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HYDROGEN IN TITANIUM ALLOYS

G. W. WILLE
J. W. DAVIS

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Office of Patent Counsel

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Prepared for
The U. S. Department of Energy
Under Contract No. DE-AC02-77ET 52039

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FORWARD

This report was prepared by McDonnell Douglas Astronautics Company - St. Louis under Contract DE-AC02-77ET52039 for the U.S. Department of Energy Office of Fusion Energy. It was administered under the direction of the Materials and Radiation Effects Branch with T. C. Reuther acting as Program Monitor. The McDonnell Douglas program was performed by G. W. Wille and J. W. Davis.

ABSTRACT

The impact of hydrogen on the mechanical properties of titanium and its alloys concerns the fusion community because it may reduce the usefulness of titanium as a candidate material for first wall and blanket structure.

The overall hydrogen embrittlement phenomena is rather complex because the effects and reactions have many interdependent variables. Factors that appear to be most significant are the temperature dependence of hydrogen solubility in alpha and beta phases, the hydrogen partial pressure around titanium, and alloy composition. Other facets that enter into the embrittlement phenomena in more subtle ways are the relative amounts of alpha and beta phases present; the prior mechanical and thermal history of the material; the stress-state and loading rate; operating temperature; and the amount of hydrogen within the titanium as well as in the surrounding region.

The titanium alloys that offer properties worthy of consideration for fusion reactors are Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-Si (Ti-6242S) and Ti-5Al-6Sn-2Zr-1Mo-Si (Ti-5621S). The Ti-6242S and Ti-5621S are being considered because of their high creep resistance at elevated temperatures of 500°C. Also, irradiation tests on these alloys have shown irradiation creep properties comparable to 20% cold worked 316 stainless steel. These alloys would be susceptible to slow strain rate embrittlement if sufficient hydrogen concentrations are obtained. Concentrations greater than 250 to 500 wppm hydrogen and temperatures lower than 100 to 150°C are approximate threshold conditions for detrimental effects on tensile properties. Indications are that at the elevated temperature - low hydrogen pressure conditions of the reactors, there would be negligible hydrogen embrittlement.

Equal numbers of hydrogen, deuterium, or tritium atom are soluble in titanium under equal conditions. No isotope effects were noted and therefore any effects noted for hydrogen should apply equally for deuterium or tritium for equal volume percent concentrations.

A thorough review of available information revealed little directly applicable data. Because of this lack of data, a sufficient data base must be generated to provide quantitative data to determine the effects of both internal and environmental hydrogen on the most favorable titanium alloys at temperatures and pressures of interest for fusion reactors. Ideally, this data base will also combine the effects of radiation damage as well as any hydrogen effects.

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1.0 INTRODUCTION AND SUMMARY

Titanium alloys appear to offer advantages for use as first wall and blanket structure in a fusion reactor based on a combination of factors which include strength, fabricability, cost, corrosion resistance, an established processing industry, and low long-term residual radioactivity. Two primary uncertainties regarding the use of titanium in a fusion reactor are radiation damage resistance and compatibility with the fusion reactor environment, particularly with respect to hydrogen. Hydrogen compatibility is particularly important because first generation fusion reactors will use deuterium and tritium as fuel. Since titanium has a high affinity for hydrogen, the potential exists for hydrogen embrittlement and increased tritium inventory in the structure.

In a fusion reactor there are four primary sources of hydrogen and its isotopes. These sources are:

- o Interactions of the deuterium and tritium (D-T) fuel in the plasma with the first wall
- o Transmutation reactions within the titanium
- o Interactions of tritium in the breeding material with the blanket structures
- o Interactions of tritium in the coolant with the first wall and blanket structures

The interactions between the D-T fuel and first wall are a combination of chemical reactions between the titanium and D-T fuel and physical/chemical reactions resulting from energetic ions incident on the first wall. During the reactor burn cycle there will be D-T ions and neutral hydrogen atoms from the plasma that travel through the plasma scrape-off zone and impinge at high speeds upon the first wall in amounts that could reach 10^{19} particles per cm^2 per second as depicted in Figure 1-1. Some ions and atoms implanted in the first wall from the plasma, will leave the first wall and reenter the scrape-off zone because of the 10^{-6} torr vacuum in the scrape-off zone. The amount of hydrogen and its isotopes that remain in the first wall will depend upon the first wall material, amount of hydrogen isotopes incident upon the wall, temperature of the wall, and hydrogen partial pressure in the scrape-off zone. During the non-burn portion of the cycle the plasma chamber will be evacuated to 10^{-4}Pa (10^{-6} torr) and then back illed with D-T fuel to 10^{-1}Pa (10^{-3} torr); therefore during this time the wall will be subjected to pure chemical interaction with D-T fuel. The former burn cycle interactions are most important since they represent the largest time segment in the operation; also the advanced tokamaks and EBT device are continuous burn machines. The equilibrium hydrogen concentrations resulting from burn cycle interactions could correspond to approximately 22,700 appm (500 wppm).

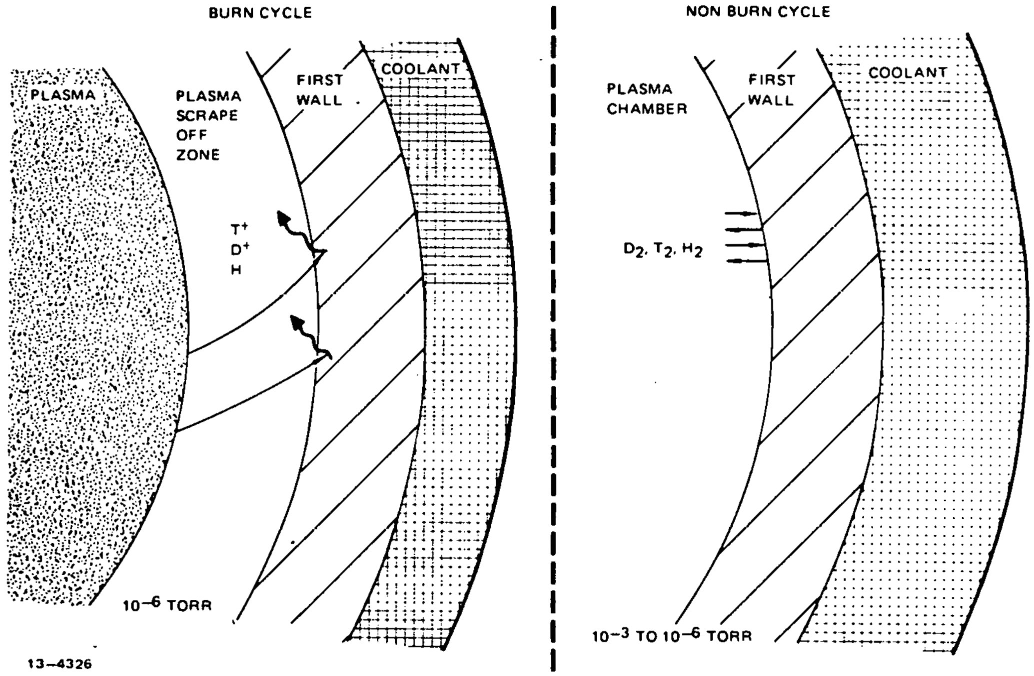

FIGURE 1–1 FUEL INTERACTIONS WITH FIRST WALL

The transmutation reactions of the 14 MeV fusion neutrons with the titanium structure results in production of hydrogen and helium throughout the material. In general, the quantity of hydrogen produced by transmutation reactions in a titanium alloy is small.

Hydrogen also results from interactions between the titanium and tritium in the breeding material and coolant. Typically, tritium will be bred in lithium containing blanket regions of a reactor. The tritium concentration in the breeding loop will depend upon the capability of the processing method used to recover the tritium. Hydrogen that has been formed in the breeder material will be present in the coolant system. The actual amount of hydrogen depends upon the system design, but for a helium cooled system could be relatively large.

Look and Baskes(1) have performed calculations that predict hydrogen concentrations in a titanium first wall of approximately 1000 appm under proposed EPR and NUWMAK operating conditions. This value of 1000 appm corresponds to 22 wppm hydrogen. These concentrations of hydrogen and its isotopes are well below the allowable maximum limits of 150 wppm (6800 appm) hydrogen allowed in present titanium material specifications. Therefore, hydrogen at these predicted concentrations would not embrittle the titanium.

However, other investigators believe that hydrogen concentrations will be higher than 1000 appm. Davis and Smith(2) have predicted equilibrium D-T concentrations in titanium of 50,000 appm which corresponds to 1100 wppm hydrogen. Hydrogen concentrations of 1100 wppm are of a magnitude that causes concern for the embrittlement effects on titanium alloys.

