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HYDROGEN EFFECTS ON THE FRACTURE OF BCC METALS.(U)
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HYDROGEN EFFECTS ON THE FRACTURE OF BCC METALS

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The deleterious effects of hydrogen on the mechanical properties of bcc metals are well known and have been extensively studied [1]. Despite the effort which has been placed on understanding these problems our mechanistic understanding is rudimentary at best. Part of the problem stems from the fact that the behavior of bcc metals with hydrogen as a solute or in a gaseous hydrogen environment cannot be accounted for on the basis of a single fracture mechanism. A second major difficulty is that the effect of hydrogen on the basic parameter of fracture, the strength of the atomic bonding is poorly understood. Despite these serious handicaps, we have made significant progress in recent years in identifying the important physical parameters of the problem, in adequately establishing the effects of hydrogen on some of these parameters and in beginning to develop a mechanistic understanding of fracture in a number of the metal-hydrogen systems. In this paper we will review some of the recent progress and attempt to highlight some of the outstanding problems which remain to be solved.

The behavior of the metal-hydrogen systems can be classified in various ways; one of the most useful being based on whether the system forms second phases such as hydrides under stress (or as a result of deformation). In the class of hydride forming systems [2,3] we will include those which have thermodynamically stable hydrides as well as systems which have hydride phases which can be stabilized by applied stresses [4,6]. Examples of hydride forming systems include the group IVb and Vb metals and their alloys (Ti, Zr, V, Nb, Ta) as well as a number of other bcc metals. All of the hydride formers are severely embrittled by hydrogen when it is present as a solute element and by hydrogen gas when transfer of H between the gas and solid phases can take place. The second category of systems is that of non-hydride formers such as Fe, Mo, W and Cr and their alloys. Some of these systems, such as those based on Fe, are severely embrittled while others such as Mo [7] and W [8] have reduced strain to failure in the presence of a high H fugacity but since they are already relatively brittle materials the effects of H are not as dramatic.

The hydrogen related failure mechanisms in these two classes of metals are clearly distinguishable. In hydride forming systems there is clear and increasing evidence [1, 9-14] that the fracture is due to the stress induced formation of a brittle hydride phase the fracture of which then leads to failure. While many questions remain concerning the details of this mechanism, it can no longer be doubted that hydrogen embrittlement results from the stress induced hydrides. This rather strong statement does not preclude the additional possibility of a second fracture mechanism occurring in the absence of hydride formation. Metals which do not form thermodynamically stable hydrides in the absence of stress may still fail by the stress induced hydride mechanism. The hydride free energy relative to the solid solution can be significantly reduced by a suitable applied

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stress field and the hydrides may form in the stress field of the crack tip [4-6].

The systems based on Fe, Mo, or W do not however fall into this latter category as the hydride free energies are too high to allow stress induced hydride formation. In these non-hydride forming systems the fracture mechanism is poorly understood despite the large amount of work which has been undertaken [1]. In part this stems from the fact that the significant parameters of this problem are only now being clearly established.

Hydride Forming Systems

Hydrogen embrittlement of the Group Vb metals, Nb, V, Ta has been extensively studied since the early 1960's [1]. The general behavior of the alloys with H as solute is shown in Fig. 1 in which the fracture ductility is plotted as a function of temperature [10, 15, 16]. The ductility minimum is characteristic of all of these systems and indeed is observed to characterize the behavior of non-hydride forming systems as well. Another characteristic behavior is the inverse strain rate dependence ie, the increase of the ductility as the strain rate is increased. Both the return of the ductility at low temperatures and the inverse strain rate dependence have been shown to reflect the embrittlement kinetics which requires a flux of hydrogen to the crack tip [10,11]. The temperature below which the ductility decrease occurs has been shown [10, 15-17] to correlate with but to be higher than the observed solvus temperatures. Severe embrittlement occurs at temperatures above that at which hydrides form on cooling in the absence of stress. Indeed, while the solid solutions may be quite ductile and the strain to failure may be very large above the solvus temperature, the actual fracture process may be a "brittle" process such as cleavage as shown in Fig. 2 [10,11].

The mechanism for fracture in these systems which seems to be able to account for these diverse observations is the stress induced hydride fracture mechanism first proposed by Westlake [9] and shown schematically in Fig. 3. As a result of the distortion field around the H interstitial, ε_{ij} its chemical potential in a stress field, μ_σ can be written [18] as

$$\mu_\sigma - \mu_o = \int \sigma_{ij} \varepsilon_{ij} dV \qquad (1)$$

where the reference state chemical potential μ_o is taken as hydrogen in solid solution at zero stress. The stress gradient which results from the presence of an elastic inhomogeneity such as a crack in a stressed solid results in an increase in the hydrogen concentration at the crack tip ($C_\sigma - C_o$) to a value

$$C_\sigma = C_o \exp \frac{\sigma^s \bar{V}_h}{RT} \qquad (2)$$

where $\sigma^s = 1/3\sigma_{ij}\delta_{ij}$ is the spherical stress component, $\bar{V}_h$ is the partial molal volume of hydrogen in solution, and only the volume change associated with the H in solution is considered. (Despite its occupancy of the tetrahedral interstitial site, H has been shown to have a cubic distortion field [19]). The increase in the local H concentration occurs at a rate which reflects the diffusion of H in the stress gradient at the crack tip and serves to eliminate the stress induced chemical potential gradient. In addition to this effect, the inhomogenous stress field at the crack tip affects the free energy between the solid solution and the hydride [4-6]; an effect which does not occur in a uniform stress field [6]. This effect has been treated in various ways but can be viewed as a decrease in the chemical potential of the hydride relative to the solid solution in the stress field of the crack tip resulting in an increase in the local solvus temperature to the value given by

