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EFFECTS OF HYDROGEN AND TEST TEMPERATURE ON FATIGUE OF VANADIUM

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DISCLAIMER

Abstract

The fatigue behavior of unalloyed 99.8% vanadium and three vanadium-hydrogen alloys: 132, 400 and 1000 ppm hydrogen, were determined in both stress control and strain control at room temperature. In addition, stress-control tests were conducted on vanadium and the 1000 ppm H_2 alloy at 400°C and 600°C in air.

S-N data obtained from stress-controlled fatigue tests revealed a pronounced improvement in fatigue life for hydrided vanadium, but little or no effect for 132 ppm H_2 in solution. Similarly, strain-control tests showed no effects of hydrogen in solution on either cyclic hardening or fatigue life, in marked contrast to previous results for vanadium containing hydride particles.

High cycle fatigue tests on vanadium and the V-1000 ppm H_2 alloy at room temperature as a function of test frequency showed a marked decrease in life for decreasing frequency for the alloy, but little effect for vanadium. These results furnish an explanation for previously reported anomolies between fatigue lives obtained in stress and strain control tests, respectively. Additional tests run as a function of oxygen content in low hydrogen alloys show that varying oxygen levels cannot account for observed changes in properties with hydrogen.

Transmission microscopy has been utilized to demonstrate differences in fatigue substructures obtained with hydrogen content. These observations are ultimately to be discussed in relation to cyclic hardening data in an effort to provide a comprehensive picture of fatigue damage in vanadium and its alloys.

I. INTRODUCTION

The objective of this program is to determine the fatigue resistance of unalloyed vanadium and to evaluate the influence of various levels of hydrogen, both in solution and in hydride form, on fatigue behavior. Fatigue tests have been conducted either in stress or strain control, as a function of test frequency and test temperature, particularly for unalloyed vanadium and an alloy containing 1000 ppm hydrogen (V-1000 H_2). In view of possible applications of bcc refractory structural alloys in advanced reactors and the relative paucity of information on fatigue resistance of these materials, the results of this research program are expected to provide guidelines for materials testing, selection and design for the reactor program.

The previous annual report (COO 3459-7)[1] provided fatigue data for vanadium and alloys containing 400 and 1000 ppm hydrogen at room temperature only. This report presents a detailed evaluation of fatigue resistance of vanadium and three vanadium-hydrogen alloys as a function of several test variables.

II. MATERIALS AND SPECIMEN PREPARATION

Vanadium utilized in this study was obtained from Wah Chang Corp. (99.8% purity). Chemical analyses of the material appears in Table I, together with that for a V-165 ppm O_2 alloy. Details of heat treatment and specimen preparation for fatigue were described in previous Annual Reports.[1,2] The material had an average grain size of about 90μ.

Three alloys were produced with hydrogen: 132 ppm H_2 (in solution) and 400 and 1000 ppm H_2 in the form of hydrides. After the final anneal to achieve constant grain size, a predetermined amount of hydrogen produced by thermal decomposition of ZrH_2 was in contact with vanadium for two hours at 873°K; a slow cool to room temperature followed. Microstructures of the hydrided alloys were shown in COO 3459-7.(1) There was a significant difference in size and volume fraction of hydride particles. The solubility limit of hydrogen in vanadium at room temperature has been reported to be about 500 ppm,(3) but there is some disagreement in the literature with this value. Westlake(4) has indicated that additional tests are to be conducted at several laboratories to conclusively establish the solubility limit as a function of temperature.

Fully reversed tension-compression fatigue tests on all materials were conducted on a closed-loop electrohydraulic machine. For stress-controlled tests, a sine wave at 20 Hz was used for most tests at 25°C; additional tests were run at 1 Hz at 25°C and 10 Hz at 400°C and 600°C. Strain-controlled tests were run with a triangular wave to maintain a constant strain rate; frequency was 0.2 to 1 Hz, depending upon maximum strain.

Cyclic hardening was monitored during constant strain tests by a Hewlett-Packard X-Y recorder. Thin foils for transmission electron microscopy were prepared by jet electropolishing in 20% H_2SO_4 in methanol.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Stress-Controlled Cycling

1. Room Temperature

The previous annual report, COO 3459-7,(1) included results of room temperature tests on vanadium and the two hydrided alloys, as shown in

Fig. 1. An σ-N plot for the solid solution V-132 ppm H_2 alloy also is shown; annealed vanadium demonstrates a 10^7 fatigue limit of about 18,000 psi. Although substantial increases in endurance limit have been obtained for hydrided material, the solid solution alloy shows only a slight increase in the σ-N curve, and a fatigue limit of about 20,000 psi. The effect of hydrogen in solution is consistent with a small increase in tensile strength, while the effect of the hydrides is much larger than can be attributed to differences in tensile strength, see Table II. The ratio of $\sigma_{max}/\sigma_{uts}$ at the fatigue limit is about 0.55 for annealed vanadium, and 0.59 for V-132 ppm H_2, both in reasonable agreement with typical levels of this ratio of 0.6 for bcc metals.[3] The ratio is on the order of 0.8 for both hydrided alloys.

In COO 3459-7[1] it was reported that σ-N data obtained from stress control tests did not agree with saturation stresses vs. number of cycles for strain control tests in the alloys containing 400 and 1000 ppm H_2, while for unalloyed vanadium the results were consistent. Fig. 2 shows similar data for V-132 ppm H_2; the agreement between stress control and strain control data is good for this solid solution alloy, again emphasizing that drastic effects of hydrogen on fatigue behavior occur only when hydrides are present.