The fusion environment at the first wall/blanket area is predicted to have operating temperatures of 300 to 600°C with hydrogen pressures of 10 to 10^{-1} Pa (10^{-1} to 10^{-3} torr). The temperature of the blanket is not expected to fall below perhaps 200°C after the reactor is in operation, therefore low or room temperature phenomena is not expected, except under fault conditions.

The hydrogen-titanium interaction has been studied since the 1930's but it was not until the early 1950's when jet engine parts started to fail as a result of hydrogen embrittlement that extensive research was initiated. As a result, considerable information has been obtained on reactions with hydrogen and its effects on properties of titanium and some of its alloys. The interaction is not a simple phenomena.

The presence of hydrogen in titanium is not always deleterious. Hydrogen embrittlement only results when hydrogen is not retained in solution or when its concentration exceeds the solubility limits of the alloy so that hydride precipitates or segregation can occur.

Generally speaking, embrittlement due to hydrogen manifests itself in two different forms: susceptibility to embrittlement at high strain rates (impact embrittlement) and embrittlement at low strain rates (low strain rate embrittlement). Impact embrittlement effects the characteristics of properties obtained at high strain rates such as Charpy impact strengths. Low strain rate embrittlement effects slow strain rate properties, such as normal tensile properties.

Factors that appear to be most significant to the embrittlement phenomena are the temperature dependence of hydrogen solubility in alpha and beta phases, the hydrogen partial pressure around the titanium, and the alloy composition. Other facets that enter into the embrittlement phenomena in more subtle ways are the relative amounts of alpha and beta phases present; prior mechanical and thermal history of the material; stress-state and loading rate; operating temperature; and amount of hydrogen present within the titanium relative to the surrounding region.

The formation of hydrides is a mechanism often attributed to the cause of embrittlement.(3)(4) This is especially true in impact embrittlement of alpha alloys where titanium hydride can precipitate from titanium during cooling from elevated temperatures due to a decrease in hydrogen solubility at room temperature. Generally, impact embrittlement is limited to alpha alloys, although in some low beta, alpha-beta, and beta alloys, impact embrittlement has been observed at hydrogen concentrations below the limit of solubility.

The presence of hydrides is not necessarily evident in slow strain rate embrittlement of alloys containing some beta. There are several thesis on the mechanism causing embrittlement in alloys containing beta, however, it is generally agreed upon that hydrogen migrates to the region of a crack tip and either causes formation of hydrides that cannot be identified by microscopy or causes distortion of the lattice to a point that propagates a crack under low strain rate.

If hydrogen is retained in solution and then precipitates or segregates under the influence of strain, low strain-rate embrittlement can take place. This embrittlement occurs in both alpha and beta alloys, possibly as a result of precipitation of small amount of hydride at the alpha-beta interfaces. Properly controlled heat treatment to keep hydrogen in solution increases the resistance of titanium alloys to low strain-rate embrittlement; however, alpha alloys experience less improvement in impact embrittlement since precipitation of hydride in the alpha phase cannot be prevented. In either case ductility is restored at elevated temperatures. Table 1-1 is a summary of embrittlement types for titanium alloys.

The solubility of hydrogen in titanium depends upon a variety of factors, many of which are interrelated, such as temperature, phase type (alpha, beta, or alpha-beta), alloying elements, and equilibrium hydrogen pressure around the titanium. No isotope effects have been observed; deuterium and tritium atoms dissolve in titanium in much the same manner as hydrogen on an atomic basis. That is, the number of deuterium or tritium atoms that will dissolve in titanium is equal to the number of hydrogen atoms that will dissolve in titanium.

Table 1-1 Titanium Alloy Embrittlement Susceptibility

Alloy Type	Embrittlement Susceptibility	Characteristics
Alpha	Impact	Increasing strain rate increases susceptibility
Near-Alpha	Low strain rate	Decreasing strain rate increases susceptibility
Alpha-Beta	Low strain rate	Decreasing strain rate increases susceptibility
Beta	Low strain rate	Decreasing strain rate increases susceptibility

A limited amount of data suggests that at elevated temperatures and low hydrogen pressures there may be no deleterious hydrogen damage to the titanium. The low hydrogen pressure in the reactor controls the solubility of hydrogen in the titanium. The 10^{-1} Pa (10^{-3} torr) hydrogen pressure would correspond to an approximate equilibrium hydrogen content in titanium at 500°C of approximately 100 wppm. At this level, it is doubtful that hydrogen would degrade the mechanical properties.

Early work on mechanical properties did not cover alloys that are commercially available now and tended to investigate higher pressure external hydrogen (10^5 Pa) rather than the 10 to 10^{-1} Pa (10^{-1} to 10^{-3} torr) for fusion. The high pressure external hydrogen pressures would, at equilibrium, correspond to higher internal concentrations than anticipated in the reactor. Work that was done with lower hydrogen pressures tended to be on either commercial or high purity titanium and not alloys of interest. There has been a resurgance in interest in hydrogen effects on titanium, primarily due to interest in titanium usage for aircraft structures and more recently for fusion reactors.

The titanium alloys that offer properties worthy of consideration for fusion reactors are Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-Si, and Ti-5Al-6Sn-2Zr-1Mo-Si.

The near alpha titanium alloys Ti-6Al-2Sn-4Zr-2Mo-.1Si (Ti-6242S) and Ti-5Al-6Sn-2Zr-1Mo-.25Si (Ti-5621S) are the preferred commercially available alloys being considered for fusion because of their high creep resistance at elevated temperatures of 500°C. Also, irradiation tests on these alloys have shown irradiation creep properties comparable to 20% cold worked 316 stainless steel.(5)

No hydrides have been observed in duplex annealed Ti-6242S charged with 24,100 appm (530 wppm) hydrogen. Because of the similarity of Ti-6242S and Ti-5621S one would expect similar, but not identical, hydrogen tolerance without hydride formation in Ti-5621S. Because of the 1 wt. percent less Al and Mo in Ti-5621S, somewhat lower solubility of hydrogen could be anticipated.

Both Ti-6242S and Ti-5621S are considered near alpha alloys but technically are alpha-beta alloys with predominantly alpha phase. These alloys would respond to hydrogen as alpha-beta alloys and therefore be susceptible to slow-strain rate embrittlement if sufficient hydrogen concentrations are obtained. It is significant to note that hydrides tend to dissolve in the microstructure at temperatures above 100 to 150°C and also hydrogen diffusion rates are increased at elevated temperatures allowing for an equalized hydrogen concentration within the material. Because of these conditions one could expect no deleterious temperatures above 150°C.

The alpha-beta alloy Ti-6Al-4V does not possess as high a creep resistance as near apha alloys, however it is candidate for use at temperatures below 500°C. The Ti-6Al-4V alloy is advantageous because of its low residual radioactivity and its large data base.

From a standpoint of maximizing the hydrogen solubility to decrease the probability of deleterious hydrogen effects, a beta alloy such as Ti-38644 would appear attractive, however, stability and creep properties of this alloy above 260°C are low.

The above conclusions are based on limited directly applicable data. A sufficient data base must be generated to provide reliable data for reactor design.

Screening tests need to be run to determine the hydrogen solubility limits of the alloys of interest at room temperature and also at the elevated temperatures (500°C) of fusion reactors. This could be accomplished by metallographic analysis to determine the concentration at which hydrides spontaneously appear at room temperature and then heating on a hot stage microscope to determine at what temperature the hydrides dissolve. The feasibility of developing coatings that will prevent or retard the absorption and subsequent diffusion of hydrogen into titanium should continue to be studied.

Subsequent to the preliminary screening tests, tensile tests need to be conducted at several loading rates to determine susceptibility to slow strain rate embrittlement.

In addition to the above screening tests an effort will be required to provide quantitative fracture mechanics data to determine the effects of hydrogen on the most favorable alloys at temperatures and hydrogen pressures of interest for fusion reactors. Ideally, this data base will also combine radiation damage and hydrogen effects.

2.0 SOLUBILITY AND ABSORPTION OF HYDROGEN IN TITANIUM

Hydrogen embrittlement of titanium is related to a decrease in solubility of hydrogen in titanium alloys near room temperature. Therefore, the effects of hydrogen can be approximated if the solubility of hydrogen in titanium alloys is known. This is especially true for the alpha alloys, since spontaneous formation of hydrides occurs when the hydrogen concentration within the metal exceeds the solubility.

It must be noted here that for titanium, and other metals of the exothermic occluding type, the difference between the solubility of hydrogen and the total amount of hydrogen which is absorbed by the metal. Since one of the major characteristics of the exothermic occluders is the formation of a hydride, it is possible to represent the equilibrium conditions of this type metal-hydrogen system by a phase diagram analagous to the phase diagrams which are used to represent normal metallic alloy systems. These can then be used to depict the difference between the two above-mentioned quantities, as follows.

