERTIES OF VANADIUM AND NIOBIUM

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by

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ABSTRACT

The influence of hydrogen on fatigue life of niobium and vanadium is described. In tests carried out under stress control conditions on unnotched material hydrogen extends fatigue life of both metals. However, in stress controlled tests on notched bars and in strain control tests on unnotched bars hydrogen is detrimental to fatigue life. Hydrided alloys are much more sensitive to notches than are the unalloyed metals. Frequency effects on fatigue life also are much more severe in hydrided alloys, lower frequency leading to shorter life.

The results of delayed failure, creep tests and elevated temperature fatigue tests also are reported. Niobium and vanadium reveal reduced fatigue lives at elevated temperatures for tests carried out in vacuum. The results of limited hold time and low frequency tests on strain controlled fatigue life also are reported. Increasing hold time increases fatigue life of niobium in the range 450-650°C.

Fractographic features change from striations in unalloyed metals to cleavage in the hydrided alloys tested at room temperature.

I. INTRODUCTION

This investigation was principally concerned with the fatigue behavior of vanadium and niobium as a function of test temperature, frequency and hydrogen content. In addition, delayed failure of V-H alloys was studied. Prior to this investigation little information on fatigue processes in unalloyed refractory metals was avaibable; existing data suggested, however, a very high ratio of endurance limit to tensile strength, on the order of 0.6-0.7, at room temperature.[1] This unusually high ratio, coupled with the high melting points, excellent ductility and favorable nuclear properties suggested that vanadium and niobium would be suitable candidate structural materials for the first wall of Tokamak-type fusion reactors. Independent analyses had shown that higher operating temperatures or longer first wall life could be achieved by use of refractory metal alloys based on either vanadium or niobium, in place of austenitic stainless steels. The principal factor likely to limit first wall life was suggested to be resistance to cyclic deformation; added consideration was given to possible contamination by isotopes of hydrogen.[2] Accordingly, this experimental program was designed to establish the fatigue resistance of unalloyed niobium and vanadium at temperatures to 800°C, under both load controlled and strain controlled cycling. Hold-time effects at elevated temperature also were measured. The effects of hydrogen on fatigue properties were evaluated principally at room temperature, although limited testing also was carried out at elevated temperatures. Fatigue crack propagation experiments were carried out at room temperature only.

Delayed failure experiments on V-H alloys also were conducted in order to determine whether hydrogen can induce slow crack growth under static loading conditions.

A few creep tests also were conducted on niobium in the range 550°C to 750°C in order to aid in the interpretation of fatigue data in the same range.

II. EXPERIMENTAL PROGRAM

Niobium (99.9 w% purity) and vanadium (99.8 w%) were used for all tests. Hydrogen charging was carried out in an evacuated furnace by thermally decomposing ZrH_2 in contact with test specimens. Fatigue testing was conducted on closed loop electrohydraulic machines in either stress or strain control. Frequency was varied for stress control tests (1 and 20 Hz for V and 1, 20 and 37 Hz for Nb) on unnotched rod, tested in fully reversed tension-compression. Notched bars were tested at 20 Hz in tension-compression. Test temperatures ranged from 25 to 700°C, with tests performed in air and others in vacuum. Crack propagation experiments were carried out in tension-tension cycling, with various ratios, R, of minimum to maximum stress intensity, on single-edge notched plate specimens. Total-strain-controlled tension-compression tests were conducted at 25°C in air, at 450°C, 550°C and at 650°C in argon at a frequency of 0.25Hz. (15cpm). Tests at 1 cpm were conducted at 450, 550 and 650°C. Cyclic hardening and softening was monitored on an X-Y recorder.

Creep tests on niobium and delayed failure tests on V-H alloys were carried out on creep frames under constant load conditions. Flowing argon atmospheres were utilized for the creep tests.

Scanning electron microscopy (SEM) was the principal tool utilized for fractographic examination of fractured samples. A limited amount of transmission electron microscopic observations were conducted on fatigued samples of vanadium and niobium.

III. RESULTS

A. High Cycle Fatigue

1. Effects of Hydrogen

Hydrides increased the room temperature fatigue resistance of unnotched vanadium, Fig. 1a) or niobium, Fig. 1b) tested at 20Hz, while hydrogen in solution had little effect. Reducing test frequency to 2Hz had little effect on the properties of unalloyed vanadium, but significantly reduced the life of V-1000 ppmH. Similar results were noted for Nb-H alloys, see Fig. 2; a marked frequency dependence was noted only for hydrided niobium.

When these metals were notched, strikingly different effects were noted. Both hydrogen in solution and in the form of hydrides produced a sharp drop in endurance limit, σ_e. The fatigue notch sensitivity factor:

$$q = \frac{K_f - 1}{K_t - 1} \qquad (1)$$

where K_f = fatigue limit unnotched/fatigue limit notched and K_t = 10.2, varied from near zero for unalloyed V to 0.6 for V-1000 ppmH, and from near zero for Nb to about 0.2 for Nb-1180 ppmH, see Fig. 3. Fractographic features in notched as well as in unnotched samples revealed a change from striated surfaces in the non-hydrogenated metals to cleavage markings, sometimes with superimposed striations, at higher H levels.

2. Effects of Test Temperature

Figs. 4 and 5 show the effects of test temperature on high cycle fatigue of vanadium. Note that there is a significant drop in life for vanadium between 400°C and 700°C in vacuum.

At 600°C, fatigue life of vanadium in air actually increased relative to room temperature, probably due to oxygen contamination from testing in air. The strengthening effect of air at 600°C relative to vacuum, is shown clearly in Fig. 4. Life vs. temperature at constant stress is displayed in Fig. 5.

