

FATIGUE CRACK GROWTH IN Nb-H ALLOYS

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The effect of temperature on the fatigue crack propagation rate has been investigated in niobium-hydrogen alloys. The study was undertaken with the ultimate goal of determining the role of hydrogen in conjunction with test temperatures on the fatigue and embrittlement processes of niobium as a representative of group VA metals. Analysis of results suggests that a mobile form of hydrogen interacting with dislocations plays an important role in the embrittlement process. This analysis is supported by calculations of the activation energy due to the effect of temperature on the critical concentration causing maximum embrittlement.

INTRODUCTION

Numerous investigations in the literature have concentrated on the effect of hydrogen on monotonic mechanical behavior of group VA refractory metals: vanadium, niobium and tantalum (1-5). Nevertheless, little attention has been directed to the influence of hydrogen on the fatigue crack propagation behavior in this group of metals. Among the early investigators in this field, Berger et al (6) recognized that hydrogen improved the high-cycle fatigue life as well as increased the tensile strength of titanium and Ti-8 wt%. Beevers (7) subsequently found that the restriction of twin formation by the hydride precipitates can increase the life of  $\alpha$ -titanium. Wilcox (8), however, reported that hydrogen in solid solution and hydride forms significantly reduced the fatigue life of tantalum. He concluded that hydrogen embrittlement was associated with the increased ease of both crack initiation and propagation.

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In contrast, Lee and Stoloff (9) reported that vanadium containing hydrogen in the form of hydride significantly improved fatigue life in the high cycle tension-compression operation. Chung and Stoloff (10) found that vanadium alloys containing hydride are more resistant to crack initiation than alloys with hydrogen in solid solution. Crack propagation rate, however, increases with increasing hydrogen content but does not differ significantly in hydrided and solid solution alloys. This study also reveals that crack initiation occupies most of the fatigue life of hydrogenated niobium, and, to a lesser extent, unalloyed niobium. Dutton et al (11) discussed the mechanisms involved in the delay of hydrogen cracking in hydride forming metals. They found that stage I crack growth rate is controlled by hydrides growing in the elastic stress gradient, while stage II is controlled by hydride growth in the plastic zone at the crack tip.

Fariabi et al. (12) investigated the effects of hydrogen on the near-threshold fatigue crack growth rate of niobium at room temperature. The results indicate that the threshold stress intensity range,  $\Delta K_{th}$ , decreases with the addition of hydrogen and reaches a minimum,  $(\Delta K_{th})_{min}$ , at a hydrogen concentration approximately equal to the solubility limit of hydrogen in niobium. As the hydrogen concentration exceeds the solubility limit,  $\Delta K_{th}$  increases with the increase of the amount of hydrogen dissolved in the specimen. From these results, it was suggested that dislocation-hydrogen interaction plays an important role in the embrittlement process. Furthermore, using microhardness measurements on fatigued specimens, Fariabi et al (13) show that the plastic zone size is controlled by extensive cyclic plasticity, and that the cyclic flow stress is similar to the static flow stress which weakly depends on hydrogen concentration.

The effect of temperature on near-threshold fatigue crack growth rate has been investigated in the niobium-hydrogen alloys at 273K and 400K by Polvanich and Salama (14). At both temperatures, the results show that the behavior of  $\Delta K_{th}$  as a function of hydrogen concentration is similar to that obtained by Fariabi et al. (12) at room temperature. It was also found that  $(\Delta K_{th})_{min}$  increases linearly with the increase of temperature.