As the hydrogen content of a metal of this type is increased from zero, the initial hydrogen addition will go into solid-solution within the metal, thereby leaving the metal in a single-phase condition. However, particles of the hydride phase will eventually begin to be formed within the metal. The solubility of hydrogen should therefore be taken as that composition at which the specimen leaves the single-phase region of the pseudo-equilibrium diagram and becomes a two-phase alloy. This definition of solubility is therefore directly equivalent to that normally applied to the solid-solutions of metallic alloy systems. However, the hydrogen content of the specimen can be increased beyond this solubility limit by the formation of the hydride-phase. Thus the total amount of hydrogen which is absorbed by an exothermic occluding metal depends upon the kinetics of hydride formation and will always exceed the solubility, as it is defined above. Ideally hydrogen should be absorbed until all the metal has been converted to the hydride of the maximum hydrogen content.(6)

2.1 SOLUBILITY

Figure 2-1 shows the titanium-hydrogen binary phase diagram at 10^5 Pa (1 atmosphere) equilibrium hydrogen pressure.(7) This shows maximum solubility of hydrogen in high purity iodide refined alpha Ti is 7.9 atomic percent (a/o) or 840 wppm and occurs at the eutectoid temperature of 319°C. The maximum solubility of hydrogen in beta Ti is considerably higher; 49 a/o or 10800 wppm and occurs at 640°C. The gamma phase is the hydride phase and does not have a fixed composition, but exists over the range of TiH to TiH_2.

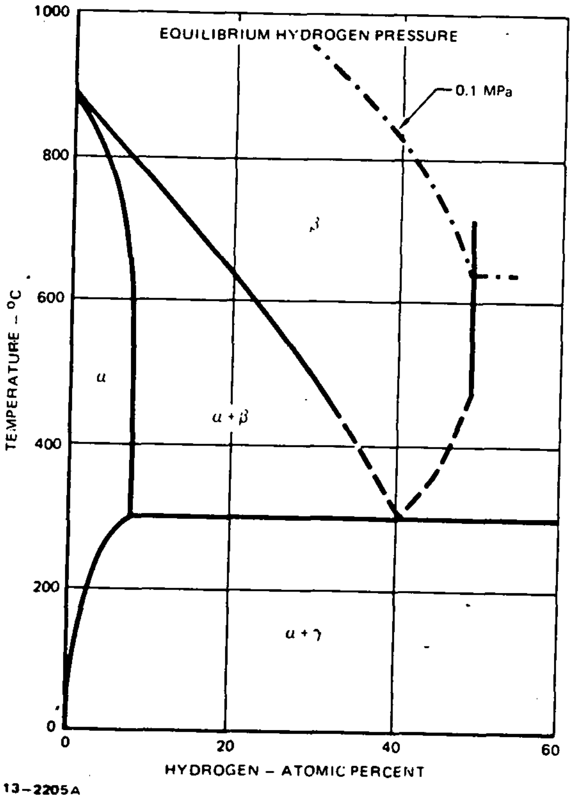

FIGURE 2–1 TITANIUM-HYDROGEN BINARY PHASE DIAGRAM

At the eutectoid temperature of 319°C the solubility of hydrogen in the beta phase is approximately 5 times that in alpha phase. When the beta and beta + gamma boundary is extrapolated to room temperature, the solubility in beta is approximately 18 a/o hydrogen. On the other hand, the low temperature portion of the alpha and alpha + gamma boundary was studied, and the solubility of hydrogen in alpha phase at room temperature was determined to be 0.1 a/o.(8) The beta phase has a much higher hydrogen solubility than alpha phase even at room temperature. Work using electron microautoradiograph has shown that in Ti-8Al-1Mo-1V, hydrogen is concentrated in beta phase and along the alpha - beta boundary. The ratio of hydrogen in beta phase to hydrogen in alpha phase was about 20 to 1 for Ti-8Al-1Mo-1V containing 40 wppm hydrogen.(9) Since a large ratio, such as 20 to

1, for solubility of hydrogen in beta to alpha phase is applicable for all titanium alloys, this explains the large increase in solubility that occurs with the presence of even small amounts of beta phase.

The effect of hydrogen pressure surrounding titanium is shown in Figure 2-2 which shows the equilibrium titanium-hydrogen phase diagram at several hydrogen pressures.(10) As equilibrium hydrogen pressure is decreased, the solubility of hydrogen is decreased, especially in the beta phase.

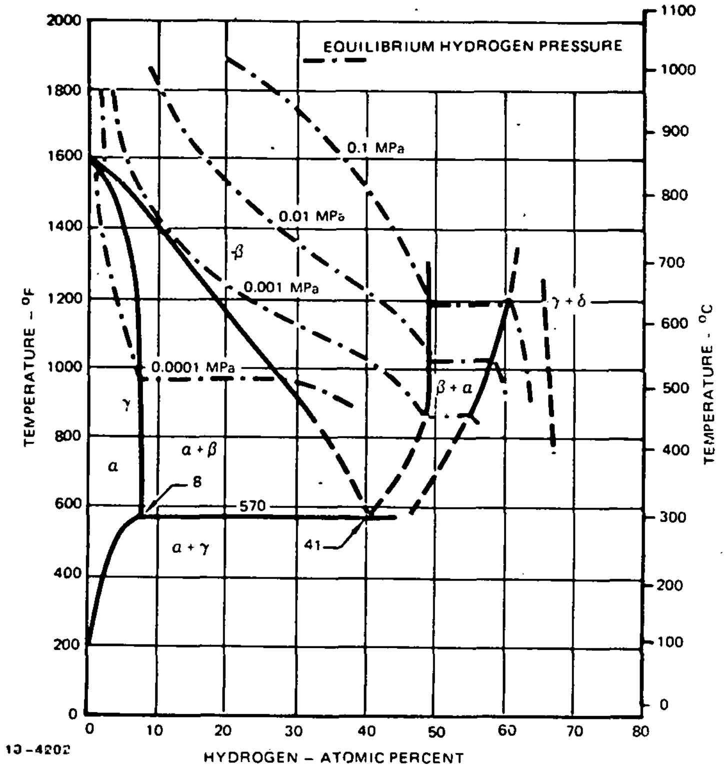

FIGURE 2–2 THE TITANIUM-HYDROGEN BINARY PHASE DIAGRAM AT SEVERAL HYDROGEN PRESSURES

The equilibrium pressure of hydrogen over high purity titanium has been measured at 500°C and pressures of 10^{-1} and 10^{5} Pa (10^{-3} to 1000 torr). Similar measurements were made for titanium-deuterium and titanium-tritium at 500°C with no isotope effects noted.(11) Figure 2-3 shows the equilibrium pressure over the titanium-hydrogen system with respect to hydrogen concentration in the titanium from several investigators. This shows that as the equilibrium pressure surrounding the titanium increases, the hydrogen concentration within the metal increases. Figure 2-4 shows a similar curve for the titanium-deuterium system.

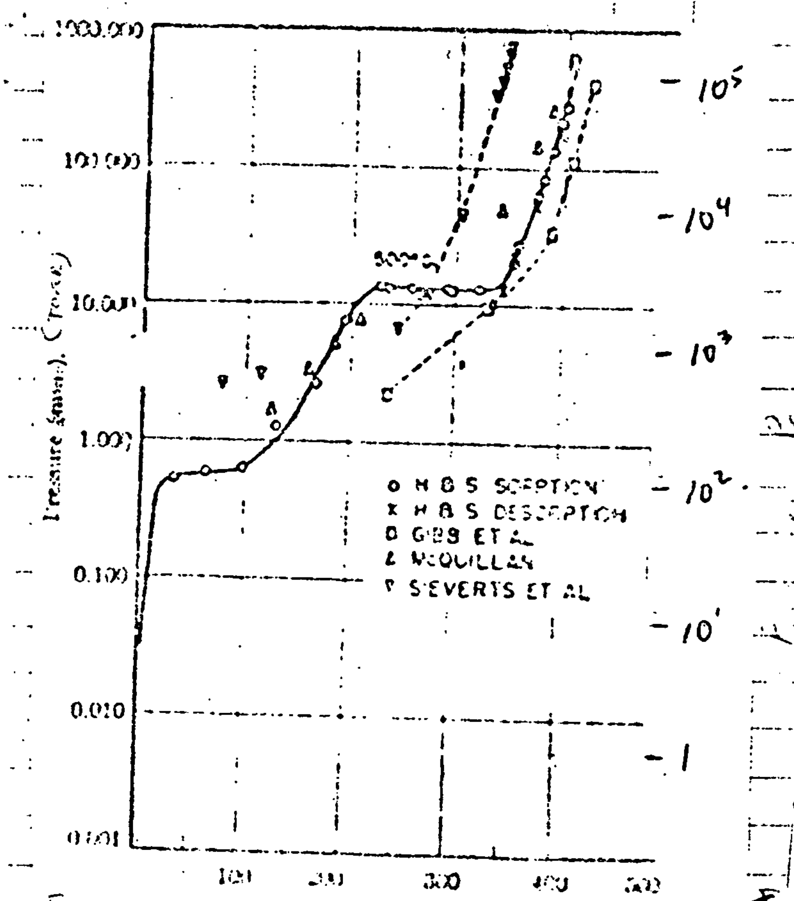

Figure II-2.
Fig. 2--Equilibrium pressure vs. hydrogen concentration (29)

Fig 2-3

2-4

Fig 2-4.