Feltner and Beardmore[8] previously had explained anomolies between stress and strain control data in molybdenum as resulting from the different test frequencies applied in the two cases. In order to determine whether frequency effects could be responsible for such differences for hydrided vanadium, a number of stress controlled tests were run at 1 Hz; the results are shown in Fig. 3a) for vanadium, and in Fig. 3b) for V-1000 ppm H_2, together with previously determined strain control data run at much slower frequencies. It is clear that reducing test frequency lowers the entire σ-N curve significantly for V-1000 ppm H_2, while the effect for annealed vanadium is much less. For both alloys the 1 Hz σ-N curve agrees reasonably well with the strain control data (obtained at frequencies as low as 1 cpm.).

Table I shows that oxygen content increased as increasing amounts of hydrogen were added to vanadium. In order to examine the possibility that the varying oxygen content might significantly alter the fatigue results reported above, a V-165 ppm O_2 alloy was prepared with identical grain size, 90μ. The resulting σ-N curve for this material was almost indistinguishable from that of unalloyed vanadium. This is consistent with the noticeable lack of effect of oxygen on tensile strength of vanadium, see Table II.

2. Elevated Temperatures

Fig. 4 shows the effects of test temperature on high cycle fatigue of vanadium and the alloy containing 1000 ppm hydrogen. Although there is a significant drop in the σ-N curve for vanadium between 25°C and 400°C, the σ-N curve at 600°C rises to a higher level than for 25°C. In view of extensive surface oxidation noted at 600°C it is reasonable to assume that atmospheric contamination is responsible for the apparent improvement in fatigue properties. We therefore conclude that in order to study fatigue processes in vanadium at temperatures in excess of 400°C, an inert atmosphere or vacuum should be employed.

At 400°C, 1000 ppm H_2 should be in solution,[3] where it might be expected that there would be little effect on fatigue properties. This is in fact the case, see Fig. 4, although some observations of hydride particles still were made on fatigue fracture surfaces. The role of stress on hydride formation at both 25°C and 400°C still remains to be studied, but it is possible that the observed hydrides were formed as a result of cycling.

B. Strain-Controlled Cycling

Fig. 5 shows the results of strain-controlled cycling on vanadium and the three hydrogen-containing alloys. A Coffin-Manson relation (based on total strain) is approximately obeyed for the four materials; however, both the slope and intercept of the plots are decreased by hydrogen. Although hydrided materials have lives distinctly inferior to that of annealed vanadium, the 132 ppm alloy exhibits properties very similar to vanadium. Table III is a summary of Coffin-Manson coefficients obtained for the four materials. The slope, α, is decreased for all alloys relative to vanadium; ε_f', the fatigue ductility coefficient (intercept) of each Coffin-Manson plot also decreases with hydrogen content, although again the major effect is for hydrided material.

Cyclic hardening data for the four test materials at 300°K are shown in Fig. 6. The slopes, n', of the cyclic strain hardening curves, are included in Table III. They decrease with increasing hydrogen content.

The increased high cycle life in the presence of hydrides may be connected with the decrease in n'. Feltner and Beardmore[6] have suggested that for increased stress cycling resistance it is desirable to decrease n', while for increased plastic strain resistance it is best to increase n'. We note that the decreased n' produced by hydrides does lead to increased stress-cycling life, consistent with the Feltner-Beardmore analysis. However, when α and n' were compared as suggested by Morrow and Sinclair[7]:

$$\alpha = -1/1+5n' \quad (1)$$

no agreement was noted, see Table III. Consequently, the role of n' is not yet fully understood.

C. Electron Microscopy and Electron Diffraction

Previous work[5] has shown that the β-hydride produced in hydrogen-charged vanadium is coherent, of monoclinic structure and possesses a {101} habit with the matrix. We have confirmed these observations by means of selected area diffraction studies of thin foils of V-1000 ppm H_2.

Specimens of annealed vanadium, cycled to failure, revealed a fairly well-developed substructure. However, V-1000 ppm H_2 reveals no dislocation substructure in failed specimens; rather, intense slip bands were noted. Studies of the development of dislocation substructure with cycle deformation are now underway. When the results of these studies are compared with the cyclic hardening data reported above, a comprehensive picture of the development of fatigue damage in vanadium should be attainable.

IV. SUMMARY

1. Hydrogen contents near and above the room temperature solubility limit increase the high cycle fatigue life, but decrease low cycle life of polycrystalline vanadium at 25°C.
2. Hydrogen in solution has little effect on low cycle or high cycle fatigue of vanadium at 25°C.
3. The beneficial effects of 1000 ppm H_2 on high cycle life persist to 400°C, although the solubility limit is not exceeded. Stress assisted hydride formation may possibly account for the results.

4. Atmospheric contamination produces anamolous fatigue strengthening of vanadium at 600°C.

5. The reduction in cyclic strain hardening rates observed in strain control tests may account for improvements in endurance limit when hydrides are present.

6. Hydrided vanadium exhibits a considerable effect of test frequency on endurance limit, again suggesting formation of stress assisted hydrides.