While researchers seem to be in relative agreement about the general features of hydrogen embrittlement in group VA metals, no clear understanding of the mechanisms involved has yet been established. Three main mechanisms have been proposed for the loss of ductility in this group of metals. These mechanisms include the cracking effects from precipitated hydrides (15), decohesion (16) and plastic deformation effects resulting from dislocation-hydrogen interaction (1). The characteristics of these mechanisms were discussed in detail elsewhere (17). The presence of two mechanisms responsible for hydrogen embrittlement in group VA has also been proposed by Farahani et al (18) from their study on single- and poly-crystal niobium. One mechanism is operative at the onset of embrittlement and involves the interaction between dislocations and hydrogen. The second mechanism has similar effects on both single- and poly-crystals and is associated with the precipitation of the hydride phase. This was also confirmed by Fariabi et al. (12) from their studies on the effects of hydrogen on near-threshold crack propagation in niobium.

In this paper, the effect of temperature on the fatigue crack propagation rate has been investigated in niobium-hydrogen alloys at 220K and 350K. The study was undertaken with the ultimate goal of determining the role of hydrogen, in conjunction with test temperatures, on the fatigue and the embrittlement processes of niobium as a representative of group VA metals.

## EXPERIMENTAL

The specimens used in this investigation were made of pure niobium (99.85 pct) furnished by Teledyne Wah Chang Corporation in the form of a sheet 1 mm in thickness. Compact tension specimens were machined out of this sheet in dimensions chosen such that a plane stress condition was satisfied. The specimen preparation as well as the method used to introduce hydrogen are described in detail elsewhere (18).

Fatigue tests were performed in tension-tension loading. The tests were performed at a load ratio  $R$  (= minimum load divided by maximum load) of approximately 0.05 and at test temperatures of 220K and 350K. The stress intensity range  $\Delta K$  was determined using the expression (19)

$$\Delta K = \frac{\Delta P}{B/w^{1/2}} f(a,w) \quad (1)$$

where  $\Delta P$  is the load range,  $B$  and  $w$  are the thickness and the width of the specimen, respectively, and  $f(a/w)$  is the compliance function, where  $a$  is the crack length.

Measurements of crack length during fatigue testing at room temperature were made by means of a travelling telescope with accuracy of  $5 \times 10^{-6}$  meter. In tests where the specimen is enclosed in the furnace or the low-temperature chamber, the change in crack length was determined by measuring changes in the electrical potential at two points across the crack where a constant alternate current was applied. The system used in measuring the crack extension as well as the method used in the measurements are described in detail elsewhere (20). The tests usually were terminated when the crack length was about 60 pct of the specimen width.

#### FRACTOGRAPHY

In order to determine the mode of fracture which occurred during crack propagation, the fracture surfaces of fatigued specimens were examined using a scanning electron microscope. Figs. 1 and 2 display the fractographs of fracture surfaces of Nb-H alloys tested at 220K and 350K respectively. These fractographs are from the regions where the stress intensity was near threshold, and the stress ratio was 0.05.

Micrograph 1a shows the fracture surface at near-threshold region of hydrogen-free niobium tested at 220K. Ductile fracture mode can be observed from random rounded irregularities on the fracture surface indicating very slow crack propagation. Fig. 1b illustrates a more brittle type of fracture surface in the specimen containing 446 ppm wt.H. The mode of fracture is transgranular slip plane cracking with a limited region of grain boundary cleavage. Figure 1c shows the transgranular cracking along a cellular path as the hydrogen content is increased to 910 ppm wt.H where the hydride phase is formed. In this figure, only small transition zones of flat fracture along the grain boundary can be observed.