$$C_e^{\sigma} = C_e^{o} \exp - (\sigma_s \Delta V_{\alpha\beta}/RT_e^{\sigma}) \qquad (3)$$

where C_e^{σ} and T_e^{σ} , and C_e^{o} and T_e^{o} are the solvus compositions and temperatures under stress and in a stress free solution respectively, and $\Delta V_{\alpha\beta}$ is the molal volume change on forming the β hydride from the α solid solution. Since the values of $\Delta V_{\alpha\beta}$ are in range of 0.1 to 0.25 and the values of the relative partial molal enthalpy of solution of H in the α solid solution relative to the β hydride, $\Delta\bar{H}_H^{\alpha}$ are small, the stresses at the crack tip can cause a significant increase in the solvus temperature (in the case where $\Delta V_{\alpha\beta} > 0$ and $\sigma_s > 0$). In addition to this effect the volume change on forming the hydrides is accommodated in part by plastic deformation in many systems eg. Nb-H [4,20]. These plastic accommodation processes can be assisted by the local stresses thus further increasing the local solvus temperature at the crack tip above the value given by Eqn. 3. In systems such as V-H, in which the hydride forms as plates and most of the volume change is accommodated elastically, this latter effect is small and the shift of the solvus is given by Eqn. 3. In addition to causing hydride precipitation above the stress free solvus temperature, the crack tip stress field affects the relative free energies of the various hydride varients and tends to bias the system towards precipitation of those variants which lie in a favorable orientation for crack propogation [13,21].

In hydride forming systems the solid solution remains ductile even at temperatures below the solvus temperature as indicated by direct observation [10-11] and by the fact that the strain to failure remains relatively high even at temperatures within the ductility minimum. Application of a stress at temperatures below the solvus results in fracture of the precipitated hydrides and the crack propogates to the interface with the solid solution. The stress concentration then causes flux of hydrogen to the crack tip and further precipitation of hydride. Cracking of the hydride occurs and the process of stress induced hydride formation and cracking is repeated leading to brittle failure. In those systems (Nb-H, Ta-H) where $\Delta V_{\alpha\beta}$ is accommodated by plastic deformation, a large hysterisis between the hydride formation and resolution temperatures is observed [4,20] as expected from the accommodation free energy terms and the cracked hydride remains along the crack surfaces [10,11,22]. In contrast to this, systems (V-H) in which the accommodation is elastic have a small hysterisis and the hydride will go back into solution once the stress field is removed as the crack propogates [12,13].

This mechanism has been supported by direct observations in the Nb-H [10,11] and V-H [12,13] systems and by appreciable indirect evidence in other systems. In the Nb-H system the fracture surface is covered by hydrides as indicated by electron diffraction and SIMS ion probe studies (Fig. 4) [22,23].

At temperature somewhat above the solvus this same mechanism will apply [10].

In this case plastic deformation and work hardening occurs prior to the initiation of fracture. As the flow stress level increases, the stress induced increase of the hydride solvus temperature also increases as indicated by Eqn. 3. In a sense the plastic deformation of the solid solution is competitive with the onset of stress induced hydrides. If the hydride solvus is shifted to the test temperature by the applied stress, hydride will form at stress concentrations such as dislocation pileups and the plasticity will be terminated by the formation and cleavage of the hydrides. If this does not occur plasticity will lead to the usual ductile fracture. The solid solution is ductile and remains so until the onset of stress induced hydrides.

In the Nb-H system hydrogen embrittlement has been observed [23] at temperatures up to 700 K at compositions greater than about H/Nb = 0.3 (Fig. 5). Since the solid solution extends to above H/Nb = 1.0 at temperatures above about 450 K it would be expected that the alloys would be completely ductile in the vicinity of H/Nb $\approx$ 0.3. The ductile-brittle transition occurs on decreasing the temperature or on increasing the H/Nb and is quite sharply defined. This behavior has been shown to be consistent with the stress induced hydride fracture mechanism except that in the high temperature region the induced hydride is the δ , NbH_2 dihydride for which the molal volume increase on forming from the α' solid solution is of the order of 20%. The boundary between the ductile solid solutions (H/Nb $\lesssim$ 0.3 and T $\gtrsim$ 700 K) and the brittle alloys can be shown to correspond to the stress shifted phase boundary between the α' solid solution and the two phase $\alpha' + \delta$ boundary.

In this fracture mechanism the stress induced hydride is expected to be a relatively brittle phase as the fracture surfaces are generally cleavage in nature. The fracture surface in the Nb-H system was shown [11] to be the {110}. Single crystals of the β hydride were shown to be extremely brittle, failing by cleavage with {110} and {100} fracture surfaces showing the same features as the low concentration Nb-H alloys [24]. Identical behavior was observed in the α' solid solution. While the V-H alloys have been shown to cleave through stress induced hydrides, single crystals of the β V_2H have been reported to be ductile [25]. The reasons for this diversity in observations is not known. While most hydrides are reputed to be extremely brittle, and support for this comes from the difficulty in preparing hydrides in any form other than powder, the reasons for this brittleness is not known. As will be discussed in a subsequent section, studies of elastic constants, phonon dispersion curves and other properties do not in general indicate that the inherent atomic bonding is reduced by the high hydrogen concentrations in the solid solutions or the hydrides. In fact an analysis of the phonon properties suggests an increase in the atomic force constants in the Group Vb hydrides relative to the solid solutions. TEM [20] and fracture [23] studies of NbH_x have indicated that dislocation motion is very limited in these hydrides and that this, rather than a decrease in atomic bonding, may cause their brittle nature.