7. Substructure development differs significantly between vanadium and the V-1000 ppm H_2 alloy.

8. Intentional addition of 162 ppm O_2 has no effect on room temperature fatigue life of vanadium.

V. ADDITIONAL CONTRACT INFORMATION

A. Effort and Compliance

The principal investigator, N. S. Stoloff, has been devoting approximately 25% time during the academic year and 1/3 time during the summer months to this program. A similar level of effort is projected for the future. However, the principal investigator, Dr. N. S. Stoloff, plans to take a sabbatical leave from Rensselaer during the Spring 1977 semester (Jan.-June 1977). During his absence the contract would be administered by either a research associate, Dr. D. W. Chung, or a faculty colleague, if this is agreeable to ERDA.

K. S. Lee, a Ph.D. candidate, has contributed to the results reported here; his Ph.D. degree should be attained by May 1976. The difficulty in obtaining graduate students for research programs has caused us to hire a post-doctoral research associate to perform most of the duties planned in the next year.

The essential tasks outlined in Proposal No. 142 (75R) B308 (2), which formed the basis for the research reported here, will have been complied with by the end of the current contract year.

B. Reports and Publications

COO 3459-8 "Effect of Oxygen on Deformation and Fracture of Polycrystalline Oxygen", by R. L. Straw and N. S. Stoloff, has been accepted for publication in Metallurgical Transactions in early 1976.

COO 3459-9* "Fatigue of Vanadium-Hydrogen Alloys", by K. S. Lee and N. S. Stoloff, was presented at the International Conference on the Effect of Hydrogen on Behavior of Materials, Sept. 7-11, 1975 at Jackson, Wyoming, and is to appear in the Conference Proceedings.

A paper entitled "The Influence of Hydrogen Content and Test Temperature on Fatigue of Vanadium" is to be presented at the AIME Annual Meeting, Las Vegas, Nevada, February 22-25, 1976.

*Erroneously marked COO 3459-8 when transmitted to ERDA

References

1. Annual Report COO 3459-7, January 1975.

2. Annual Report COO 3459-5, January 1974.

3. C. W. Owen, D. H. Sherman and T. E. Scott, Trans. Met. Soc. AIME, 1967, v. 239, p. 1666.

4. D. L. Westlake, Argonne National Laboratory, private communication.

5. S. Takano and T. Suzuki, Acta Met., v. 22, 1974, p. 265.

6. C. E. Feltner and P. Beardmore, in ASTM STP 467, p. 77, American Society for Testing and Materials, Philadelphia, Pa., 1970.

7. J. Morrow and G. M. Sinclair, in ASTM STP 237, p. 83, American Soc. for Testing and Materials, Philadelphia, Pa., 1958.

8. P. Beardmore and P. H. Thornton, Met. Trans., v. 1, 1970, p. 775.

Table I. Chemical Analyses of Alloys

Alloy	H_2 (ppm)	O_2 (ppm)
V	5	90
V-132 H_2	132 ± 10	125 ± 10
V-400 H_2	400 ± 40	210 ± 20
V-1000 H_2	1000 ± 100	300 ± 30
V-162 O_2	5	162 ± 6

Table II. Tensile Data for Alloys

Alloy	Temp. $^{\circ}C$	0.2% σ_y ksi	U.T.S. ksi	Total ε %	Uniform ε %
V	25	20	33	42	22
V	400	10	32.5		32
V-132 H_2	25	21.8	34	> 65	22
V-400 H_2	25	25.6	36.7	40	22
V-1000 H_2	25	27.2	42	24.4	18.6
V-1000 H_2	400	11.3	33.8		28
V-162 O_2	25	18	33	106	62.5

Table III. Effect of Hydrogen on Coffin-Manson Coefficients

Alloy	α	ε'_f	n'	$\frac{-1}{1 + 5n'}$
V	-0.49	0.29	0.33	-0.37
V-132	-0.35	0.13	0.297	-0.40
V-400	-0.39	0.066	0.159	-0.55
V-1000	-0.32	0.023	0.08	-0.71

Figure Captions

Fig. 1. Effect of hydrogen content on high cycle fatigue life of vanadium at 25°C.