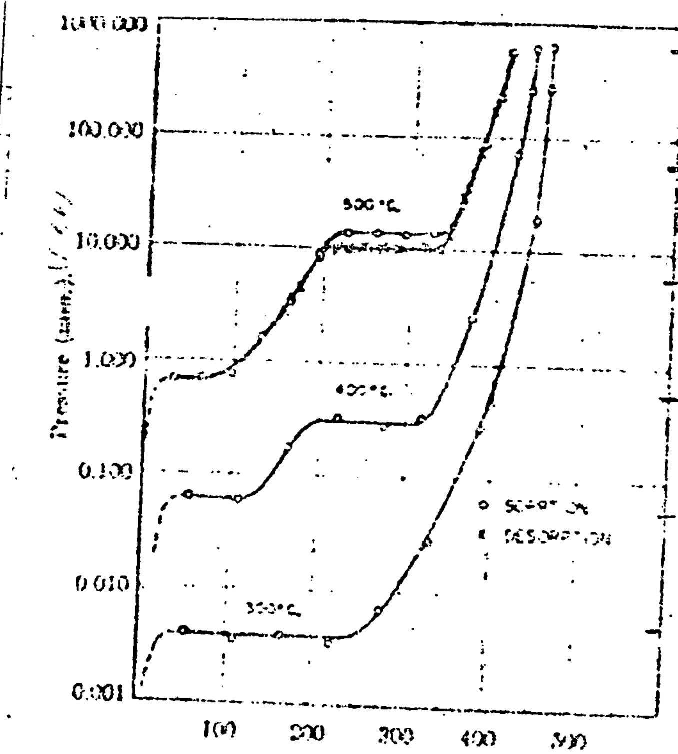

Figure II-3.
Fig. 3--Equilibrium pressure vs. deuterium concentration

A comparison of the two figures for a 500°C temperature shows equal volumes of hydrogen and deuterium concentrations in the titanium; the same characteristics were observed for titanium-tritium. Therefore, no isotope effects on solubility are expected to occur in reactor.

Nagasaka and Yamashina(12) have investigated the solubility of hydrogen and deuterium in high purity alpha titanium in the pressure range of 10^{-2} to 1 Pa (10^{-4} to 10^{-2} torr). Figures 2-5 and 2-6 show the results of this investigation.

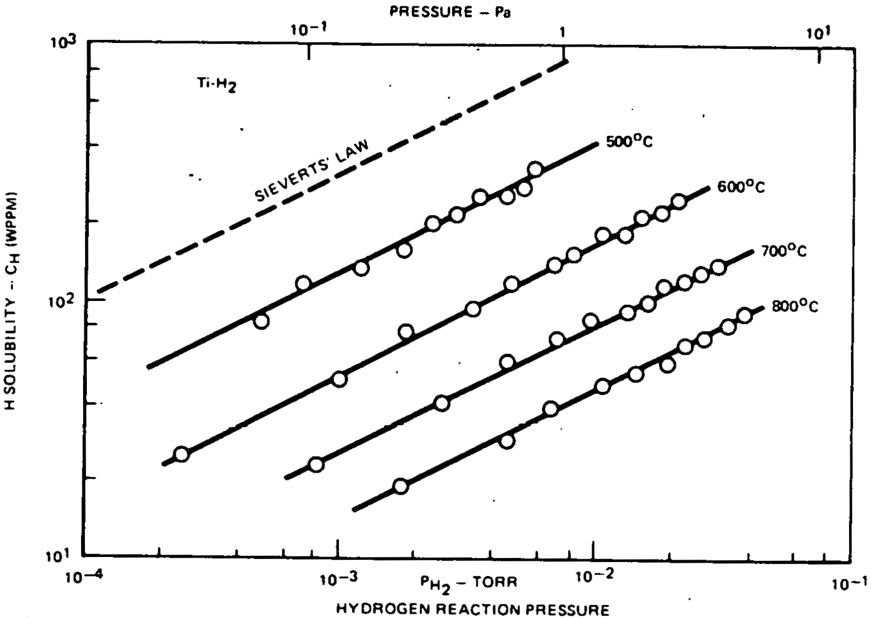

FIGURE 2–5 SOLUBILITY OF HYDROGEN IN α-Ti

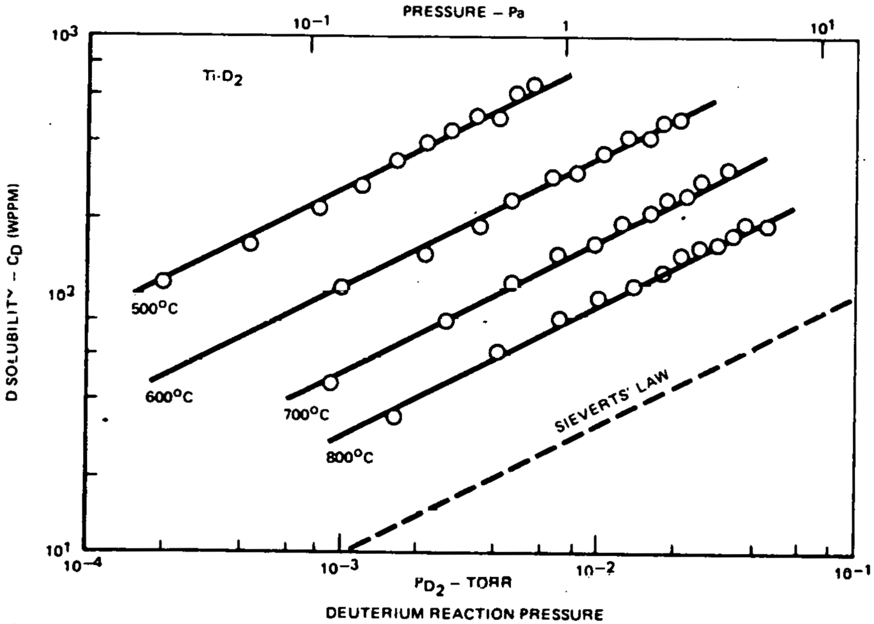

FIGURE 2–6 SOLUBILITY OF DEUTERIUM IN α-Ti

For typical reactor temperatures and pressures such as 500°C and 10^{-1} Pa (10^{-3} orr) the solubility would be approximately 100 wppm for hydrogen in titanium and 200 wppm for deuterium in titanium. These are concentrations by weight, therefore the number of hydrogen and deuterium atoms dissolved in the metal are nearly equal under the same conditions of temperature and pressure. The equations of solubility of hydrogen and deuterium in alpha and beta titanium in the pressure range of 10^{-2} to 1 Pa (10^{-4} to 10^{-2} torr) are shown in Table 2-1(12).