The kinetics of hydrogen embrittlement in the hydride forming systems have not been extensively studied. Some indication that the fracture growth rate is associated with H diffusion to the crack tip has been obtained in the Zr-H [26] and Ti-H [27] systems. A recent study [28] of crack propogation in kinetics in the Nb-H system has shown definitively that this is the case where the H is present as a solute. Several different types of kinetics can be obtained depending on the temperature range relative to the solvus temperature and depending on the type of loading employed (increasing K, decreasing K or constant K type of test where K is the crack tip stress intensity). In decreasing K tests well below the solvus, the crack growth rate is expected to be determined by the flux of H to the stress induced hydride which forms at the crack tip and to be characterized by a linear dependence of ln(v) vs K behavior as is observed (Fig. 6). The strong isotope dependence in the H diffusivity [29] is reflected in the fracture rates. The ratio of the velocities for Nb-H and Nb-D alloys is observed to be 15 at 77 K in excellent agreement with the expected ratio from the diffusivities. This good agreement with the kinetics calculated on the basis of the fracture model is observed over the entire temperature range.

At temperatures closer to the solvus the kinetics of fracture are controlled by both the stress induced formation of hydrides at the crack tip and diffusion of hydrogen to these hydrides from the surrounding solid solutions. This results in a three stage ln(v) vs K_I curve as shown in Fig. 7. The high stress intensity Stage III corresponds to ductile overload failure which occurs when the fracture is driven at a rate which exceeds the ability of the hydrogen flux to form hydrides at the crack tip. The low K_I Stage I regime corresponds to the threshold stress intensity below which the hydrides are not nucleated and failure does not occur. The Stage II behavior is steady state formation and fracture of crack tip hydrides at rates which reflect the flux of hydrogen to the crack tip. The kinetics are described by a modified theory based on Simpson and Puls [30];

$$V = \eta D_H \overset{o}{C}_H \exp \frac{W^{inc}}{RT} \quad \exp \frac{W^a}{RT} \tag{4}$$

where D_H is the hydrogen diffusivity, $\overset{o}{C}_H$ is the concentration of hydrogen in solid solution, W^{inc} is the elastic strain energy of the hydride and matrix due to $\Delta V_{\alpha\beta}$ and W^a is the interaction energy of the hydride with the crack tip stress field. The temperature dependence of Stage II velocities is given by an Arrhenius relation with the activation enthalpy

$$\Delta H = \Delta H_H + W^{inc} + W^a \tag{5}$$

where ΔH_H is the diffusion enthalpy for hydrogen. We can estimate the activation enthalpy to be 6-7 KJ/mole. As seen in Fig. 8 the data fit an Arrhenius relation very well and the measured activation enthalpy is 6.6 ± 1.5 KJ/mole in good agreement with the expected value. A more extensive treatment of the kinetics of crack propogation in the Nb-H system has shown that the stress induced hydride fracture mechanism discussed above is in good quantitative agreement with the measured parameters.

Based on the proposed mechanism several effects of alloying with interstitial and substitutional solutes may be expected. Any solute which causes significant strengthening of the solid solution, such as C,N or O will result in higher stresses at elastic inhomogeneities and hence in larger shifts in the local solvus temperatures. Thus strong alloys should exhibit increases of the temperatures below which the brittle fracture mode is observed as has been noted in Nb-O-N-H alloys [10]. On the other hand, it has recently been shown that substitutional alloys of Nb with Mo, Ti and V have greatly increased solubility for H before the onset of hydride precipitation [31]. In these alloys the increased thermodynamic stability of the solid solution relative to the hydride should result in a decrease in the temperature below which brittle fracture is observed. Trapping of H by solutes may also result in the same effect as this would decrease the rate at which the hydride could form at the crack tip. An inhibition of embrittlement resulting from alloying Nb has been observed [32].

Despite the general understanding of hydrogen embrittlement in the hydride forming systems there are a number of major outstanding problems. One of these is understanding of the deformation and fracture of the hydrides themselves. Except for the suggestion [24] that the β NbH is brittle due to the difficulty of dislocation motion and the observation of ductility in VH [25], there is little information about the hydride properties. Another observation which is poorly understood is the "high temperature ductility minimum" first reported by McIntyre and Hardie [15] and confirmed by Gahr and Birnbaum [10]. This minimum in ductility, which is only a few degrees in width, occurs just above the high temperature loss in ductility in Nb-H and V-H alloys. In situ crack propogation and fractographic studies [10,11] do not show any distinctive features associated with this ductility minimum which differ from the behavior above and below the minimum. While it has been suggested [10] that this minimum reflects an ordering reaction in the hydride there is no strong evidence in support of this suggestion. Another area which deserves additional study is the high temperature embrittlement which has been observed in Nb-H alloys [23] and which may occur in other systems. At the present time only a few studies of the effects of alloying on the embrittlement are available. This area is an important one for developing our understanding as well as possibly developing methods of alleviating the practical problems of using materials in aggressive environments and should be further explored.

Non - Hydride Forming Systems

Our mechanistic understanding of hydrogen embrittlement in systems which do not form hydrides (even in the presence of a stress bias at the crack tip) is in a much more rudimentary state than for the hydride forming systems. The behavior of these materials has been extensively characterized but often by investigations which have not been sufficiently well controlled to allow the development of mechanistic understanding. A number of proposed mechanisms have been put forth and as these have been recently reviewed [1] only a few possibilities will be discussed here.