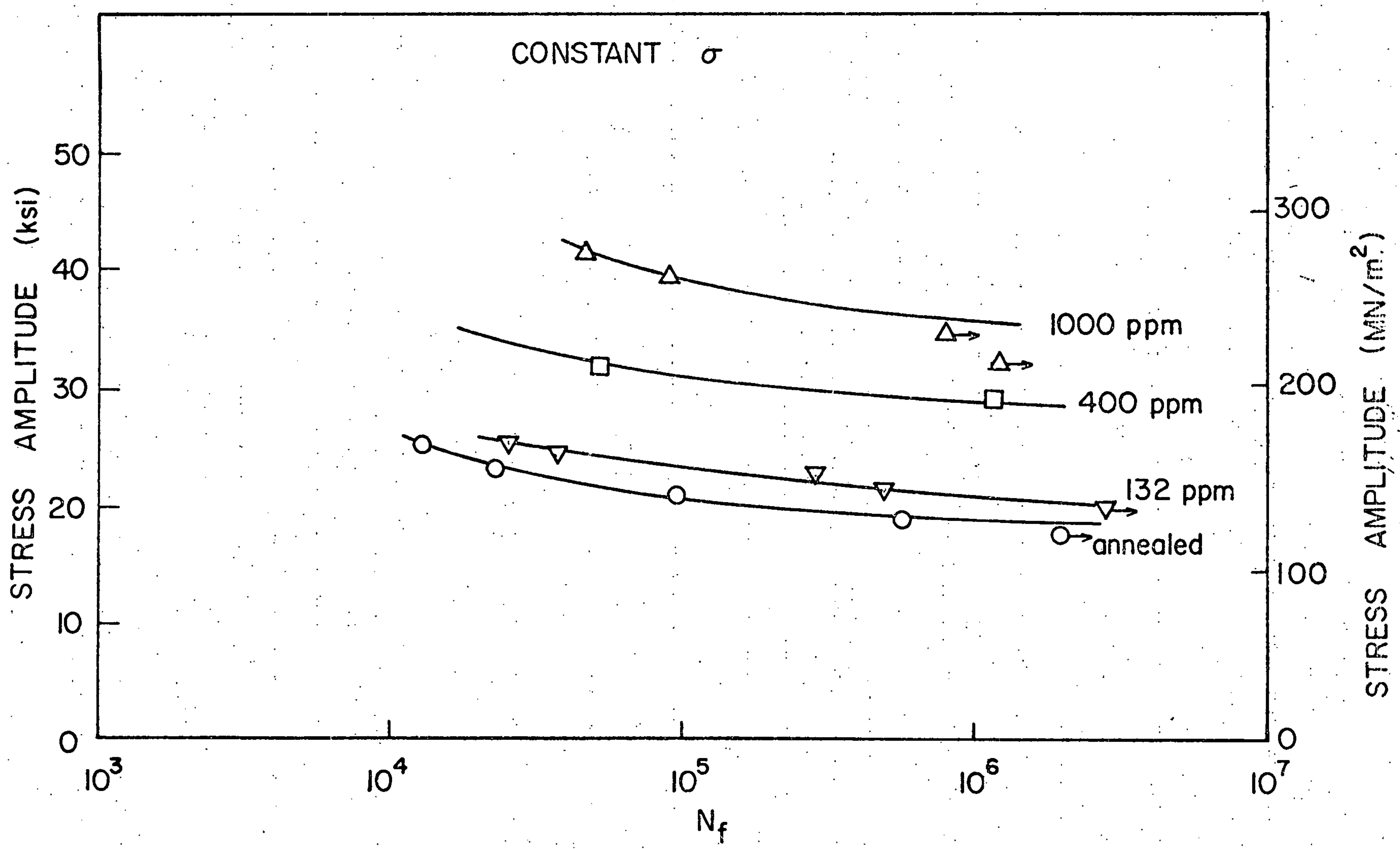
Fig. 2. σ-N data from Fig. 1 compared with saturation stresses computed from strain control tests, V-132 ppm H_2.

Fig. 3. Effect of test frequency on high cycle fatigue life, 25°C.
a) vanadium b) V-1000 ppm H_2