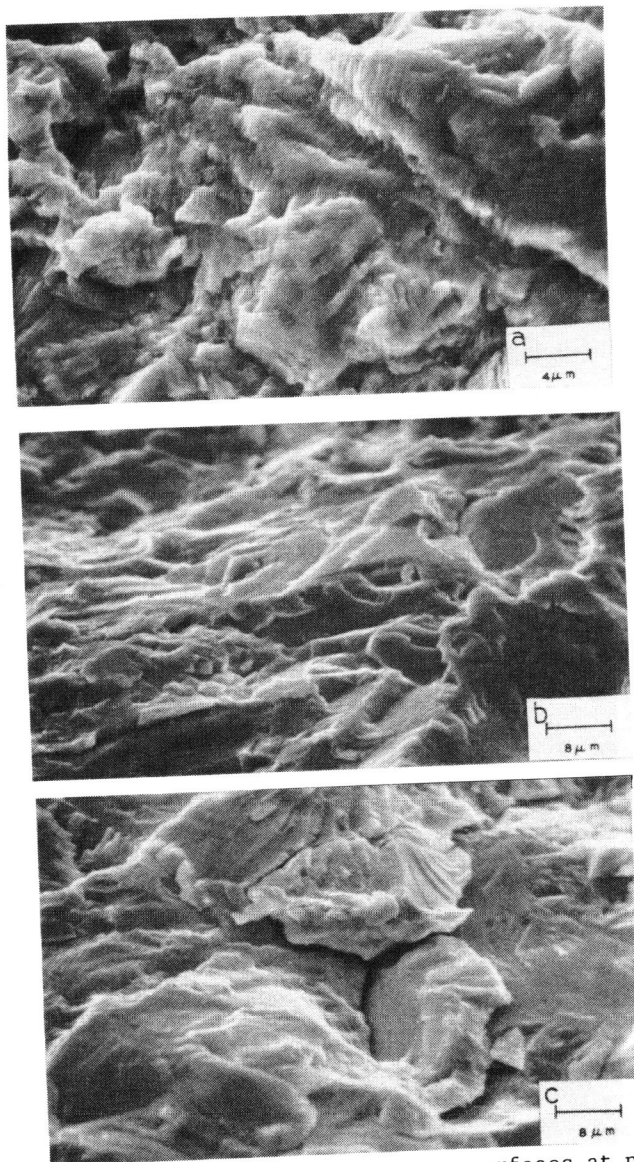


Fig. 1. SEM fractographs of fracture surfaces at near-threshold regions of Nb-H alloys at  $T = 220\text{K}$  for a) hydrogen-free Nb, b) Nb + 446 ppm wt.H. and c) Nb + 910 ppm wt.H.