One rather remarkable observation is that the phenomenology of the embrittlement due to solute hydrogen or gaseous H is very similar for both the hydride and non-hydride forming systems. While in the past this has led to some confusion, it is clear that this similarity results from the kinetics of embrittlement rather than the mechanism of fracture. Thus the observation of a ductility minimum vs temperature, of an inverse strain rate effect on the ductility, of three stage ln(v) vs K dependence and many other observations reflect the kinetics of transport of hydrogen to the crack tip and not the mechanism of fracture. One example will be used to illustrate this point. As previously discussed the ductility minimum in the hydride forming systems results from the fact that above a certain temperature the stress is not sufficient to form a hydride and plastic failure occurs. Below a certain temperature the mobility of the hydrogen is limited and within the time scale of the test a sufficiently high concentration does not occur at the crack tip to form the hydride and the plastic failure occurs. The same general explanation accounts for the behavior in the non-hydride forming systems. A critical concentration of hydrogen, the value of which depends on the local stress, is required for brittle fracture [33]. At low temperatures the hydrogen mobility is limited and within the time of the experiment the critical concentration is not achieved resulting in ductile failure. Above a certain temperature the stress level at stress singularities is not sufficiently high to increase the local hydrogen concentration to this critical value and again ductile failure occurs. Thus although the detailed phenomena differ in the hydride forming and non-hydride forming cases, the low temperature limit of the ductility minimum is set by the kinetics of hydrogen diffusion to the crack tip and the high temperature limit is set by the thermodynamics at the crack tip. Both types of systems require a critical hydrogen concentration for fracture but for completely different reasons. While understanding the kinetics of fracture is important, the kinetics do not determine the fracture mechanism.

In several important respects the phenomenology of embrittlement differs in the two classes of material. One example is that the fracture is generally intergranular in the non-hydride forming metals and transgranular in the hydride formers. High strength single crystal whiskers of Fe exhibit ductile fracture in H_2 and H_2S gas atmospheres under conditions where equivalent strength steel fractures in a brittle intergranular mode [34]. In many cases the fracture surface is associated with segregated elements such as S, P, Sb, As and others although the relation of this segregation to hydrogen embrittlement is not established [35]. Another aspect in which the behavior differs is the effect of solute hydrogen on the plastic behavior. In Nb, V and Ta solute hydrogen results in an increase in the yield and the flow stresses by an amount which increases as the temperature is decreased [36]. In contrast, high purity iron exhibits a marked decrease of the flow stress when electrolytically charged with H (at low current densities) and the effect increases as the temperature is decreased [37,38]. In low purity iron the effect is opposite to this and the introduction of solute H solution strengthens the material. Once again the mechanism for these effects are not established although it has been suggested that H decreases the energy for kink nucleation on screw dislocations. While the softening effect is large in pure iron this material does not exhibit hydrogen embrittlement and the relation between H effects on dislocation behavior and embrittlement, if any, is not known.

The most commonly accepted mechanism of embrittlement in the non-hydride forming metals is "lattice decohesion" which was first suggested by Troiano [39] and developed by Oriani [40] and others. The essence of this mechanism is that solute H decreases the strength of the atomic bonds at the crack tip and this leads to fracture when the H concentration exceeds a critical value. Evidence in support of this mechanism is rather indirect as theoretical or experimental treatments of the effects of H on atomic bonding are very difficult to develop. Measurements such as elastic constants and phonon dispersion curves examine the effects of H on the lattice potential close to the equilibrium position. In the group Vb metals these measurements indicate an increase in the phonon frequencies for all of the phonon branches [41] and an increase in c_{44} and B and decrease in c' [42] as the H concentration is increased. Analysis of these results leads to the conclusion that hydrogen increases the atomic force constants. Measurements of this type are difficult to carry out in the ferrous systems due to the low H solubility. In the only measurement available it was reported that the polycrystalline shear modulus, G decreases with H additions to Fe [43]. (These measurements were carried out at low frequencies and must be treated with some causion.)

The conclusion which must be drawn from the available experimental evidence, imperfect as it is, is that no evidence exists to support the assumption that H in solid solution decreases the strength of atomic bonding. While some of the evidence suggests that a strengthening of the atomic bond actually may occur, this conclusion must be considered to be extremely tentative. Theoretical treatments are equally inconclusive.

Measurements of the effect of solute H on the surface energy of Nb (α′ solid solution at H/Nb = 0.82) and of the surface energy of the β NbH hydride have been carried out using fracture mechanics techniques and have shown that the solid solution and the hydride have about the same surface energy as pure Nb [24]. A similar result was obtained [44] for solid solutions of H in Ni (admittedly not a bcc metal) at elevated temperatures where the equilibrium surface energy was determined. The above experiments are directed towards the effect of a uniform distribution of H on the surface energy and do not preclude the possibility that the surface energy of these metals are decreased by the segregation of H to the surface. Indeed, this follows from the positive heat of adsorption of H to the surface which leads to an excess surface concentration in equilibrium. Thus while H in solid solution does not decrease the surface energy, in agreement with conclusions drawn from phonon dispersion data and elastic constants, H segregated at surfaces such as grain boundaries does reduce the boundary energy and as a consequence may reduce the stress to cause fracture along the boundary.

One other class of measurement which may add to our understanding is photoemission studies of adsorbed H on surfaces. These have not been carried out on bcc metal surfaces but on Ni (111) surfaces they indicate bonding of the H to the surface via sp bands [45]. The changes in the surface electronic structure do not clearly establish the effect of H on the Ni bonding and additional work of this sort should be carried out.