At 25°C and especially at 400°C, extensive surface cracking starting at slip bands was noted in unalloyed vanadium. These cracks also were found in a V-1000 ppm H specimen which did not show any such cracks at room temperature; the life of this material was much lower at 400°C (air) than at 25°C.

The high cycle fatigue resistance of niobium also was measured as a function of temperature, see Fig. 6, but tests at elevated temperatures were conducted only in vacuum (1.3×10^{-4} Pa). The fatigue life decreased rapidly between 25°C and 600°C, with a further small drop at 800°C. The ratio of σ_e/σ_{UTS} decreased from 0.60 at 25°C in air (typical of bcc metals) to 0.55 at 600°C and 0.40 at 800°C. Specimens tested at 600°C and 800°C necked to a point, indicative of a severe thermal ratcheting effect during fatigue. No fatigue zone could be distinguished, unlike room temperature specimens, which displayed distinct fatigue and overload zones. Dimples on the fracture surface at 600°C and intense wavy slip on the outer surface at 800°C, Fig. 7, were observed.

TEM studies of niobium tested at 800°C revealed a cellular dislocation substructure. Dislocations were visible within the cells.

B. Crack Propagation

The crack propagation rate of vanadium and several V-H alloys obeys the relation:

$$\frac{da}{dN} = C\Delta K^m \qquad (2)$$

where ΔK is stress intensity range, and C and m are constants. Increasing hydrogen content produced a significant increase in m, Fig. 8. Data for vanadium with the ratio, R, of $\sigma_{min}/\sigma_{max}$=0.4 are compared with data for niobium, tested with R = 0.1, at a slightly higher Δσ, Fig. 9. Note that crack growth is more rapid in niobium, and m = 3.1, compared to m = 2.6 for vanadium. Previously, we had estimated m = 4.3 for niobium based upon fully reversed (R=-1) tests on pre-notched bar samples.[4]

C. Low Cycle Fatigue

1. Room temperature

Results of strain-controlled experiments in air on niobium, vanadium and two hydrided alloys at 25°C are shown in Fig. 10. Clearly, hydrides have a detrimental effect on life at the low frequencies utilized for these tests. The results for unalloyed niobium compare well with the data of Coffin[5] for many structural materials (scatterband), as had previously been noted by others for a niobium alloy, D-43.[6]

2. Elevated temperature

Low cycle fatigue experiments on niobium also were carried out in argon at 450°C, 550°C and 650°C, see Fig. 11. Note that life increases somewhat with increasing temperature and increasing frequency.

3. Frequency and Hold-Time Effects

Lowering test frequency from 15 cpm to 1 cpm had a deleterious effect on fatigue life of niobium at 450, 550 and 650°C, as was shown in Fig. 11. This behavior is attributed to creep-fatigue interaction, since increased environmental contamination at low frequencies should lead to prolonged fatigue lives, which was not the case.

Results of hold-time experiments on niobium at 450, 550 and 650°C are summarized in Fig. 12. These show that increased hold time actually increases the number of cycles to failure, perhaps due to recovery of material at the crack tip with increasing time at maximum load.

4. Cyclic Strain Hardening and Softening

Cyclic strain hardening at higher rates than monotonic strain hardening were noted in both vanadium and niobium tested in strain control at room temperature. Typical results for niobium are shown in Fig. 13.

However, maximum stress levels monitored during cyclic straining of niobium decreased steadily with number of cycles at all temperatures in the range 450 - 650°C for $\Delta\varepsilon_p = 1.5\%$, and 2.25%. Test frequency had no consistent effect on the results, but saturation stress clearly decreased with temperature.

D. Creep Experiments

Steady state creep rates were determinated in niobium at temperatures in the range of 550°C - 750°C with the data recorded in Fig. 14. Activation energy was stress dependent, with Q = 234 kj/mole = (56 kcal/mole) at σ at 73 MPa (10.5 ksi) and Q = 167 kj/mole (40 kcal/mole) for σ = 65 MPa (9.4 ksi).

E. Delayed Failure

Static loading experiments on several V-H alloys resulted in two patterns of behavior: non-embrittlement in annealed vanadium and alloys with hydrogen in solution, and high susceptibility to delayed failure in dydrided alloys, see Fig. 15. Hydride reorientation under stress was noted, but hydrides at crack tips did not crack. It appeared that hydrides indirectly enhanced embrittlement by increasing the matrix yield stress, thereby reducing the plastic zone radius at the crack tip and reducing crack blunting.

IV. DISCUSSION

The characteristics of high cycle fatigue in unalloyed niobium and vanadium resemble those of other refractory metals such as molybdenum. (1,7) The observed high ratio of endurance limit to tensile strength in these metals is probably an inherent property, due perhaps to the high ratio of elastic limit to ultimate tensile strength.

Hydrides have a strengthening effect in fatigue of vanadium and niobium only when testing is conducted on unnotched material in stress control. Hydrided alloys are much more notch sensitive than the pure metals, so that a pronounced degredation in notched fatigue lives with hydrogen content is noted. Test frequency has a very significant effect on fatigue life of hydrided niobium and vanadium, while there is little effect on the pure metals or solid solution alloys with hydrogen. These effects appear to be related to the difficulty in forming a cellular dislocation substructure in hydrided material.

The high cycle life of vanadium and niobium at elevated temperatures is very sensitive to the test environment. Tests on vanadium and V-1000 ppm H show that above 400°C fatigue strengthening in air occurs due to oxygen contamination. When tests were carried out in vacuum, on the other hand, niobium showed a continuous drop in fatigue resistance from 25 to 800°C. The lack of a distinct fatigue zone at 600°C and 800°C (all specimens necked to a point) indicated a substantial creep or thermal ratcheting effect on fatigue life.