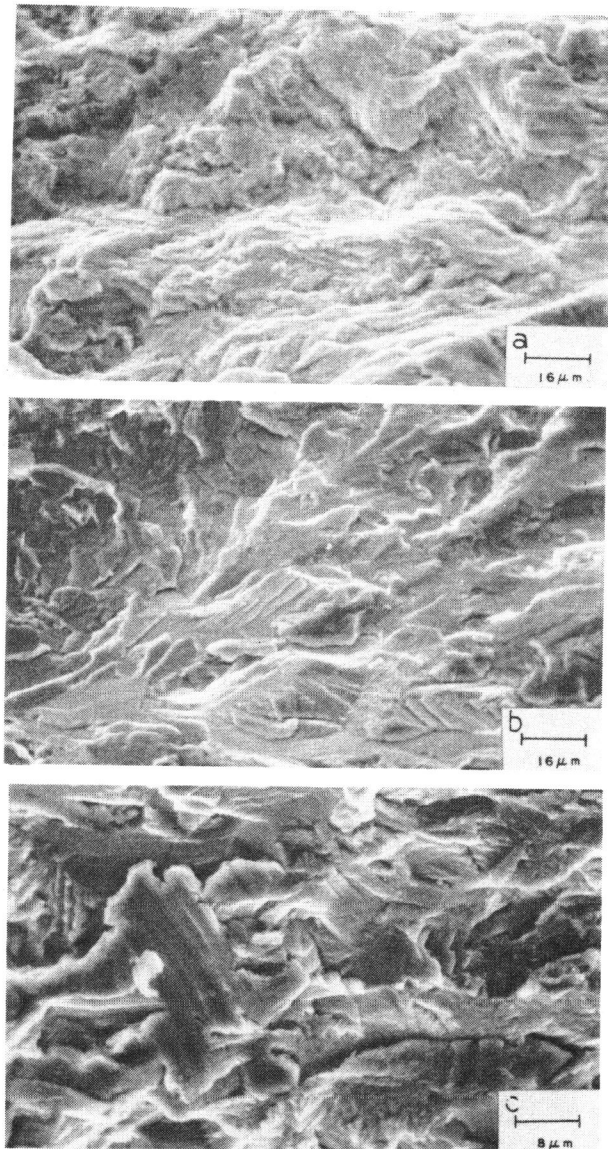


Fig. 2. SEM fractographs of fracture surfaces at near-threshold regions of Nb-H alloys at  $T = 350\text{K}$  for a) Nb + 77 ppm wt.H, b) Nb + 293 ppm wt.H. and c) Nb + 902 ppm wt.H.

## FRACTURE CONTROL OF ENGINEERING STRUCTURES – ECF 6

Micrographs in Fig. 2 show the fracture surface of niobium at near-threshold region tested at 350K. Micrograph 2a is for the specimen containing a low hydrogen content of 77 ppm wt.H. The micrograph shows a combination of random round irregularities in the fracture surface as are often observed in slow crack propagation in ductile material. To a lesser degree, one can see the presence of structure of intersecting planes with the crack path proceeding along several systems of relatively flat, parallel surfaces. Fig. 2b illustrates another type of fracture surface in the specimen containing 293 ppm wt.H. Transcrystalline cleavage facets with river markings in which the cleavage planes are joined by steps with a cellular appearance are predominant on the fracture surface. Although brittle fracture appears on the fracture surface, crack propagation is stable in this case. Micrograph 2c is for niobium containing 902 ppm wt.H and is comparable to that of micrograph 1b. The fracture surface in this micrograph indicates a mixture of cracking by grain boundary cleavage and regions of transgranular slip plane cracking.

### RESULTS

Figure 3 shows the crack growth rate  $da/dN$  as a function of stress intensity range  $\Delta K$  for all specimens tested at  $T = 220K$ . The crack growth rate  $da/dN$  was calculated using the increase in the crack length during the number of cycles  $N$  between successive crack tip readings. The results obtained at  $T = 350K$  are shown in Figure 4. The majority of the curves in both figures represents the crack growth rates in stages I and II. In several specimens, however, the tests were extended to cover stage III or part of it. From both Figs. 3 and 4, it can be seen that at low growth rates (near-threshold) there is a strong dependence of  $da/dN$  on  $\Delta K$ , and the slope of this behavior is not much affected by the presence of hydrogen.

The near-threshold stress-intensity  $\Delta K_{th}$  as a function of hydrogen concentrations for both  $T_{th} = 220K$  and  $350K$  are plotted in Fig. 5. Also shown in this figure are the results obtained by Fariabi et al (12) at room temperature and by Polvanich and Salama (20) at 273K and 400K. From Fig. 5, one can see that, at a constant temperature,  $\Delta K_{th}$  of hydrogen-free niobium is

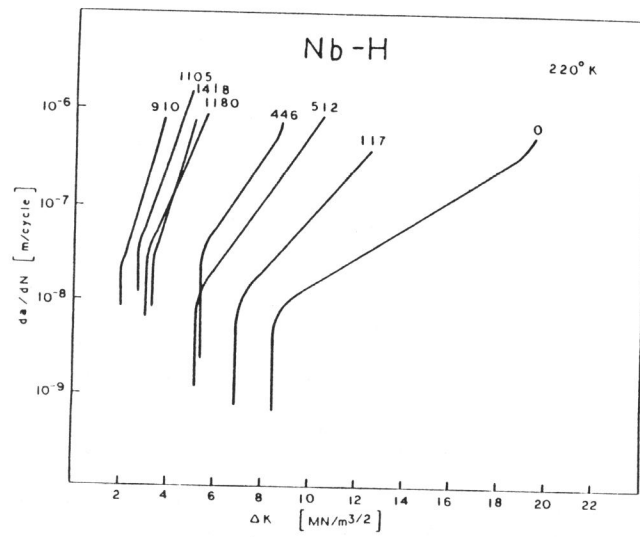


Fig. 3

Fatigue crack propagation rate,  $da/dN$ , vs. stress intensity range  $\Delta K$  in Nb-H alloys at 220K.