The solubility of hydrogen in titanium has been found to conform to Sieverts Law, which is $C = A \quad P \exp(-H_S/RT)$ where:

C = solubility in wppm
A = constant
P = hydrogen equilibrium pressure in torr
H_S = enthalpy of dissolution in cal g-at^{-1}
R = gas constant, 1.987 cal/mole/^{o}K
T = temperature, ^{o}K

TABLE 2-1 EQUATIONS OF SOLUBILITY OF HYDROGEN AND DEUTERIUM IN TITANIUM IN PRESSURE RANGE 10^{-4} TO 10^{-2} TORR

System	Temperature Range, °C	$c/\sqrt{p}$ (wppm torr$^{-1/2}$)	$c/\sqrt{p}$ (atomic ratio torr$^{-1/2}$)
$Ti\text{-}H_2$	500-800	$(0.48 \pm 0.04)_{exp}$ (12600/RT)	$(2.3 \pm 0.1) \times 10^{-5}$exp (12600/RT)
$Ti\text{-}H_2$	900-1150	$(1.4 \pm 0.2)_{exp}$ (14200/RT)	$(6.5 \pm 0.9) \times 10^{-5}$exp (14200/RT)
$Ti\text{-}D_2$	500-800	$(0.97 \pm 0.08)_{exp}$ (12600/RT)	$(2.3 \pm 0.1) \times 10^{-5}$exp (12600/RT)
$Ti\text{-}D_2$	900-1150	$(2.9 \pm 0.4)_{exp}$ (14200/RT)	$(6.5 \pm 0.9) \times 10^{-5}$exp (14200/RT)

To clarify the above table, the solubility of hydrogen in α-titanium could be calculated from the expression

$$C = (0.48 \pm 0.04)_{exp}{}^{(12600/RT)}$$

The influence of oxygen and nitrogen on the solubility of hydrogen in pure titanium at temperatures below the eutectic point was investigated by Lenning, Spretnak and Jaffee.(13) Hydrogenated specimens were annealed at 400°C for 64 hours, cooled to a desired temperature, held at this temperature for 24 hours, and then water quenched. These data show that neither oxygen nor nitrogen has an appreciable influence on the solubility of hydrogen in titanium at room temperature. However, above 378°C both of these elements slightly increase the solubility of hydrogen in titanium.(9)

The previously discussed work has dealt with high purity unalloyed titanium. The addition of alloying elements affects hydrogen solubility both from microstructural and hydrogen capacity standpoint. The solubility of hydrogen in titanium and its alloys varies with the amount and type of phase present(2)(8)(10)(14). Metallographic examination of titanium alloys indicate that, generally the alloys consisting primarily of alpha phase have a lower solubility of hydrogen than alloys that consist primarily of beta phase. In the case of mixed phase alloys (alpha + beta), the solubility increases with increasing amounts of beta phase.

Alloying elements such a Mo, Nb, Cr, V, Mn, and Fe stabilize the beta phase at lower temperatures and therefore increase the overall hydrogen solubility at these temperatures as compared with unalloyed titanium. In addition to affecting the amount of beta phase present, specific alloys appear to allow for higher hydrogen solubility than others. Of the beta stabilizing elements, Mo appears to allow for higher hydrogen solubility than Nb, Cr, or V. Manganese and Fe have very little effect on the hydrogen solubility.

The alpha stabilizers are Al, Zr and Sn. Of these, Al is most significant because it is used in large concentrations in both alpha and beta alloys. The apparent effect of Al is to increase the hydrogen solubility at low temperatures as shown in Figure 2-7(15) while at elevated temperatures the Al decreases the

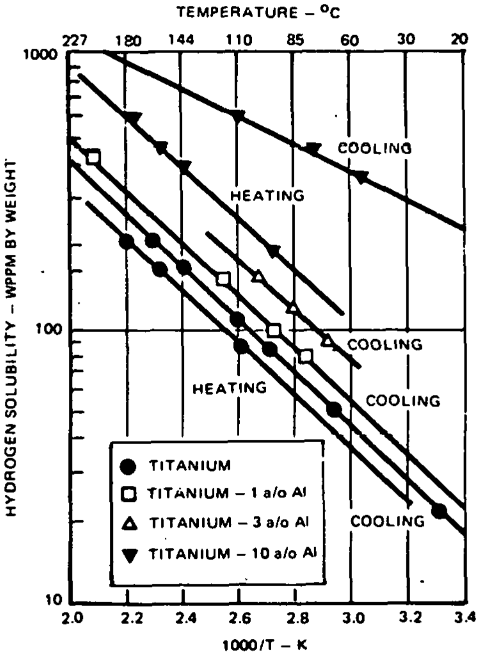

FIGURE 2–7 ARRHENIUS PLOT OF SOLUBILITY LIMIT VS RECIPROCAL TEMPERATURE FOR SEVERAL Ti ALLOYS

solubility as shown in Figure 2-8.(2) It can be seen in Figure 2-7 that at room temperature the hydrogen solubility was 21 wppm in unalloyed alpha titanium and the solubility increased to 250 wppm for titanium with 10 atomic % Al. In addition to the increase in hydrogen solubility, Paton, et al(16) noticed that hydride nucleated and grew with difficulty in Ti-10 a/o Al. This finding supported earlier work(16) that Al suppressed hydride precipitation. Paton, et al,(15) explained that along with hydride precipitation, there was a volume expansion, and that this expansion had to be taken up by the matrix through elastic and plastic work. The high strength of the Ti-Al alloy made elastic and plastic work more difficult, consequently a higher supersaturation was needed for nucleation and growth of the hydride phase.

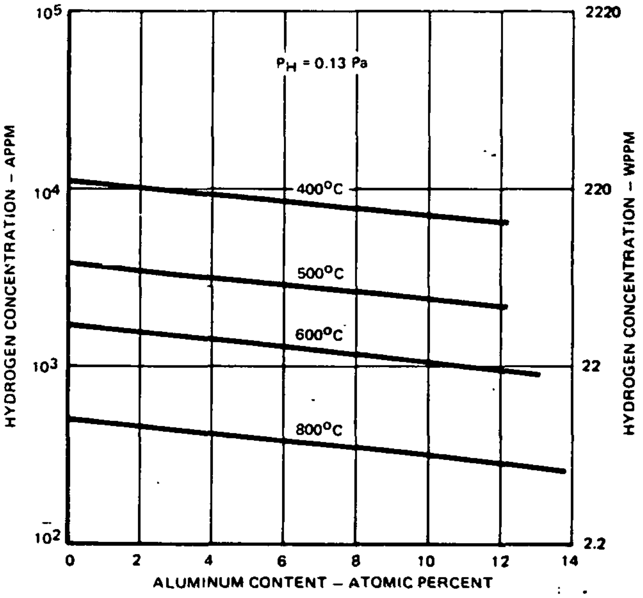

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FIGURE 2-8 INFLUENCE OF TEMPERATURE AND ALUMINUM CONCENTRATION ON APPARENT EQUILIBRIUM CONCENTRATION OF HYDROGEN IN TITANIUM

Hydrogen present in titanium is in a state of dynamic equilibrium between the ionized atom or proton and hydrogen atoms in the interstitial site. There are two types of interstitial sites in titanium, octahedral and tetrahedral. Octahedral sites can accommode atoms of radius 0.59 A and tetrahedral sites can accommodate atoms of radius 0.315 A. Since the hydrogen atom has a radius of 0.41 A, the majority of interstitial hydrogen atoms will occupy octahedral sites. Additions of aluminum decrease both the "c" and the "a" parameters of the hexagonal titanium lattice, consequently octahedral sites will be slightly smaller than 0.59 A. A etter fit of hydrogen atoms in octahedral sites results and this appears to be the reason why aluminum increases the hydrogen solubility of the alpha phase. Beta phase has a tetrahedral hole of 0.44 A radius in which hydrogen could fit very well. This is generally believed to be the reason why hydrogen solubility in the beta phase is so much higher than in the beta phase.(9)

Hall(17) reports that hydride precipitation in room temperature alpha-beta Ti-6Al-4V was strongly dependent upon both microstructure and hydrogen content. This indicates that the formation of hydrides is affected by additional factors other than solubility. In equiaxed Ti-6Al-4V gamma-hydride precipitation began at approximately 9100 appm (200 wppm) hydrogen; in the fully transformed condition-hydride precipitation began at approximately 36,400 appm (800 wppm) hydrogen; and in equixed alpha plus transformed beta microstructure gamma-hydride precipitation began at approximately 50,000 appm (1100 wppm) hydrogen.

The significance of microstructure in hydrogen absorption by titanium is indicated by studies in which cathodically charged samples were examined.(18) In predominantly alpha alloys, hydrogen absorption was limited to a thin surface layer of hydride. When a beta network was present, hydrogen penetrated much more deeply into the alloy. Acicular structures having a more continuous beta network showed greater absorption than equiaxed structures. Large amounts of hydrogen were absorbed in alloys containing moderate amounts of beta with no evidence of hydride at the surface or in the alloy. One alloy (Ti-8Mn) absorbed 12,100 wppm (37 atomic per cent) during cathodic charging without visible signs of hydride in the structure.

Hall(19) also reports precipitation of gamma-hydride at approximately 13,600 appm (300 wppm) hydrogen in room temperature alpha Ti-5Al-2.5 Sn alloy. He also noted that prolonged heating even at 100°C was sufficient to cause the hydrides to decompose.

Wille and Pao(20) have not observed hydrides in duplex annealed Ti-6Al-2Sn-4Zr-2Mo-0.08 Si (Ti-6242S) charged with 24,100 appm (530 wppm) hydrogen. An electron micrograph of this sample is shown in Figure 2-9. The Ti-6242S is considered a near-alpha alloy because it is a weakly beta stabilized alpha-beta alloy. However, because it does have a continuous network of beta surrounding the alpha phase it will react to hydrogen in a manner more similar to the alpha-beta alloys and dissolve higher concentrations of hydrogen before hydrides will precipitate. This is indicated somewhat by the presence of hydrides at 13,600 appm (300 wppm) hydrogen in alpha alloy Ti-5Al-2.5Sn reported by Hall and lack of hydrides at 4,100 appm (530 wppm) hydrogen concentration in Ti-6242S alloy.