Crack growth rates, da/dN in vanadium, niobium and their alloys with hydrogen could be described by the Paris-Erdogan equation: (see Eq. 2), where experimental constants C and m varied with hydrogen content. In general, m and da/dN increased with hydrogen, suggesting that hydrides accelerate crack propagation. Since hydrides extend the lives of unnotched material, hydriding must delay crack initiation; this conclusion was verified by measuring the time needed initially to extend a fatigue crack in vanadium. Increasing hydride content substantially delayed initial crack growth.(8)

Low cycle fatigue experiments on unalloyed vanadium and niobium revealed general agreement with Coffin-Manson relation:

$$N_f^{a} \Delta\varepsilon_p = C_2$$

where a and C_2 are experimental constants. Data for niobium and vanadium fell within the scatter band for ductile engineering alloys published by Coffin,(5) while data for hydrided niobium and vanadium fell well below the scatter band. These results may be attributed to decreased tensile ductility in hydrided alloys, thereby reducing C_2.

The reduced low cycle fatigue lives noted when frequency was reduced is attributable to a creep-fatigue interaction. However, hold-time experiments showed a small increase in number of cycles to failure with increasing hold-time. The latter can be explained by increased recovery at the crack tip, during the longer hold at maximum load, or perhaps by crack blunting.

Apparent activation energies, Q, for steady state for creep in niobium was recently reported by Singh(9) for stress levels of 40, 50 and 65 MPa at 676°C, 640°C and 604°C, respectively. The activation energy increased from 259 kj/mole (∿60 kcal/mole) at 50 MPa (7250psi) to 305 kj/mole (∿76 kcal/mole) at 65 MPa (9420 psi). These values, which agree reasonably well with earlier results of Brinson and Argent[11] for niobium tested in compression, are somewhat higher than those found in the present study in a similar temperature range. By comparison, the activation energy for self diffusion in niobium is about 410 kj/mole (98 kcal/mole). Therefore, creep in this temperature range, 550 - 750 C, does not seem to be climb controlled; rather, cross slip may control creep. The stress-dependent activation energy was attributed by Singh [9] to a higher dislocation density at higher stresses, leading to a lower activation volume.

V. SUMMARY AND CONCLUSIONS

The major findings of this investigation are:

1) Hydriding increases high cycle fatigue life of unnotched vanadium and niobium, but decreases high cycle life of notched material due to the high notch sensitivity of hydrided alloys.

2) Fatigue lives of hydrided alloys at 25°C are reduced at lower frequencies, while frequency has little effect on lives of unalloyed material.

3) Fractographic features are altered significantly by hydriding prior to test: striated fracture surfaces in unalloyed material give way to cleavage surfaces in alloys with high hydrogen contents.

4) Crack growth rates are increased by hydriding, but crack initiation is delayed.

5) Low cycle fatigue lives of unalloyed niobium and vanadium fall within the Coffin-Manson data band for ductile alloys; low cycle lives are decreased sharply in hydrided material due to reduced ductility of the latter.

6) Temperature effects on fatigue lives in both high and low cycle fatigue tests depend upon environmental factors. Specimen contamination produces anamolously long fatigue lives above 400°C when tests are conducted in air.

7) Evidence for creep-fatigue interactions was obtained at low cyclic frequencies in strain-controlled tests on niobium.

8) Cyclic softening occurs at elevated temperatures in unalloyed niobium; little effect of frequency was noted on the softening, but saturation stress decreased with increasing temperature.

9) Delayed failure occurs in hydrided V-H alloys.

10) Activation energies for creep of niobium at temperatures in the range 550 - 750 C are stress dependent.

VI. REFERENCES

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3. R.E. Gold and D. L. Harrod, J. Nucl. Mat. V. 85/86, 1979, pp. 805-815.
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9. S. Singh, PhD Thesis, U. of Illinois at Champaign, Urbana, 1980.
10. G. Brinson and B. B. Argent, J. Inst. Met., V. 91, 1961-62, p. 293.

VII. PRESENTATIONS

1. Fatigue of Vanadium-Hydrogen Alloys, Conf. on Effect of Hydrogen on Behavior of Materials, Jackson, Wyo., August 1975.
2. Metallurgy and Low Temperature Fracture, TMS-AIME Annual Meeting, Atlanta, Ga., March 1977, (Invited).

3. The Influence of Hydrogen on High Cycle Fatigue of Polycrystalline Vanadium, Sec. Int. Congress on Hydrogen in Metals, Paris, France, June 6-22, 1977 (with D. W. Chung, K. S. Lee).

4. Fatigue Behavior of BCC Refractory Metals, TMS-AIME Fall Meeting, St. Louis, Mo., Oct. 1978.

5. Cyclic Deformation of Refractory Metals for First Wall Application, First Topical Conf. on Fusion Reactor Materials, Miami, Fl., June 19-30, 1979.

6. Hydrogen Effects on Fatigue of Refractory Metals, TMS-AIME Fall Meeting, Louisville, Ky., Oct. 14, 1981 (Invited).

7. Effects of Temperature and Environment on Fatigue of Vanadium and Niobium, TMS-AIME Annual Meeting, Dallas, TX, Feb. 1982 (with R. Choudhury, P. Xiao, S. Ashok.)