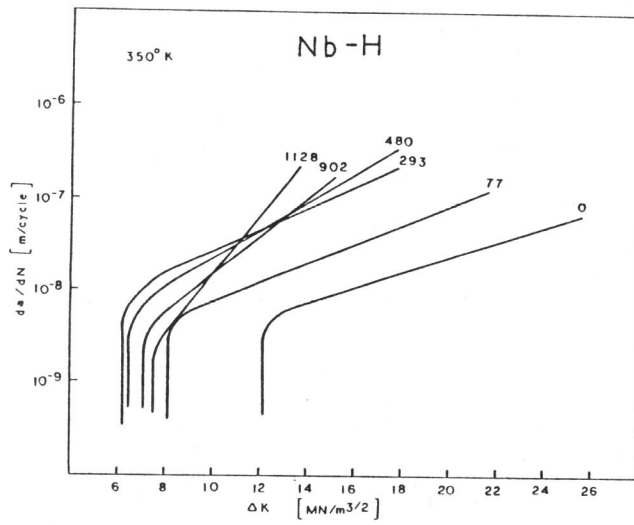


Fig. 4

Fatigue crack propagation rate,  $da/dN$ , vs. stress intensity range  $\Delta K$  in Nb-H alloys at 350K.



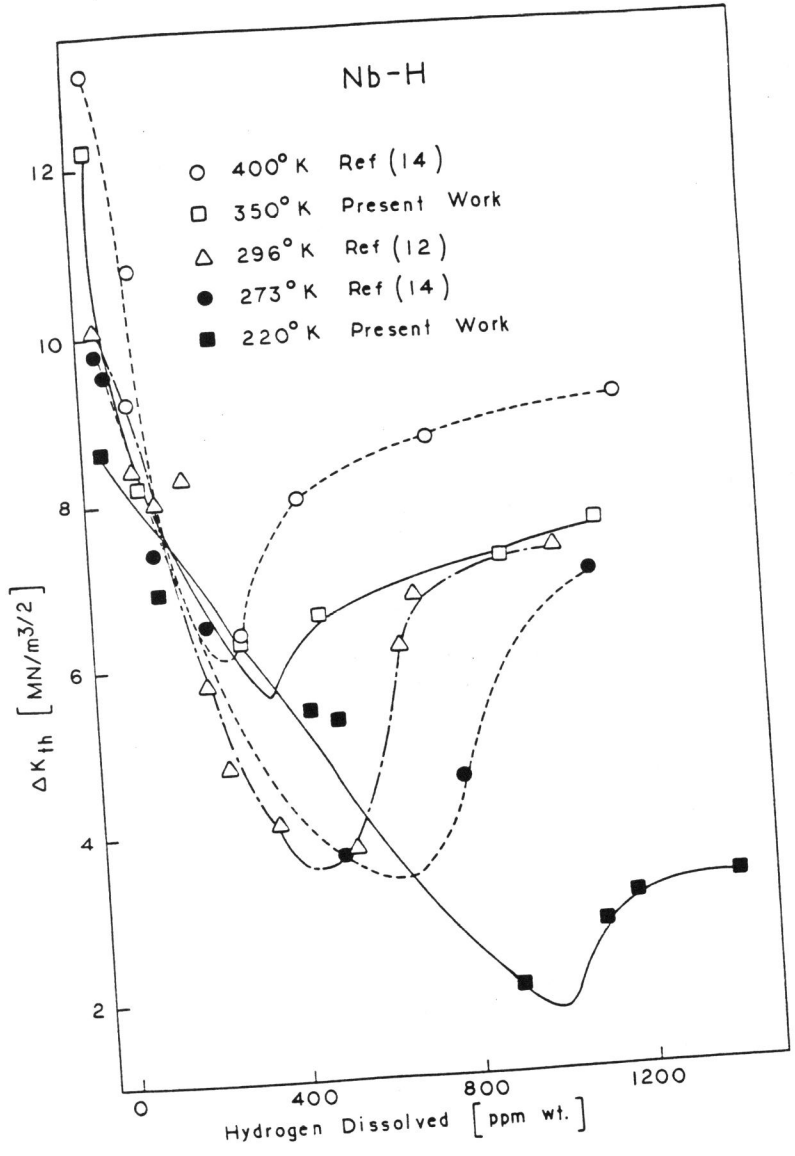


Fig. 5  
 Dependence of threshold stress intensity range  $\Delta K_{th}$  on hydrogen concentration in Nb-H alloys.

the highest, but decreases rather sharply as hydrogen is introduced. The decrease of  $\Delta K_{th}$  with hydrogen is almost linear until it reaches a minimum value at a hydrogen concentration characteristic of the test temperature used in the fatigue experiments. Above this hydrogen concentration,  $\Delta K_{th}$  increases as the amount of hydrogen dissolved is increased, and levels off as the amount of hydrogen is further increased.

DISCUSSION

Dependence of  $\Delta K_{th}$  on Temperature

From Fig. 5, one can see that for all temperatures  $\Delta K_{th}$  reaches a minimum value,  $(\Delta K_{th})_{min}$ , which represents the maximum embrittlement in the material at this temperature. The hydrogen concentration at the point where the maximum embrittlement occurs can be considered as the critical concentration,  $C_{cr}$ , required for maximum embrittlement by hydrogen. As the amount of hydrogen dissolved exceeds  $C_{cr}$ ,  $\Delta K_{th}$  increases as a function of hydrogen concentration and seems to level off at very high concentrations.

Table 1. Variations of the Critical Concentration at maximum embrittlement  $C_{cr}$  and the Solubility Limit  $C_o$  as a function of Temperature.

T(K)	$C_{cr}$ (ppm wt.H.)	$C_o$ (ppm wt.H.)	Reference
220	990	75	Present Work
273	650	253	Ref. 14
296	450	402	Ref. 13
350	350	775	Present Work
400	260	1271	Ref. 14