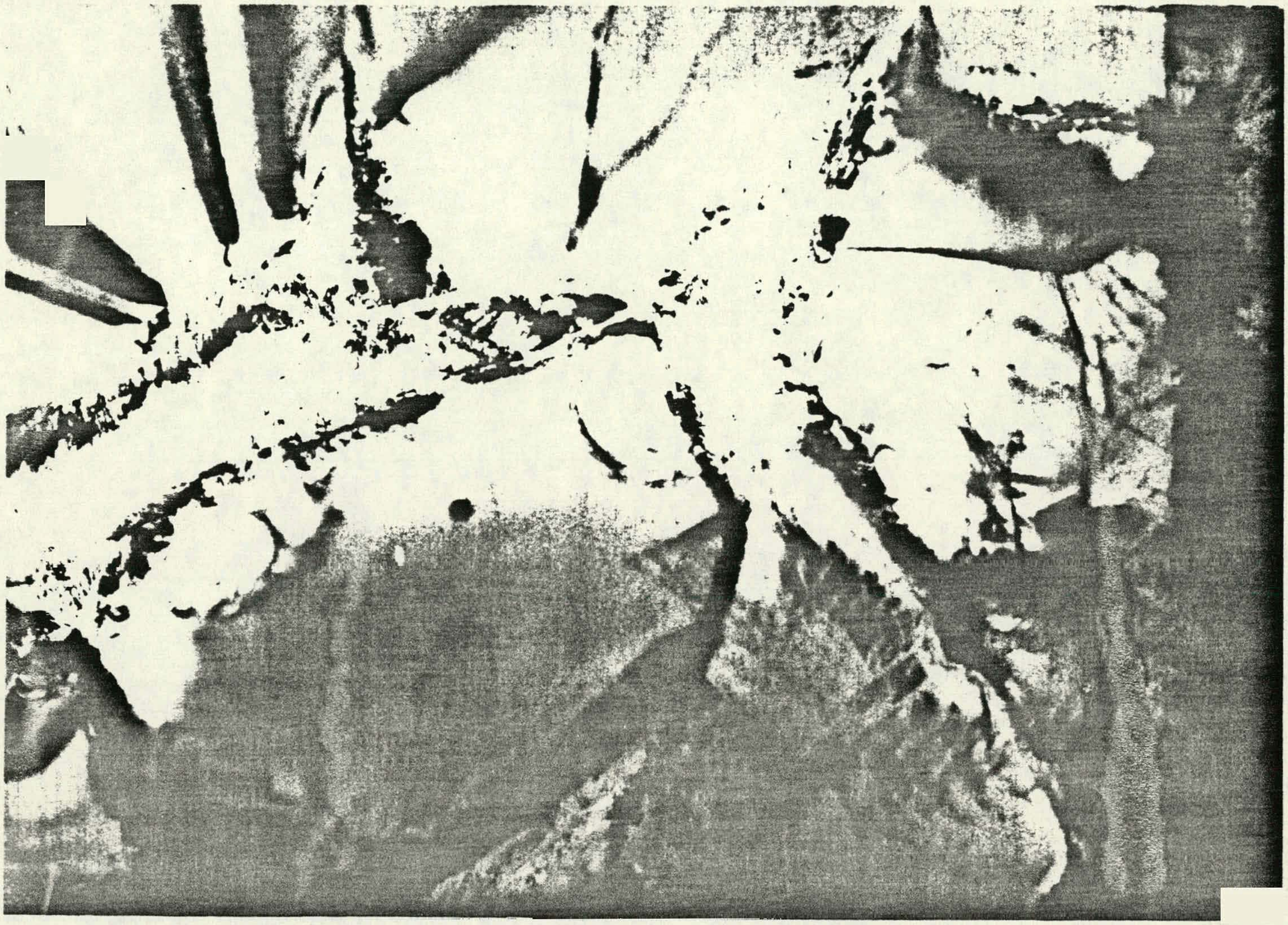
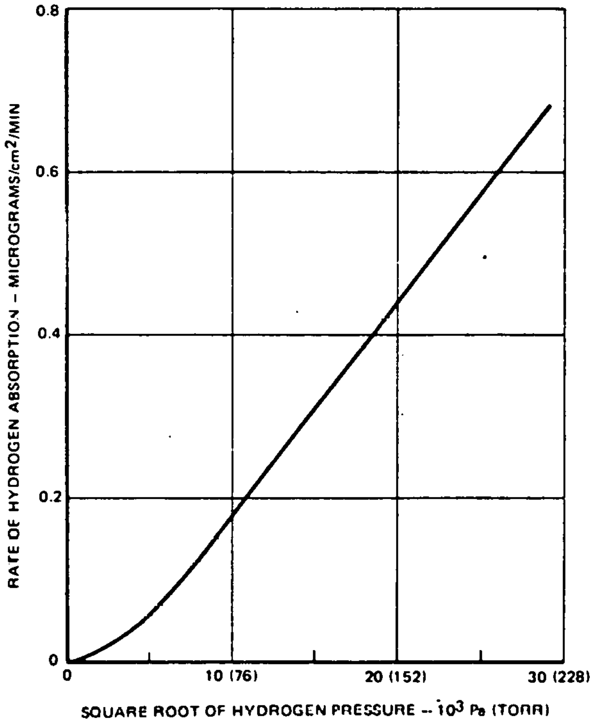


Figure 2-9 Transmission Electron Micrograph of Ti-6242S with 24,100 appm (530 wppm) H. No Hydrides are visible.

2.2 TOTAL ABSORPTION - After the solubility of hydrogen in titanium is exceeded, the titanium will continue to absorb hydrogen, with the additional hydrogen forming hydrides. The formation of additional hydrides could continue until all the titanium has been converted to a hydride of the maximum hydrogen content if ideal conditions exist.

The total amount of hydrogen that can be absorbed by titanium is controlled by surface conditions effecting the adsorption of atomic or molecular hydrogen, and then diffusion of the adsorbed surface hydrogen into the bulk of the material. Variables affecting absorption are the surface cleanliness, temperature, and hydrogen partial pressure. The absorption of hydrogen at 274°C as a function of hydrogen pressure is shown in Figure 2-10(21). Shown is the linear dependence of adsorption upon the square root of the hydrogen pressure, indicating that the dissociation of molecular to atomic hydrogen is occuring at the surface. Also, the rate at which hydrogen is absorbed will be quite dependent on surface area, so that the amount absorbed in a given time will increase as the ratio of surface area to volume increases.



13–4712

FIGURE 2–10 EFFECT OF PRESSURE ON THE RATE OF HYDROGEN ABSORPTION BY IODIDE TITANIUM AT 274°C

The presence of an oxide film on the metal surface can considerably retard absorption of hydrogen by titanium.(22)(23) Presumably, this effect is due to the prevention of the absorption of the adsorbed layer of hydrogen or hydride on the surface. An indication of the effectiveness of an oxide layer is shown in Figure 2-11.(22) If sufficient time is allowed for the oxide film to be absorbed into the metal, absorption of hydrogen occurs at its normal rate. This is indicated by the behavior of the sample, in Figure 2-11 having a very thin oxide layer. Cooling the sample to room temperature after formation of the oxide film, followed by reheating, results in loss of much of the protective qualities of the oxide film, apparently because of cracking.