Fig. 4. Effect of test temperature on high cycle fatigue life of vanadium and V-1000 ppm H_2. Elevated temperature tests run at 10 Hz.

Fig. 5. Low cycle fatigue data, 25°C.

Fig. 6. Cyclic hardening data from strain-controlled cycling, 25°C.



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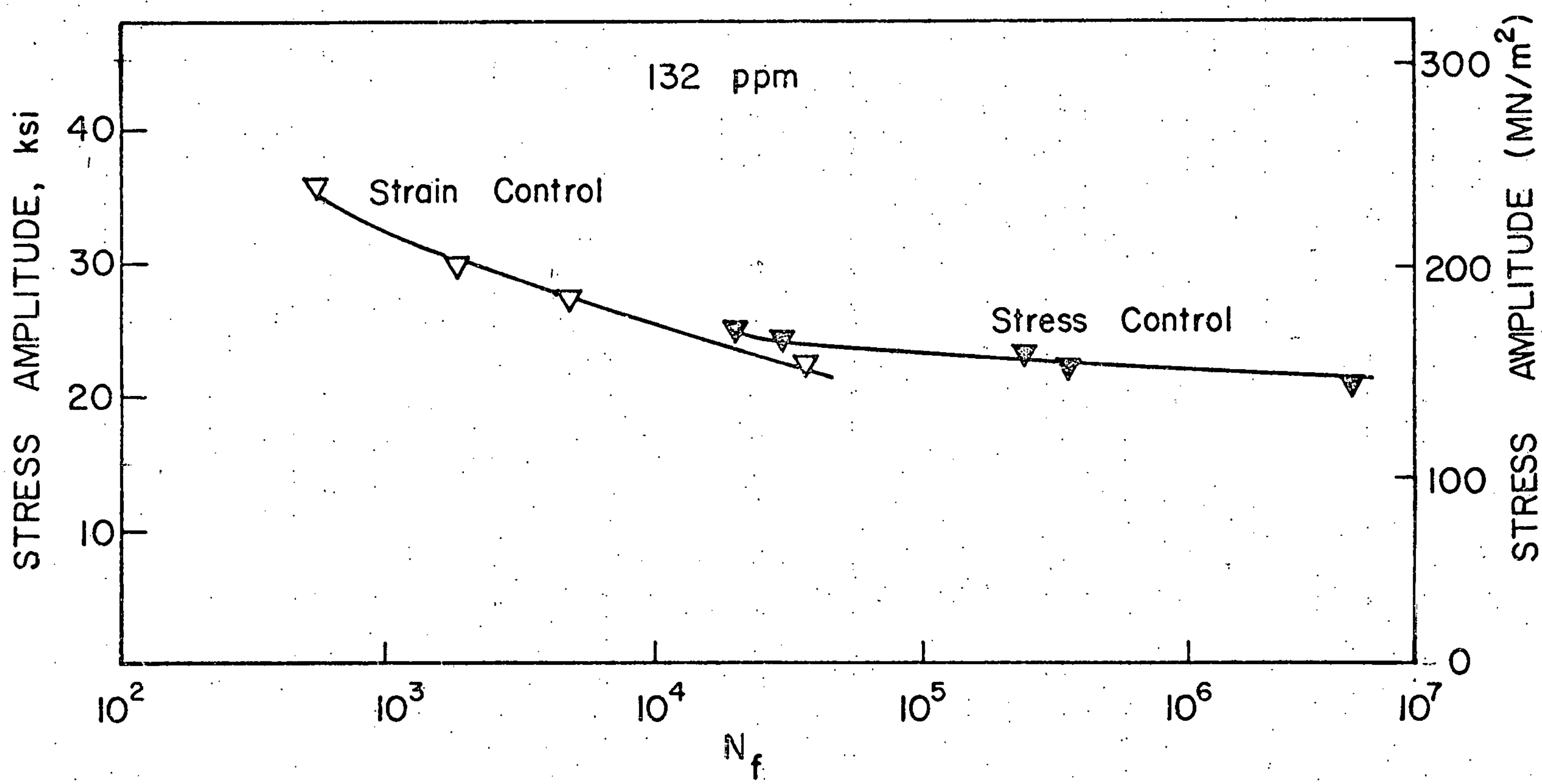