In directing attention to the behavior of H at grain boundaries we are being consistent with the bulk of observations which suggest that hydrogen embrittlement in the non-hydride forming systems is principally a grain boundary fracture phenomenon. This should not imply that transgranular brittle fracture would not occur in the absence of grain boundaries at a sufficiently high H fugacity. The embrittlement in many systems is also associated with the presence of other segregated species having positive heats of adsorption and which consequently decrease the surface energy. Segregation of species such as S may weaken the bonding across the grain boundary by forming directional metal - S bonds using electrons which in the absence of the segregant would take part in the metal - metal bonds. There is some recent experimental [46] and theoretical evidence [47] (albeit on Ni surfaces) that this may indeed occur. Hydrogen, when present as a segregated species at the grain boundaries may act in the same way as these other species to decrease the boundary energy and perhaps the atomic bonding across the grain boundary. It differs from these other segregants in that it retains its high mobility in the lattice at the temperature of the mechanical test. Hydrogen can therefore accumulate at the grain boundary during the stressing by various transport mechanisms such as diffusion or dislocation transport in response to stress concentrations resulting from plastic deformation which precedes fracture. Recent SIMS studies of ^2H in nickel have shown segregation at grain boundaries both in the presence of segregated S and in its absence [48].

The fact that segregation of H at grain boundaries occurs and the expectation that this has a concomitant decrease in the surface energy does not establish this as the mechanism of hydrogen embrittlement. The fracture energy greatly exceeds the thermodynamic surface energy and hence plastic deformation processes must play a significant role in the fracture. It has been suggested [49] that the amount of plastic work scales with the surface energy. A detailed understanding of this coupling is not available but it can result from several sources. As the surface energy is decreased the stress to cause bond rupture is also reduced leading to lower values of the local stresses and hence to smaller plastic zones and less plastic work. Other effects related to the influence of H on the dislocation behavior will be of significance in ways which are not yet established. In particular a localization of the slip in front of a crack due to H solutes, as has been observed in nickel [50] can lead to a decrease in the total plastic work and an increase in the normal stresses in front of the crack tip [51]. A decrease in the stress to move dislocations caused by H can have a significant influence on these processes.

In summary, examination of the available experimental and theoretical information does not lead to any definitive conclusion about the mechanism of hydrogen embrittlement of the non-hydride forming metals. The information required for the mechanistic understanding (such as the effects of H on the atomic bonding, the nature of the interactions of H and other segregants with boundaries, the nature of the interactions between H and these other segregants, the effect of H on the plastic deformation processes) is first being developed and considerable additional work is required. If however, we measure progress by the extent of our recognition of the problem, then appreciable progress has been made.

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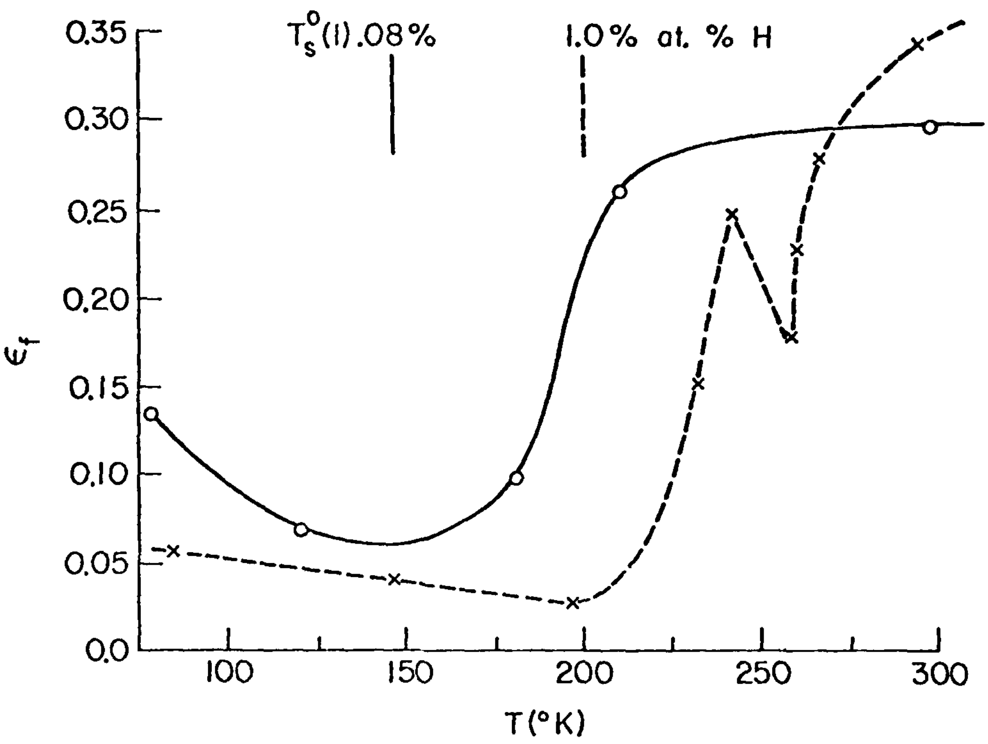

Fig. 1a Strain to failure vs temperature for Nb - H alloys.
(------) 1.0 at % H
(———) 0.08 at % H
The stress free solvus temperatures are indicated by the vertical lines. This data was taken at strain rates of 10^{-4} sec^{-1}.