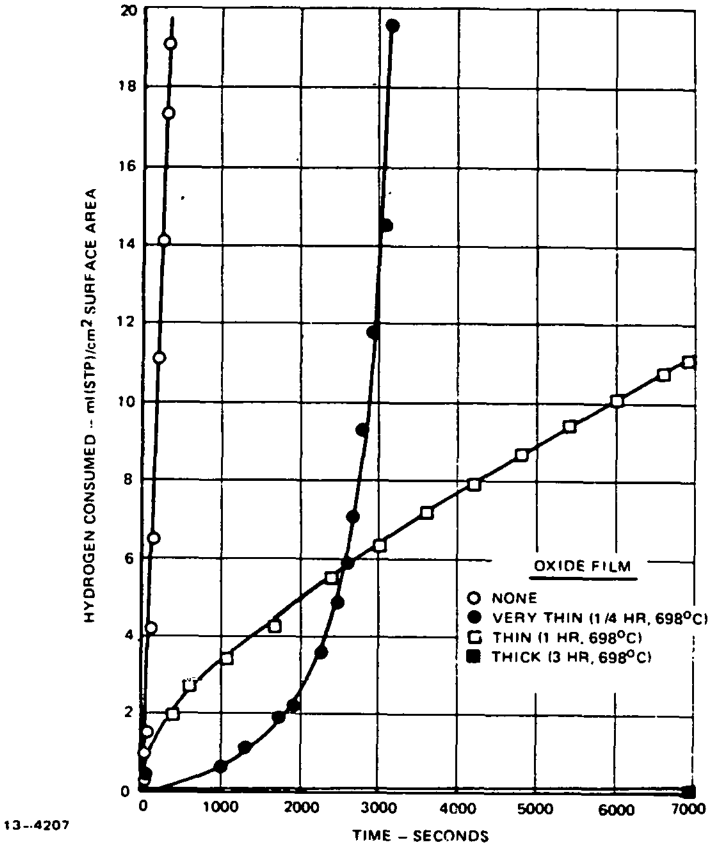


FIGURE 2–11 REACTION RATES AT 698°C AND PRESSURE OF HYDROGEN WITH HIGH-PURITY TITANIUM HAVING VARIOUS OXIDE-FILM THICKNESSES

If the oxide film is unstable or has been damaged by abrasion, hydrogen absorption can occur. Covington(24),(25) reports that absorption of hydrogen from hydrogen containing environments can occur more rapidly at temperatures above 80°C. Laboratory tests have shown that 2% moisture in hydrogen gas effectively passivates titanium so that hydrogen absorption does not occur at pressures of 5.6 MPa (800 psi) and temperatures to 315°C.

Any abrasion to destroy the continuous oxide film increases susceptibility to hydrogen absorption. Cotton(26) reports that abrasion with iron is particularly deleterious because hydrogen readily diffuses in iron, and a microscopic particle of iron embedded in the titanium surface so as to penetrate the oxide film affords ready access for hydrogen to the base titanium.

Charlot and Westerman(27) report that vapor blasting or sandblasting made a titanium surface very susceptible to hydrogen absorption, whereas a pickled surface was least susceptible to hydrogen absorption.

Van Deventer and Maroni(28) have performed studies on Ti-6Al-4V and Ti6242S that indicate order of magnitude decreases in permeability through samples with either anodized or nitrided surfaces. Similar results have been reported by Braganza(29) for Ti_2N coated high purity titanium. These decreases in permeability result from changing the absorption characteristics of the titanium surfaces.

The influence of temperature on the absorption of hydrogen in titanium is shown in Figure 2-12.(21) The high purity titanium absorbed approximately 14 times more hydrogen at 299°C than at 249°C after 100 minutes.

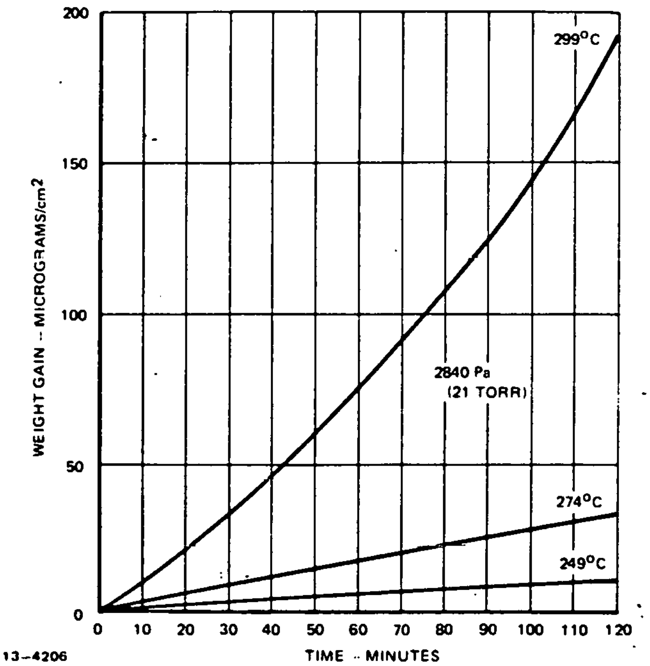


FIGURE 2-12 EFFECT OF TEMPERATURE ON HYDROGEN ABSORPTION OF IODIDE TITANIUM AT A HYDROGEN PRESSURE OF 2840 Pa

The importance of alloy content on the absorption of hydrogen in titanium is indicated by the data shown in Figure 2-13.(22) Absorption occurs very rapidly at 698°C in all four materials, the leveling off of the curves indicating an approach toward the equilibrium concentration of hydrogen. It is seen that absorption was most rapid in Ti-8Mn, less rapid in iodide and interstitial-containing titanium, and Ti-4Al-4Mn alloy. As will be shown in Section 3, the diffusion coefficient varies in the order of largest to smallest in iodide titanium, Ti-4Al-4Mn, commercial-purity titanium, and Ti-8Mn, therefore, it must be assumed that some factor in addition to composition, possibly microstructure, is also affecting the results.

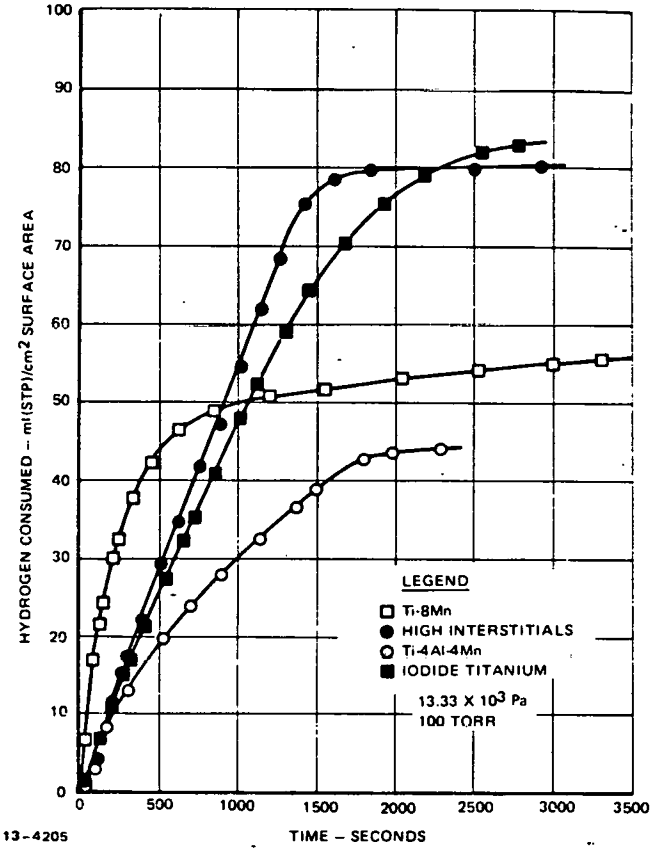


FIGURE 2–13 REACTION RATES OF TITANIUM ALLOYS WITH H_2 AT 698°C AND 13.3 X 10^3 Pa PRESSURE

2.3 FUSION APPLICABILITY - For fusion energy applications, it is advisable to maximize the hydrogen solubility in titanium, within the constraints of tritium inventory, to prevent hydride formation; therefore titanium alloys containing aluminum and molybdenum should contribute to this goal. Hydrides were not evident at room temperature in the near-alpha Ti-6Al-2Sn-4Zr-2Mo-0.08Si (Ti6242S) alloy with 24,100 appm (530 wppm) hydrogen, indicating that reasonably high levels of hydrogen can be accommodated. Temperatures above 100°C have been reported to decompose hydrides. This is an important point in fusion reactors because walls in commercial reactors are expected to be at elevated temperatures. Since solubility is strongly dependent upon alloy composition and microstructure, it will be necessary to conduct tests to accurately determine solubility of alloys and heat treatments being considered.

The total amount of hydrogen that can be absorbed into titanium is greater than the solubility of hydrogen in titanium, because titanium is an exothermic occluder. Various surface treatments should be evaluated which could limit or control the hydrogen that could be absorbed through the surface layer, thus decreasing the titanium inventory.

3.0 DIFFUSION RATES OF HYDROGEN IN TITANIUM

Diffusion rates, solubility, and absorption of hydrogen are helpful to assess the potential of titanium for certain fusion reactor components. Hydrogen diffusion into and out of a titanium first wall structure during operational cycling may be critical with regard to the effect, if any, on the properties of the titanium.

Hydrogen is dissolved in titanium interstitially, and diffuses rapidly through the metal. The diffusion rates differ, depending upon purity and/or alloy composition of the titanium and whether the microstructure is alpha or beta.

The diffusion coefficient can be expressed by the following equation:

$$D = D_0 \exp - \frac{E}{RT}$$

where: D = diffusion coefficient, cm^2/sec

T = temperature, °K

E = activation energy constant, cal/mole

D_0 = constant, cm^2/sec

R = gas constant, 1.9865 cal/mol°K

The variation of diffusion coefficient has been investigated for commercially pure and high purity iodide titanium, alpha and beta titanium, and in several titanium alloys. These findings are presented in Table 3-1.