VIII. PUBLICATIONS

1. K. S. Lee and N. S. Stoloff, "Fatigue of Vanadium-Hydrogen Alloys" in Effect of Hydrogen on Behavior of Materials, A. W. Thompson and I. M. Bernstein, Eds., AIME, New York, 1976, pp. 404-414.

2. D. W. Chung, K. S. Lee and N. S. Stoloff "The Influence of Hydrogen on High Cycle Fatigue of Polycrystalline Vanadium" in Proc. Sec. Int. Congress on Hydrogen in Metals, Paris, France, June 6-11, 1977, paper 3C11.

3. D. W. Chung and N. S. Stoloff "Effect of Hydrogen on Fatigue Crack Propagation in Vanadium", Met. Trans. A, V. 9A, 1978, pp. 7178.

4. D. W. Chung and N. S. Stoloff "Fatigue Behavior of Niobium-Hydrogen Alloys", Met. Trans. A, V. 9A, 1978, pp. 1387-1399.

5. N. S. Stoloff "Cyclic Deformation of Refractory Metals for First Wall Application", in J. Nucl. Mat. V. 85/86, 1979 pp. 855-859.

6. D. W. Chung and N. S. Stoloff "Delayed Failure of Vanadium-Hydrogen Alloys", in Proc. ICM3, V. 2. Cambridge, England, Aug. 1979, pp. 421-429.

7. S. Ashok, P. Xiao, R. Choudhury and N. S. Stoloff, "Elevated Temperature Fatigue Behavior of Niobium and Vanadium", to be submitted to Met. Trans. Fall, 1981.

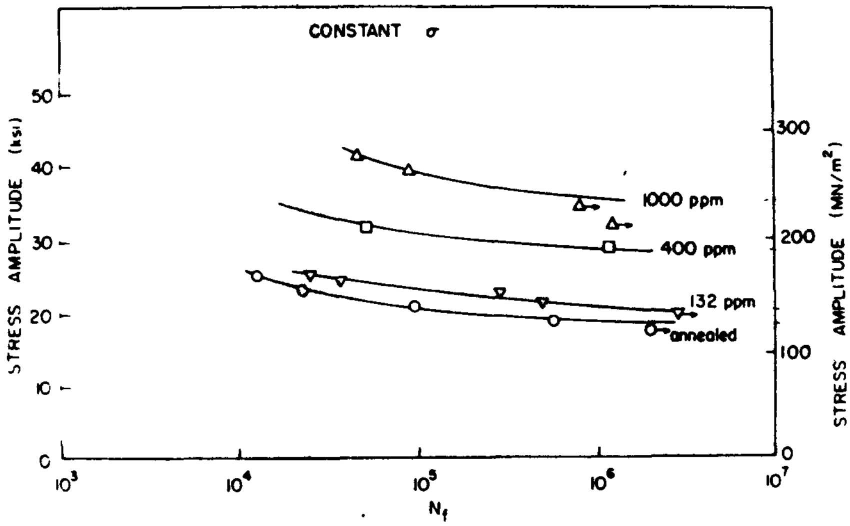
IX. THESES

PhD

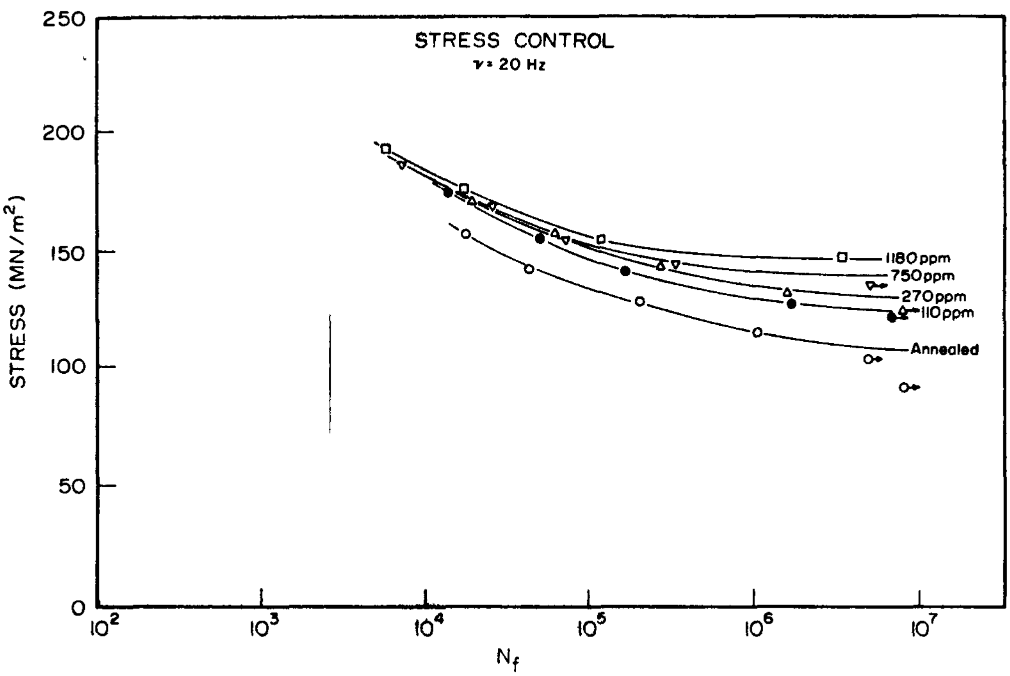
K. S. Lee, "Fatigue of Vanadium", May 1976.

M.S.

R. K. Choudhury, "The Effect of Temperature on Fatigue of Niobium", June 1980.



a) V-H alloy



b) Nb-H alloys

Fig. 1 - Stress amplitude, σ, vs. cycles to failure, N_f; unnotched, 25°C. a) V-H alloys b) Nb-H alloys.