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Figure 3. Effect of test frequency on high cycle fatigue life, 25°C.

a) vanadium

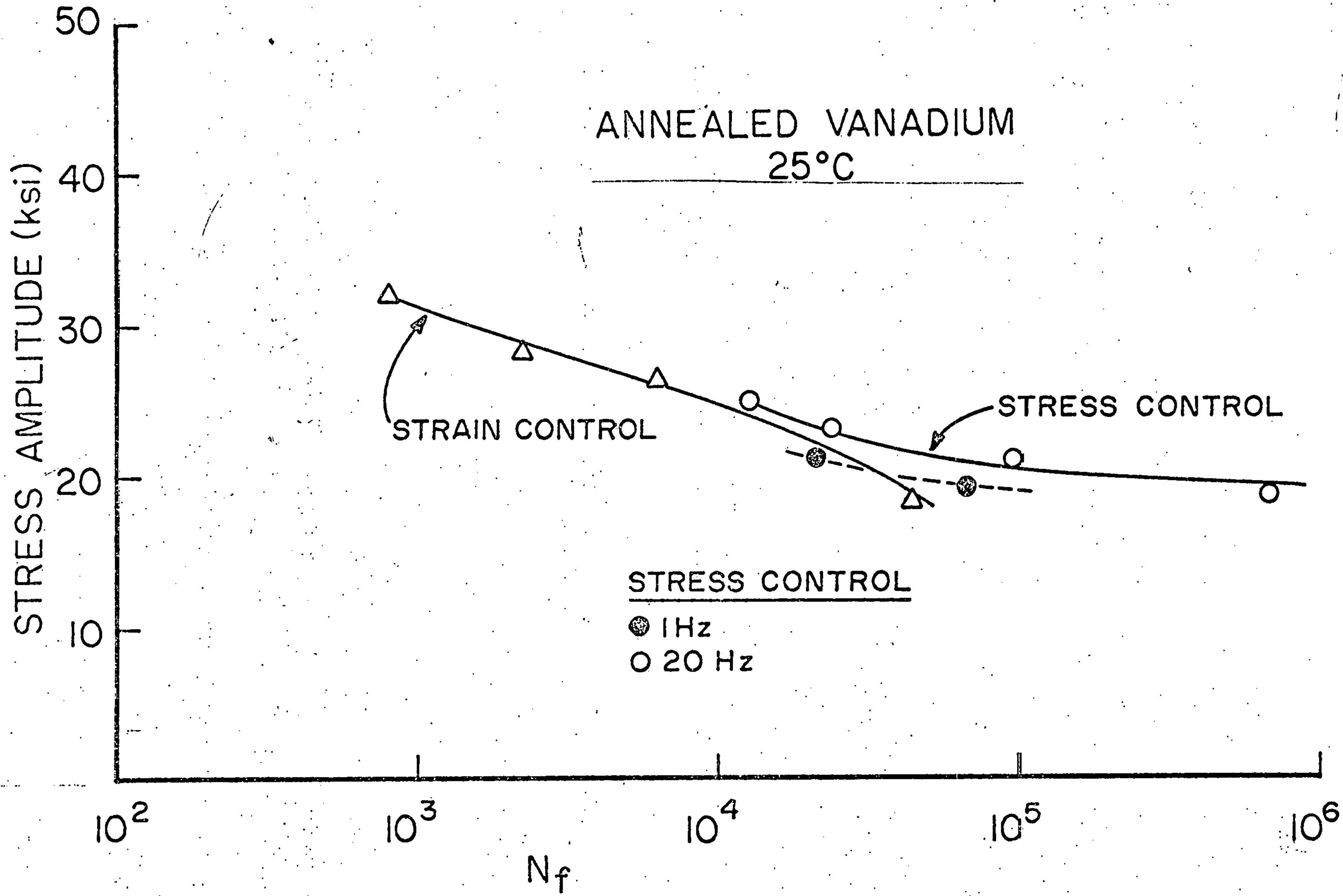


Figure 3. Effect of test frequency on high cycle fatigue life, 25°C.