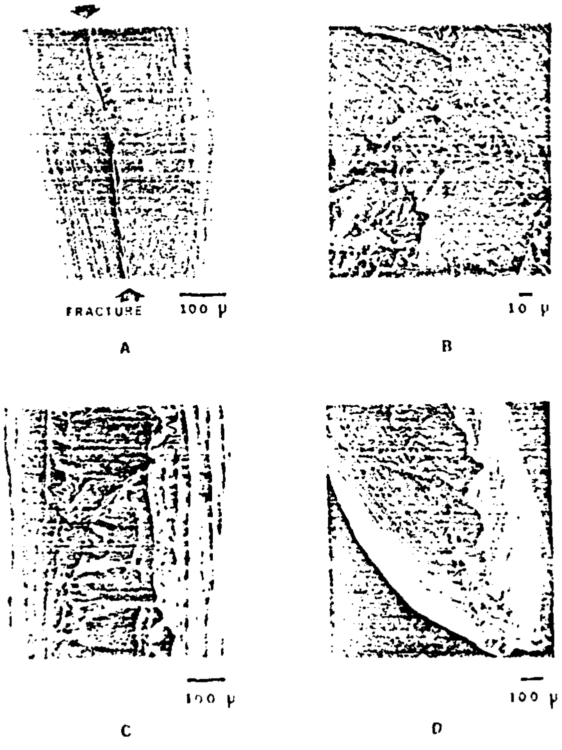

Fig. 1b Fracture surfaces of Nb - H alloys containing 0.08 at % H.
(A) 210 K
(B) 180 K
(C) 120 K
(D) 77 K

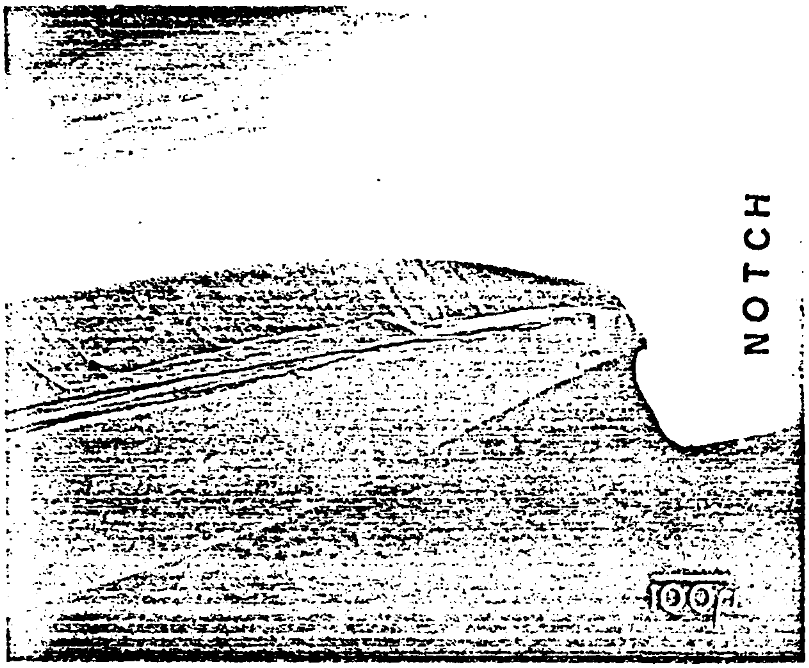

Fig. 2 Fracture surface of a Nb specimen containing 1 at % H which was stressed at 230 K. The initial width of the specimen is equal to the notch width and is about 500 μ. The fracture surface is {110} cleavage despite the large reduction in area preceding fracture.

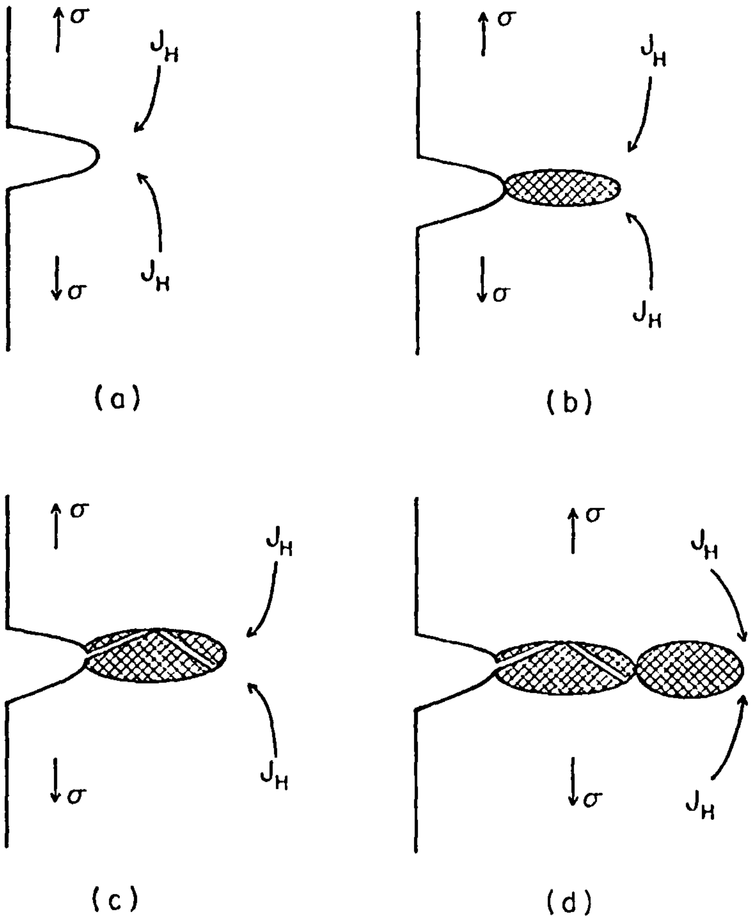

Fig. 3 Schematic representation of the stress induced hydride fracture mechanism. (a) Stress induced flux of hydrogen to the crack tip. (b) Stress induced formation of hydride at the crack tip. (c) Cleavage of the hydride (d) Repeat of (a) and (b).