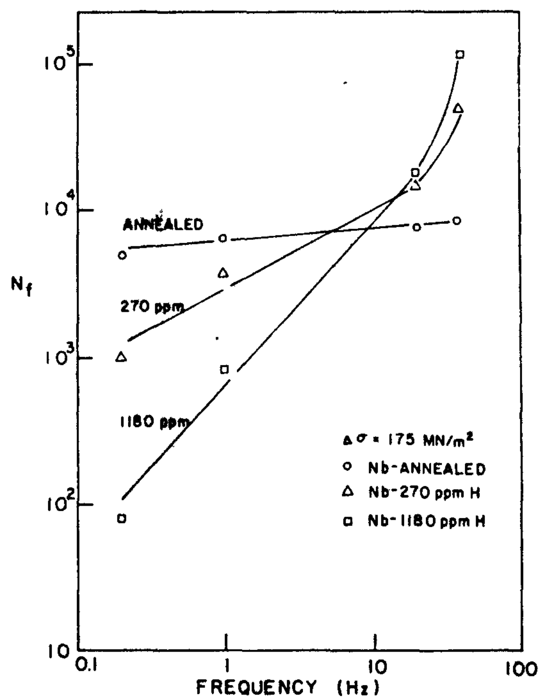


Fig. 2. Frequency dependence of fatigue life in Nb and Nb-H alloys, 25°C.

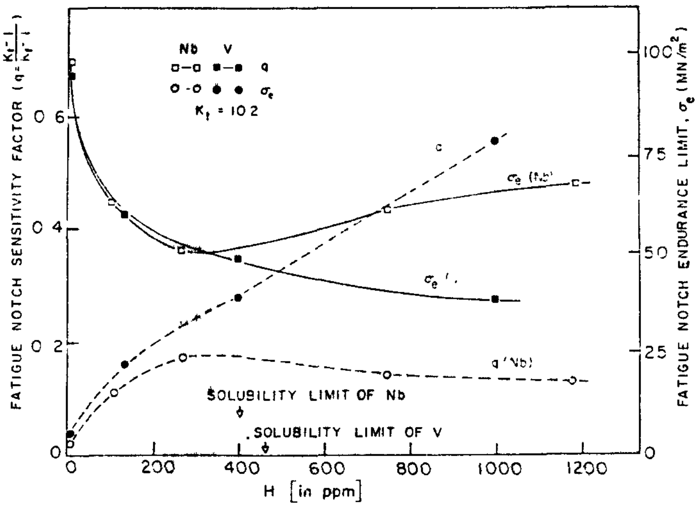


Fig. 3 Fatigue notch sensitivity ratio vs. hydrogen content in Nb and V.

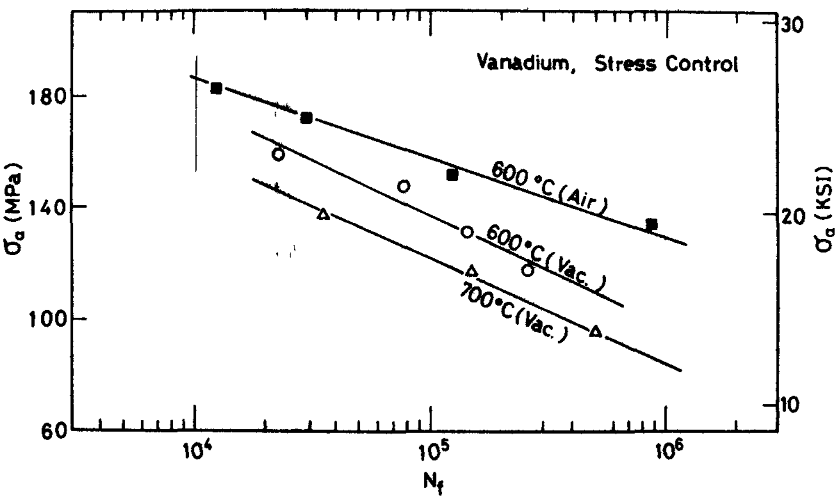


Fig. 4 Effect of temperature and encironment on fatigue of unalloyed vanadium.

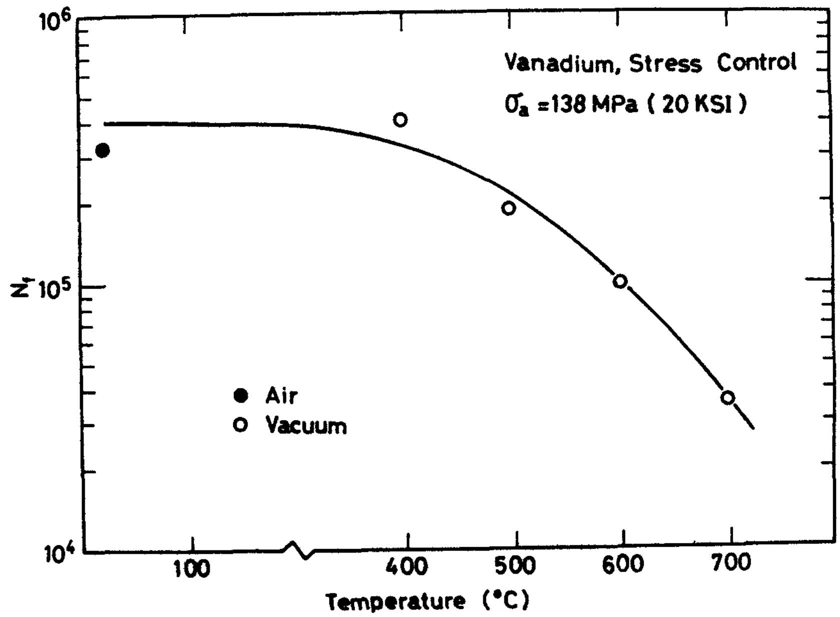


Fig. 5 Effect of temperature in fatigue life of vanadium at constant stress.