This behavior indicates the presence of two mechanisms which are responsible for the embrittlement of niobium with hydrogen. One mechanism causes the sharp decrease of  $\Delta K_{th}$  when the amount of hydrogen added is less than that of  $C_{cr}$ , while the other mechanism, which partially offsets the embrittlement occurring at lower concentrations, operates when the hydrogen concentrations exceed that of  $C_{cr}$ . The values of  $C_{cr}$  at temperatures used in these investigations are listed in Table 1. The stress-free solubility limit  $C_0$  of hydrogen in niobium at these temperatures (15) are also listed in this table and indicates that there is no correlation between  $C_{cr}$  and the formation of hydride as it was reported earlier (12). This also indicates that the two embrittlement mechanisms are operative when hydrogen is in the solid-solution as well as in the hydride phase, and the presence of hydride cannot be responsible for the decrease of  $\Delta K_{th}$ . If hydride rather than some more mobile form of hydrogen was responsible for embrittlement,  $\Delta K_{th}$  should have reached its minimum value when the hydride phase starts to form and  $\Delta K_{th}$  drop precipitously after that.

Critical Hydrogen Concentration at the Crack Tip

Also from Figure 5, one can see that the minimum values of the threshold stress intensity range,  $(\Delta K_{th})_{min}$ , for the five test temperatures follow the general behavior of fatigue fracture toughness of most materials where  $\Delta K_{th}$  decreases as the test temperature is decreased. Figure 6 displays a plot of  $(\Delta K_{th})_{min}$ , as a function of temperature T, and indicates a linear relationship between the two quantities. The slope of this linear relationship  $(\Delta K_{th})_{min}/T = 0.024 \text{ (MN/m}^{3/2}\text{) per 1K}$ .