b) V-1000 ppm H_2

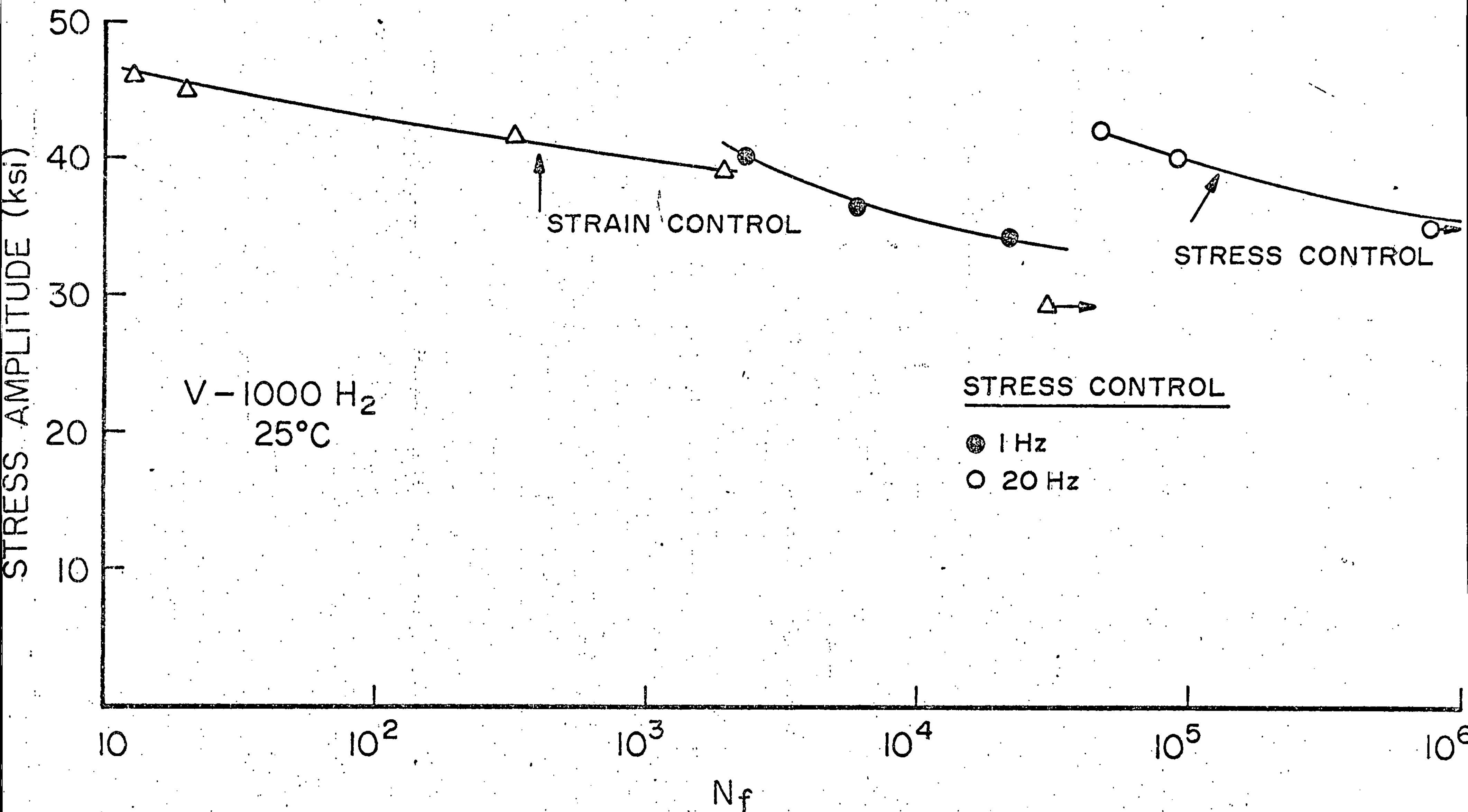
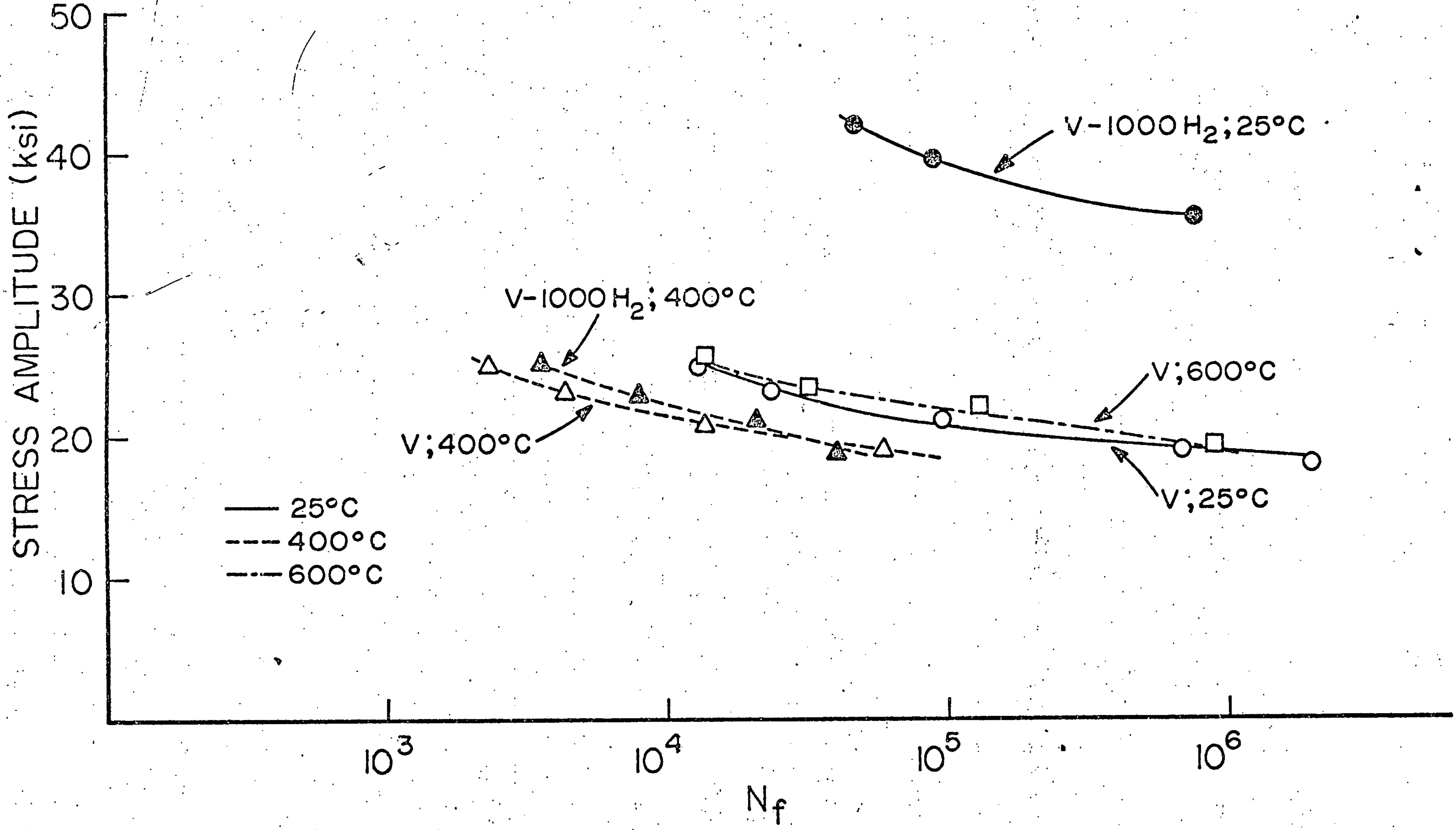