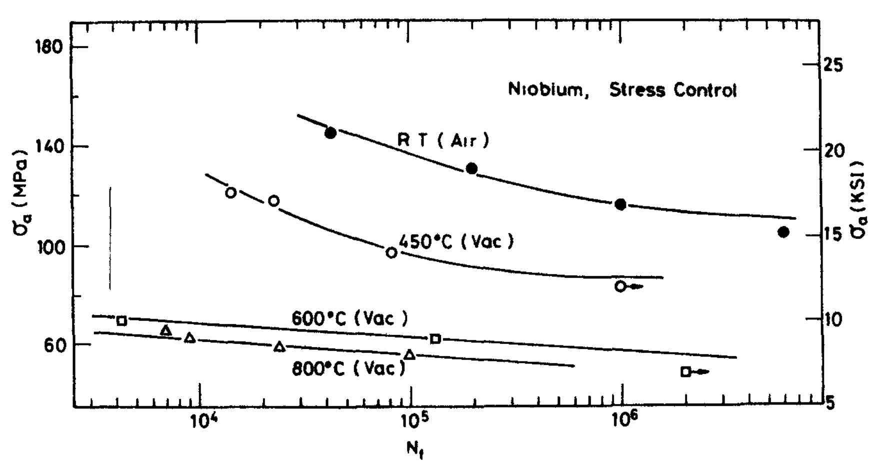


Fig. 6 Effect of temperature and environment on fatigue life of unalloyed niobium.

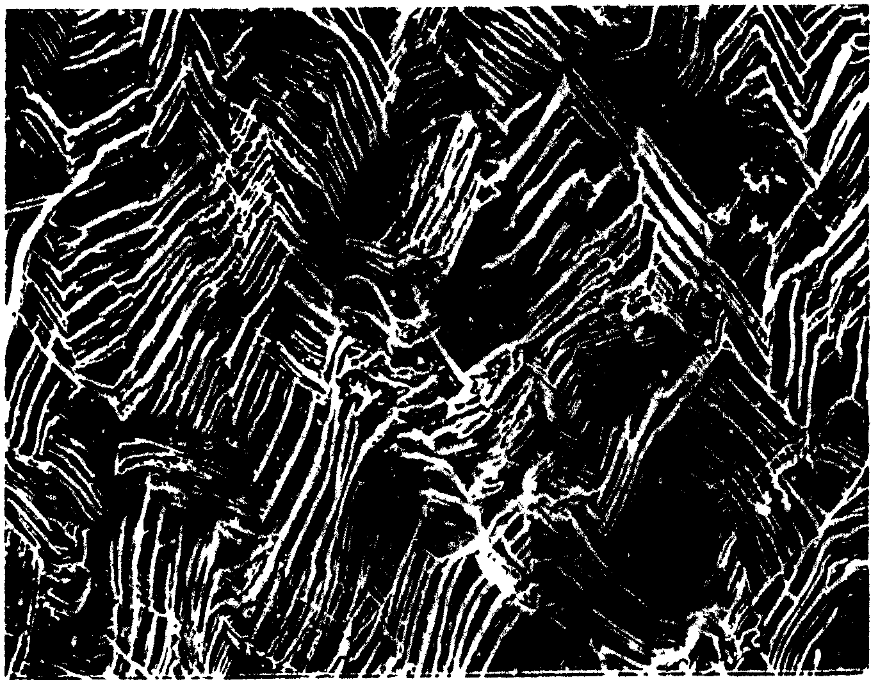


Fig. 7 Wavy slip in niobium cycled in stress control at 800°C, x 500.

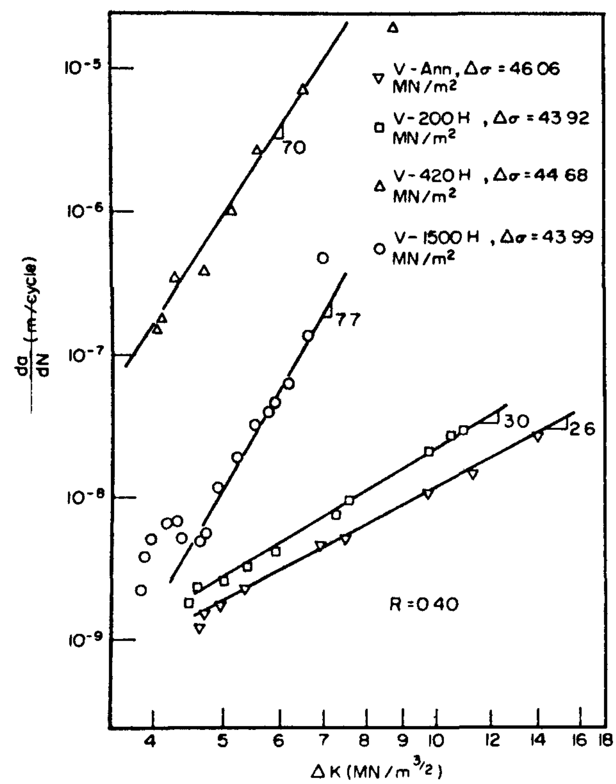


Fig. 8 Fatigue crack propagation rates, da/dN, plotted as a function of stress intensity factor range, ΔK, for various hydrogen concentrations.