The solute concentration built-up in a stress field,  $C_r$ , at a distance r has been calculated by Liu (21) as

$$C_r = C_0 \exp\left[\frac{2(1+\nu)}{\sqrt{2\pi r}} \cdot \frac{V_H \Delta K}{3RT}\right] \quad (2)$$

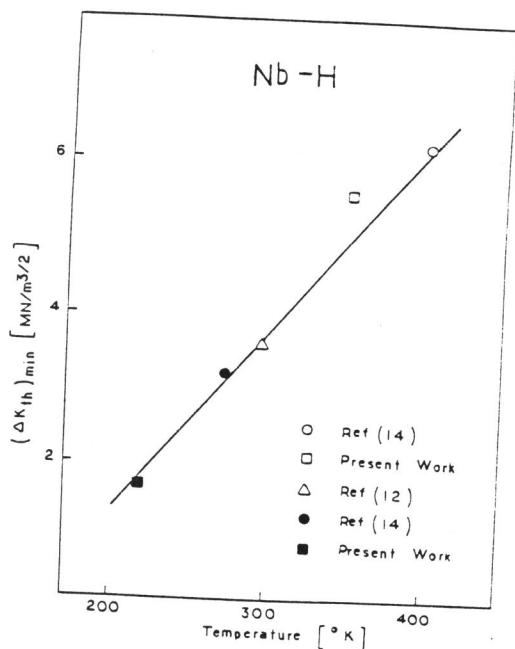
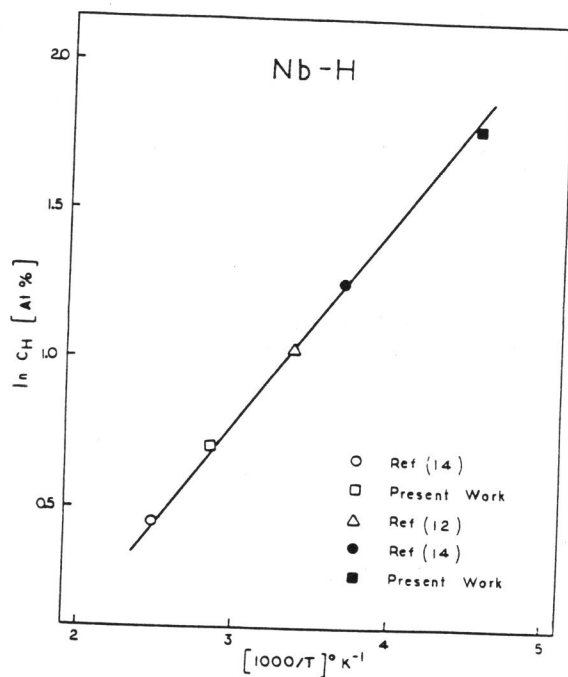


Fig. 6  
Minimum threshold stress intensity range ( $\Delta K_{th}$ )<sub>min</sub> as a function of temperature

Fig. 7  
The logarithm of hydrogen concentration at minimum threshold stress intensity range (maximum embrittlement) vs. inverse of temperature



where  $C_o$  is the solute concentration in the bulk,  $V_H$  is the partial molal volume,  $\nu$  is the Poisson's ratio and  $R$  is the gas constant. From microhardness measurements at  $T=296K$  and  $T=400K$  and  $273K$ , Fariabi et al (13) and Polvanich (20) determined the plastic zone size in niobium specimens containing various amounts of hydrogen and found that  $r$  does not change much as a function of hydrogen dissolved  $C_o$  and its value at  $(\Delta K_{th})_{min}$  varies between 0.4 and 2.5 mm. These results are also confirmed at  $T=220K$  and  $350K$  in the present investigation.