Figure 4. Effect of test temperature on high cycle fatigue life of vanadium and V-1000 ppm H_2. Elevated temperature tests run at 10 Hz.



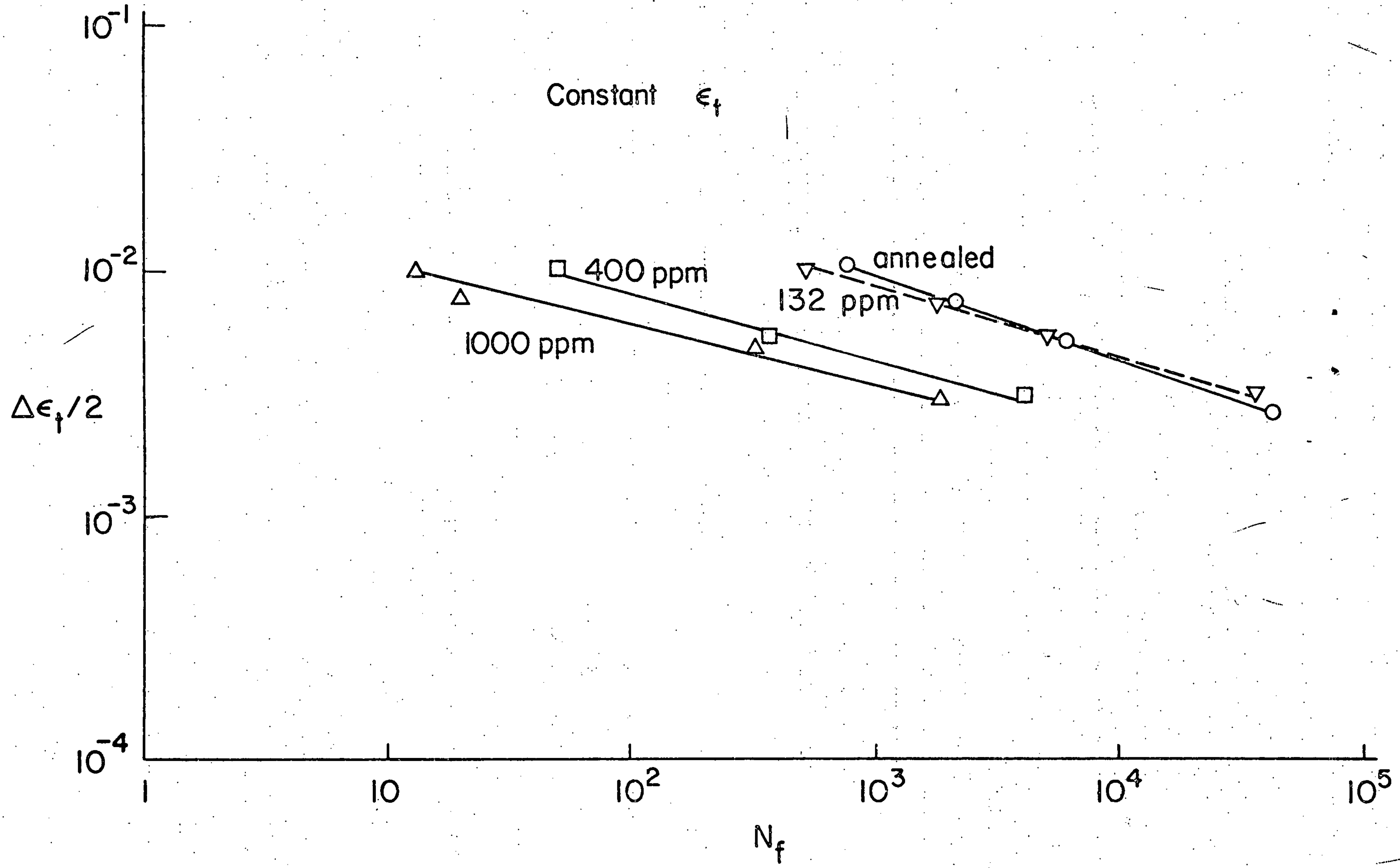


Figure 5. Low cycle fatigue data, 25°C.

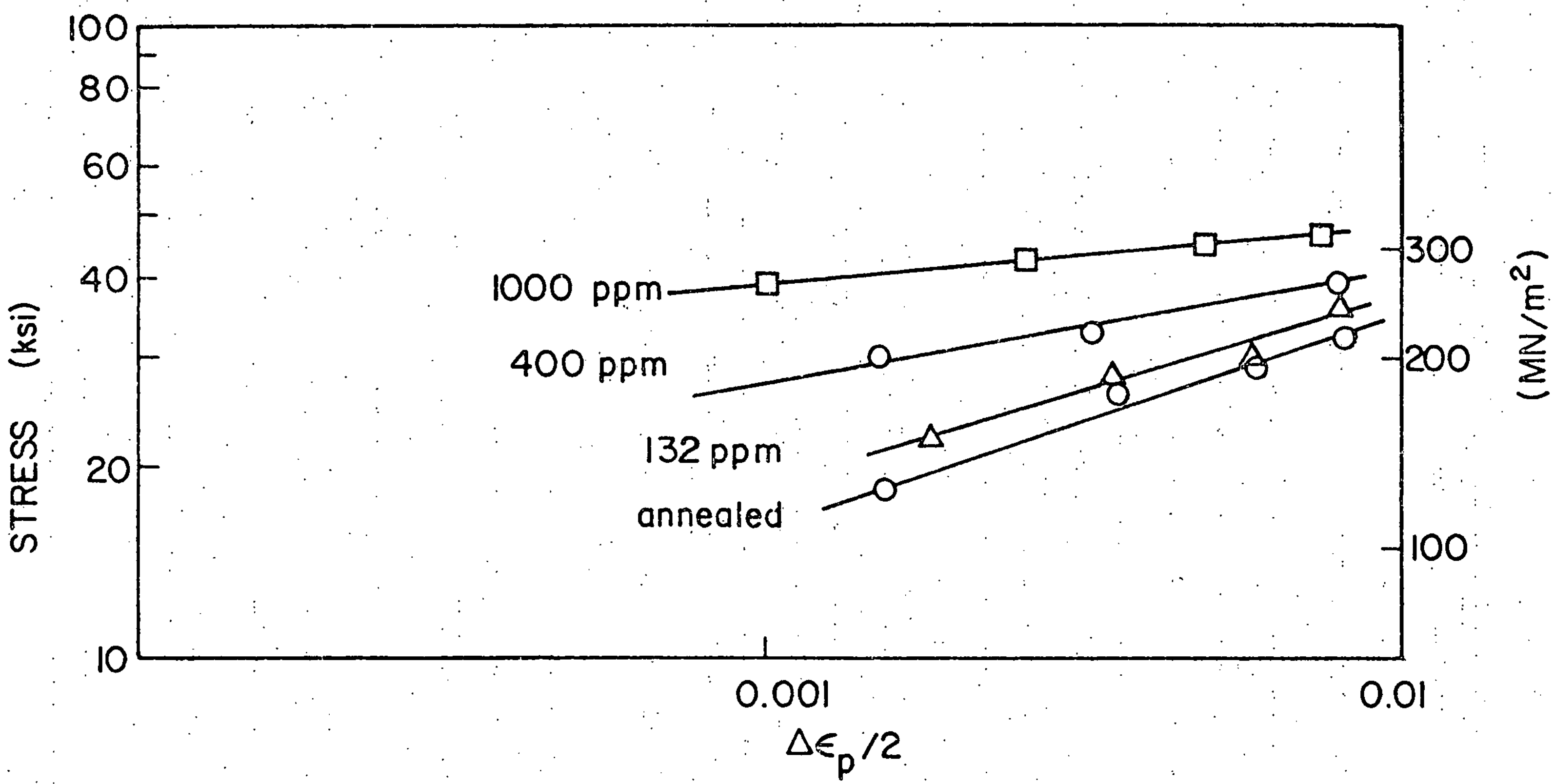


Figure 6. Cyclic hardening data from strain-controlled cycling, 25°C.