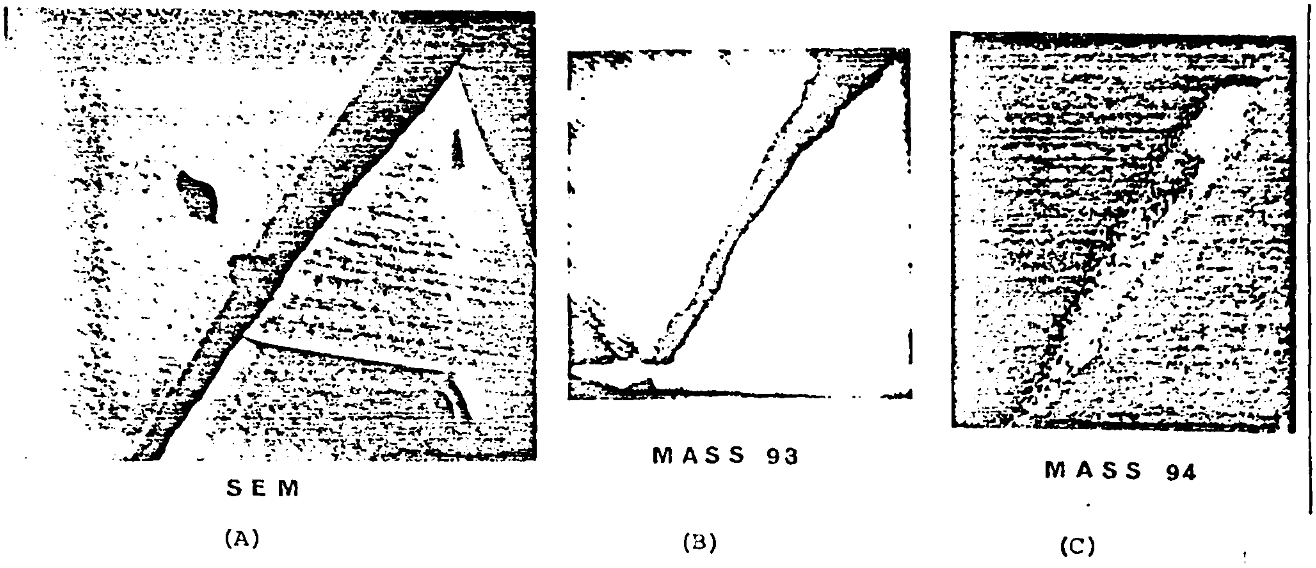

Fig. 4 Fracture surface in Nb - H alloy showing formation of the NbH hydride along the fracture surface.
(A) SEM image of the fracture surface.
(B) SIMS image of the fracture surface using mass 93 Nb ions.
(C) SIMS image of the fracture surface using mass 94 NbH ions.