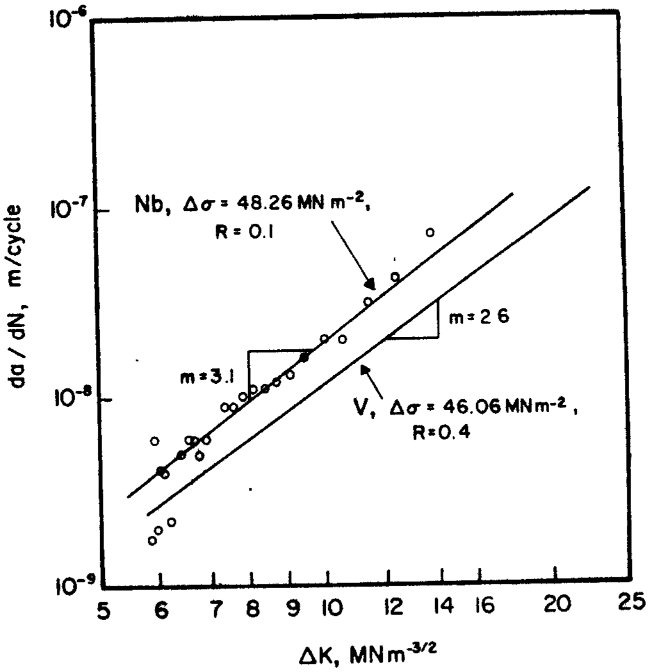


Fig. 9 Fatigue crack growth in niobium and vanadium; 25°C.

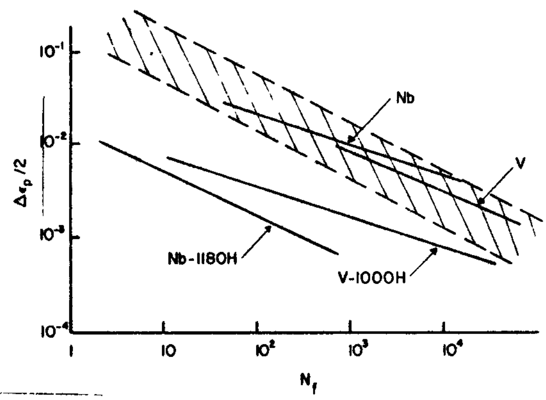


Fig. 10 Plastic strain range vs. cycles to failure for Nb, V and alloys with hydrogen at 25°C. Scatterband for about 20 structural materials from ref. 5.

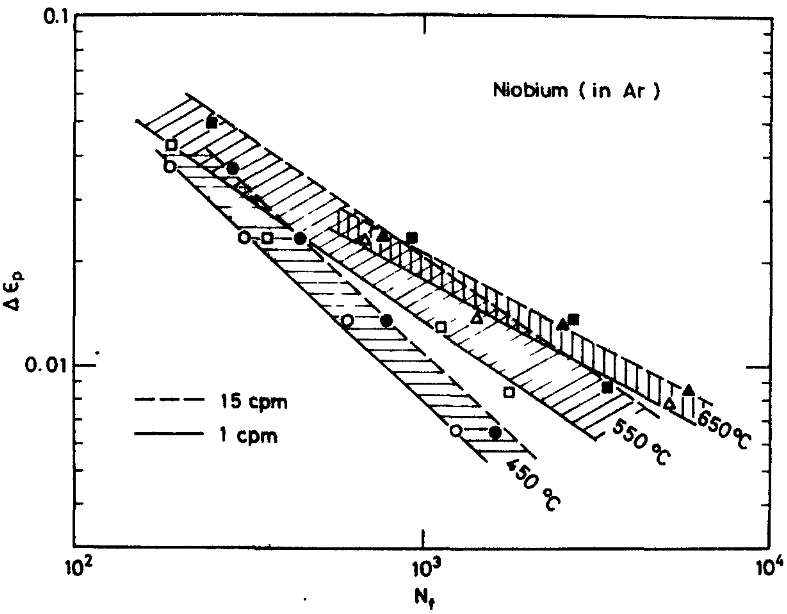


Fig. 11 Effects of frequency and temperature on low cycle fatigue of niobium in argon.

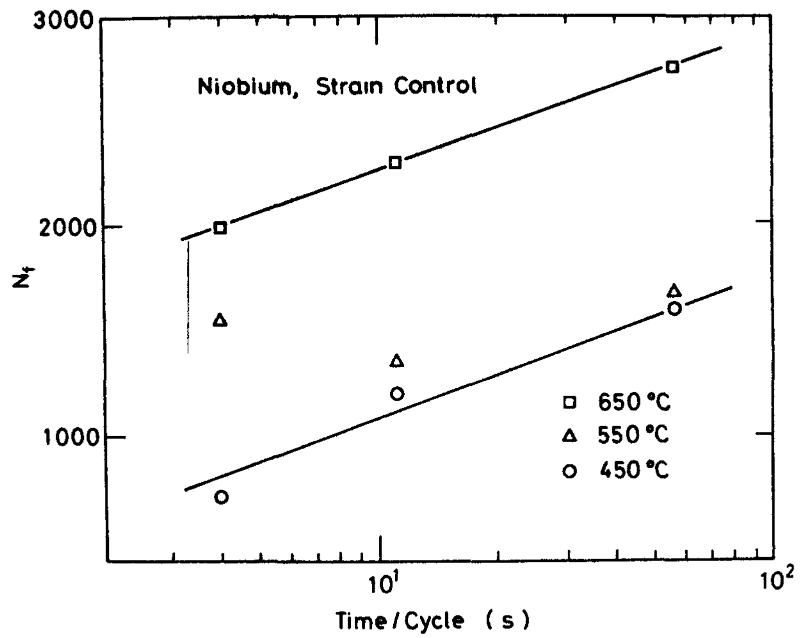


Fig. 12 Effect of Hold time on fatigue life of niobium.