Using these values for  $r$  along with the value obtained from Fig. 6 for  $(\Delta K_{th})_{min}/T = 0.024$   $MN/m^{3/2}/K$ , in Eqn. 2, the ratio of the hydrogen concentration at a distance  $r$  from the crack tip,  $C_r$ , and in the bulk,  $C_o$ , will then vary between 1.09 and 1.04. In these calculations  $\nu = 0.37$ ,  $R=8.3$  Joules/moles.K, and  $V_H=1.7 \times 10^{-6} m^3$ . This result indicates that at  $(\Delta K_{th})_{min}$ , there will be no migration of hydrogen from the bulk to the crack tip stress field, and  $C_r$  represents the critical hydrogen concentration required for maximum embrittlement.

This result supports the quantitative correlation obtained by Gerberich and Chen (22) who suggest the existence of  $\Delta K_{th}$ , defined as the stress intensity below which no cracking will occur under hydrogen-assisted cracking conditions. Those authors also proposed that the controlling mechanism for  $\Delta K_{th}$  depends on a critical concentration of hydrogen whose propensity to form is governed by yield strength, initial concentration, state of stress and temperature. The agreement, however, is only for the minimum values of  $\Delta K_{th}$  or for the maximum embrittlement at a given temperature.

#### Activation Energy of Maximum Embrittlement

Figure 7 illustrates a plot of the natural logarithmic of hydrogen concentration (in percentage of atomic ratio) for maximum embrittlement as a function of the inverse absolute temperature ( $1/T$ ). This plot indicates the increase of hydrogen concentration for maximum embrittlement as the test temperature is decreased. From this figure one also can see that a straight line passes through the data points, and the slope of this line represents an activation energy of a process which can be represented by the relationship

$$C_{cr} = C \exp(Q/RT) \quad (3)$$

where  $C$  is a constant. The value of the activation energy  $Q$  calculated from Fig. 7 is equal to 1370 cal/mole or 0.059 eV.

From their anelastic studies of hydrogen diffusion in niobium, Baker and Birnbaum (23) have found that, at low temperatures, hydrogen exists as pairs of H-H clusters, and the energy of interaction of these pairs is 1265 100 cal/mole. The agreement between this value and that calculated from Fig. 7 suggests that at  $(\Delta K_{th})_{min}$  hydrogen exists as pairs of H-H clusters, and the concentration of these clusters increases as the temperature is decreased. One of the mechanisms proposed earlier (16) for hydrogen embrittlement was based on decohesion resulting from mobile hydrogen in solution or as clusters. The presence of H-H clusters can also be more effective as obstacles to dislocation mobility. Earlier studies by Farahani et al (1) and Fariabi et al (12) gave evidence in support of dislocation hydrogen interaction as a mechanism for hydrogen embrittlement in niobium.

#### CONCLUSIONS

From the results obtained in the present research, the following conclusions can be drawn:

1. The threshold stress intensity range,  $\Delta K_{th}$ , of niobium is very much influenced by the presence of hydrogen. It decreases as the amount of hydrogen dissolved is increased and reaches a minimum at a critical concentration where the maximum embrittlement occurs. As the hydrogen concentration exceeds this critical concentration,  $\Delta K_{th}$  increases with the increase of hydrogen content in the specimen.  $\Delta K_{th}$  is also found to be affected by temperature and decreases as the temperature is lowered. The critical concentration at the crack tip, however, increases as the temperature is decreased.

2. The behavior of the near threshold stress intensity range as a function of hydrogen concentration suggests the presence of two mechanisms to be responsible for the embrittlement of niobium with hydrogen. One mechanism causes the sharp decrease of  $\Delta K_{th}$  when the amount of hydrogen is below  $C_{cr}$ , while the other mechanism which partially offsets the embrittlement occurring at higher concentrations, operates when the hydrogen concentration exceeds  $C_{cr}$ .
3. The analysis of temperature effects on  $\Delta K_{th}$  versus hydrogen concentration suggests that the dislocation-hydrogen interaction plays an important role in the hydrogen embrittlement of niobium. The analysis also indicates that the decohesion mechanism does not have a major effect in the embrittlement process.

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