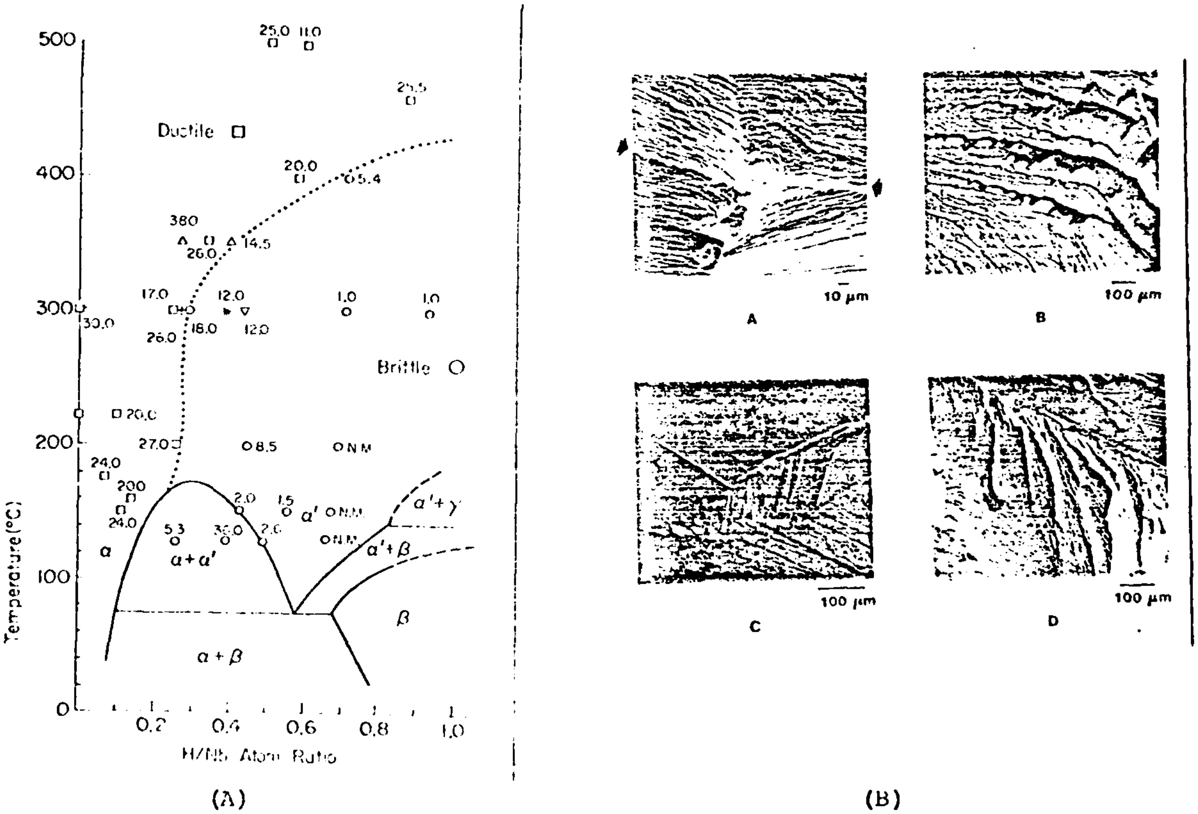

Fig. 5 High temperature embrittlement of Nb - H alloys
(A) Phase diagram of the Nb - H system showing the high temperature ductile - brittle transition in the solid solution phase field. The data points indicate the compositions and temperatures tested and the numbers next to each point indicate the strain to failure.
(B) Fracture surfaces for specimens tested at 575 K with the compositions (a) $NbH_{0.28}$ (b) $NbH_{0.30}$ (c) $NbH_{0.71}$ (d) $NbH_{0.93}$

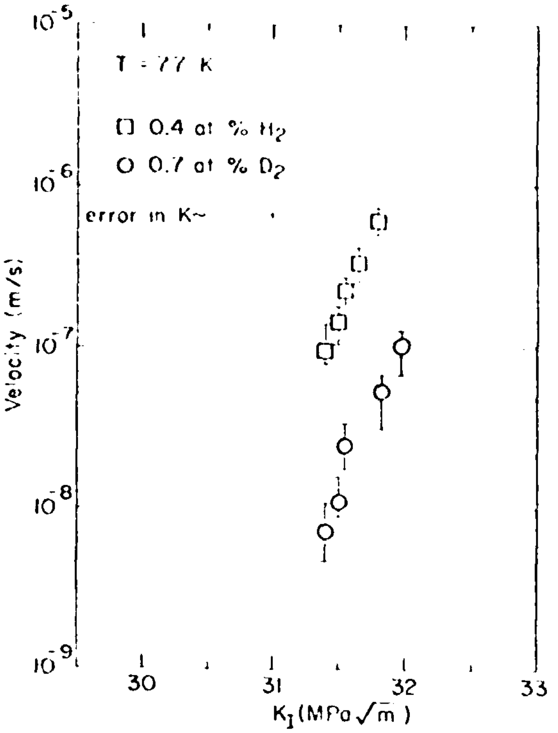

Fig. 6 Crack velocity (v) vs stress intensity (K_I) for Nb-H and Nb-D specimens of the indicated compositions tested at 77 K. The ratio of the crack velocity at constant K_I reflects the anomolous isotope effect for the diffusion of H or D to the crack tip. The actual concentration of H or D in solution at the test temperature is determined by the solvus.

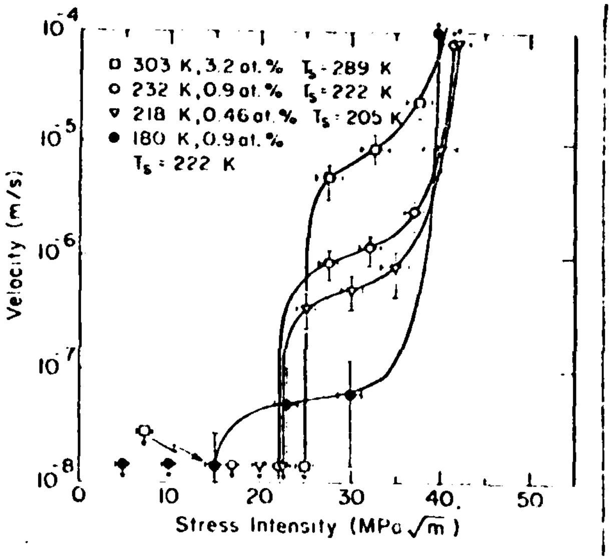

Fig. 7 Crack velocity (v) vs stress intensity (K_I) for Nb specimens containing the indicated H concentrations and tested at the indicated temperatures. The tests were carried out at constant stress intensities and exhibit three stage behavior. These tests were carried out near the stress free solvus temperatures, T_s which are indicated.

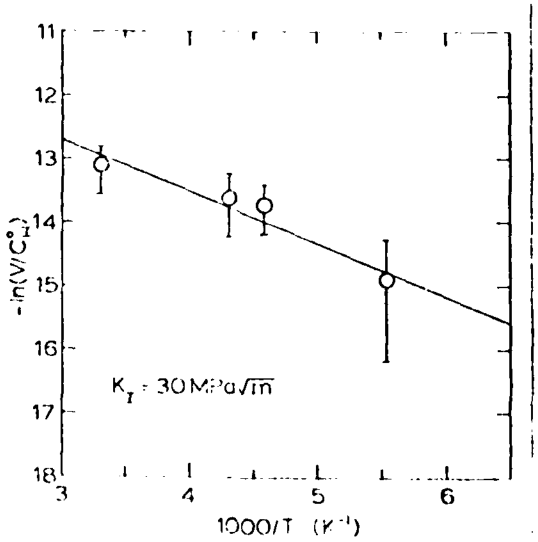

Fig. 8 Arrhenius plot of the temperature dependence of the stage II velocity for the data shown in Fig. 7. This form is in agreement with the theoretical expression, Eqn. 4.

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