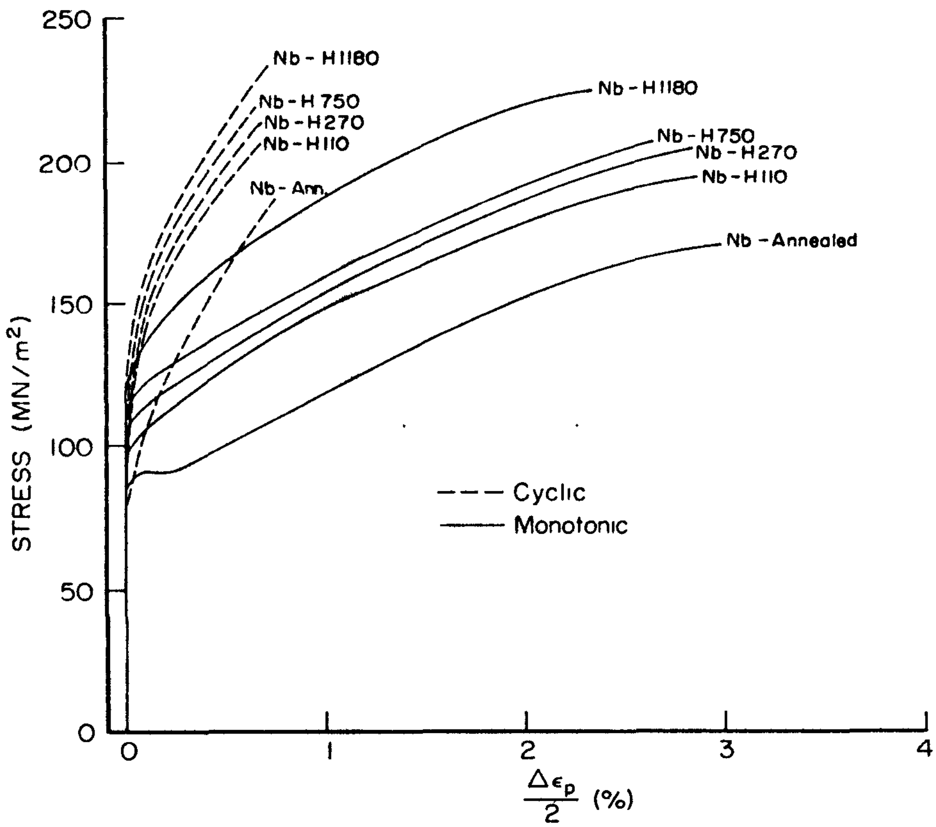


Fig. 13. Cyclic and monotonic stress-strain curves of niobium and niobium-hydrogen alloys.

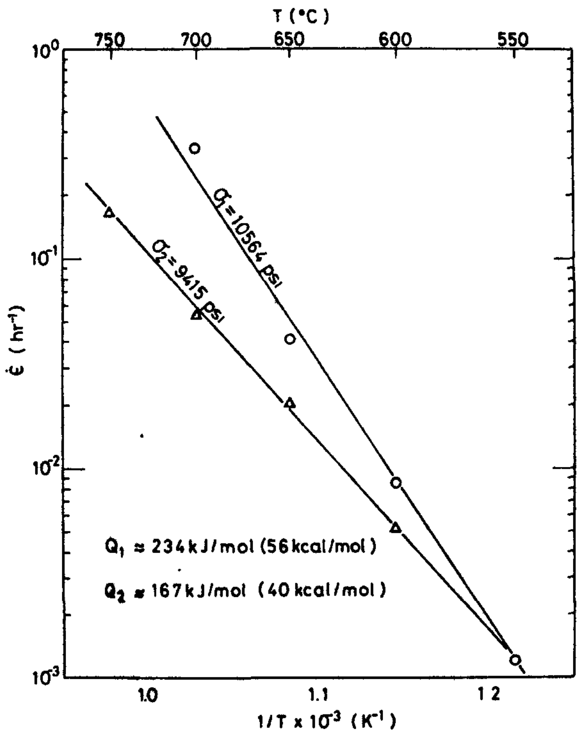


Fig. 14 Effects of temperature and stress on creep rate of niobium in argon.

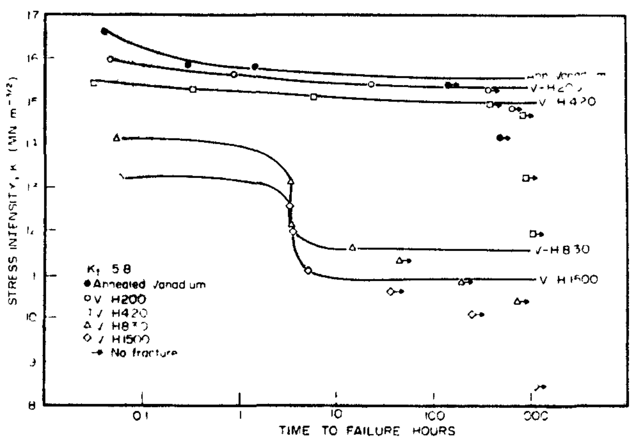


Fig. 15 Stress intensity vs. time to failure in vanadium-hydrogen alloys.