Measurements made during degassing studies were used to approximate the diffusion coefficients for items g through k above. In the absence of surface effects, the degassing coefficient is equal to the diffusion coefficient.

From the diffusion coefficients calculated in Table 3-1, the diffusion rate in beta titanium at a temperature of 699°C, (Item g) is higher than that in alpha Ti (Items e and f). Also evident is the similarity of the diffusion coefficients for alloyed titanium (items h through m) except for highly beta 13V-11Cr-3Al (Item m). A suggested explanation for the similarity of diffusion coefficients for most titanium alloys (Items h through l) is that alloying blocks free movement of hydrogen through the metal.(10) An explanation for the much higher diffusion coefficient for 13V-11Cr-3Al alloy (Item m) is not apparent. Holman, et al.(30) compared their results with diffusion coefficients on high purity Ti,(31) as shown in Figure 3-1. In this case it appears that alloying increased the diffusion coefficient to levels higher than those of high purity all beta titanium.

TABLE 3-1 DIFFUSION COEFFICIENTS

$$D = D_O \exp - \frac{E}{RT}$$

Item	Material	Type	D_O, cm^2/sec	E cal/mole	D, cm^2/sec at 699°C	Reference
a	Comm. Pure Ti	alpha	0.9×10^{-2}	12,400	1.45×10^{-5}	10,22
b	Comm. Pure Ti	alpha	0.27×10^{-2}	14,200	0.17×10^{-5}	10,41
c	Comm. Pure Ti	alpha	-	-	1.0×10^{-5}	10,14,22
d	Comm. Pure Ti	alpha	0.06×10^{-2}	14,400	0.03×10^{-5}	24
e	Iodide Ti	alpha	1.8×10^{-2}	12,380	2.92×10^{-5}	10,31,42
f	Iodide Ti	alpha	1.55×10^{-2}	12,800	2.04×10^{-5}	10,22
g	Iodide Ti	beta	1.95×10^{-3}	6,640	6.24×10^{-5}	31,42
h	Ti-4Al-4Mn		1.8×10^{-3}	9,000	1.6×10^{-5}	10,14,22
i	Ti-5Al-2.5Sn		-	-	1.7×10^{-5}	10,14,22
j	Ti-8Mn		3.6×10^{-3}	6,900	0.9×10^{-5}	10,14,22
k	Ti-2Mo-2Cr-2Fe		-	-	1.2×10^{-5}	10,14,22
l	Ti-3Al-5Cr		-	-	1.2 x 10-5	10,14,22
m	Ti-13V-11Cr-3Al		1.58×10^{-3}	5,140	11×10^{-5}	30

Waisman, et al.(32)(33) have investigated the diffusion of hydrogen in titanium with respect to composition, temperature and stress gradient contributions. Their work, which was conducted on commercially pure (CP) titanium and Ti-6Al-4V, indicates that the diffusion of hydrogen is affected by the above factors.

Pontau, et al.(17), have investigated deuterium concentration profiles in Ti, Ti-6Al, and Ti-6Al-4V after 10 keV D_3^+ implantation at room temperature. The single phase alpha Ti and Ti-6Al alloys retained the deuterium near the surface, within 0.5 m, while in the alpha-beta Ti-6Al-4V alloy, only about 5 percent of the deuterium remained near the surface 3.9 hours after implantation. (See Figure 3-2). The behavior of the Ti and Ti-6Al are similar with the aluminum slightly

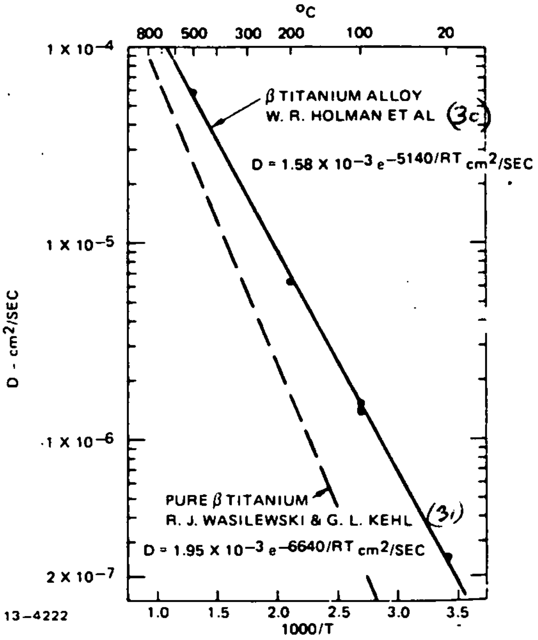


FIGURE 3–1 DIFFUSION COEFFICIENT VS TEMPERATURE

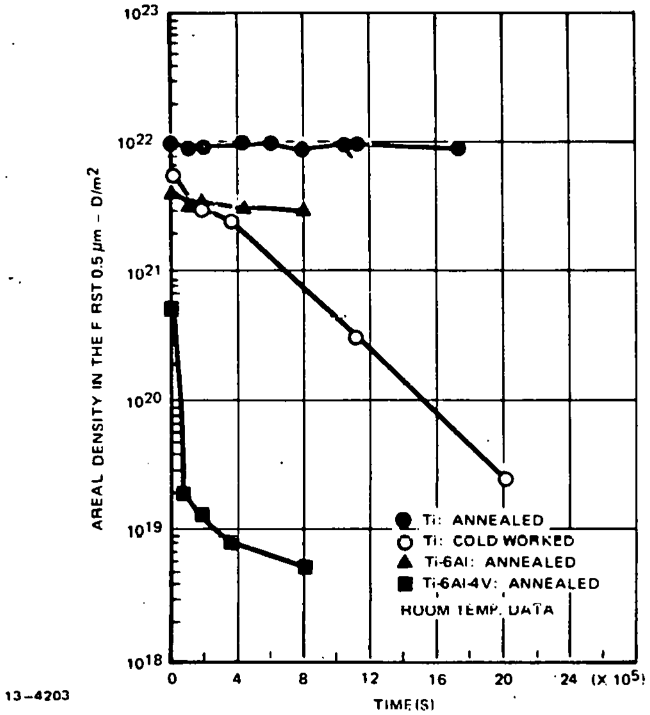


FIGURE 3–2 DEUTERIUM RETENTION VS TIME FOR ANNEALED Ti, COLD-WORKED Ti, ANNEALED Ti-6Al, AND ANNEALED Ti-6Al-4V ~~α/β~~, FLUENCE = 1 X 10^{22} D/m^2

increasing the solubility of the deuterium in the alloy. The presence of the beta phase in the Ti-6Al-4V causes the deuterium to rapidly diffuse into the bulk of the alloy, thus no deuterides form. The time dependence of the deuterium retention at the surface of samples at room temperature is also shown in Figure 3-2.(17) Pure annealed Ti and Ti-6Al samples maintained nearly constant deuterium levels during the test. Of particular interest is that the deuterium concentration of cold worked pure titanium decreased steadily in the first 0.5 m surface, indicating enhanced diffusion rate from the cold working, such that nearly all of the deuterium migrated from the near-surface region within 27 hours.

An indication of diffusion rates is the rate at which a gas permeates through a metallic membrane. Several investigations have been conducted on permeability of hydrogen through titanium.

Van Deventer and Maroni(28) have performed hydrogen dissolution and permeability studies on Ti-6Al-4V and Ti-5Al-6Sn-2Zr-1Mo-Si. They state that the permeability of the titanium alloys as compared to conventional 300 series stainless steel was approximately 1000 and 3000 times greater for the Ti-6Al-4V and Ti-5Al-6Sn-2Zr-1Mo-Si alloys, respectively. They also report that Ti-6Al-4V with either anodized or nitrided surfaces had permeabilities about an order of magnitude less than that of uncoated Ti-6Al-4V. The data for the nitride-coated Ti-6Al-4V is shown in Figure 3-3.

The presence of a surface layer to inhibit hydrogen permeation into the titanium has been investigated. Braganza, et al.(29), have reported that a layer of interstitially built Ti_2N can reduce the hydrogen permeation into high purity titanium by orders of magnitude. They concluded that titanium nitrided at temperatures below the alpha-beta transformation displays a stronger inhibiting effect on inward hydrogen diffusion than when nitriding is performed near the alpha-beta transformation temperature.

The currently available information on diffusion rates does not lend itself to a clearly reliable quantitative analysis useful to predict the characteristics of the titanium alloys being considered for fusion reactors. Since diffusion data is so dependent upon alloy composition and microstructure, it will be necessary to conduct tests on the alloys and heat treatments of interest to determine exact diffusion rates.

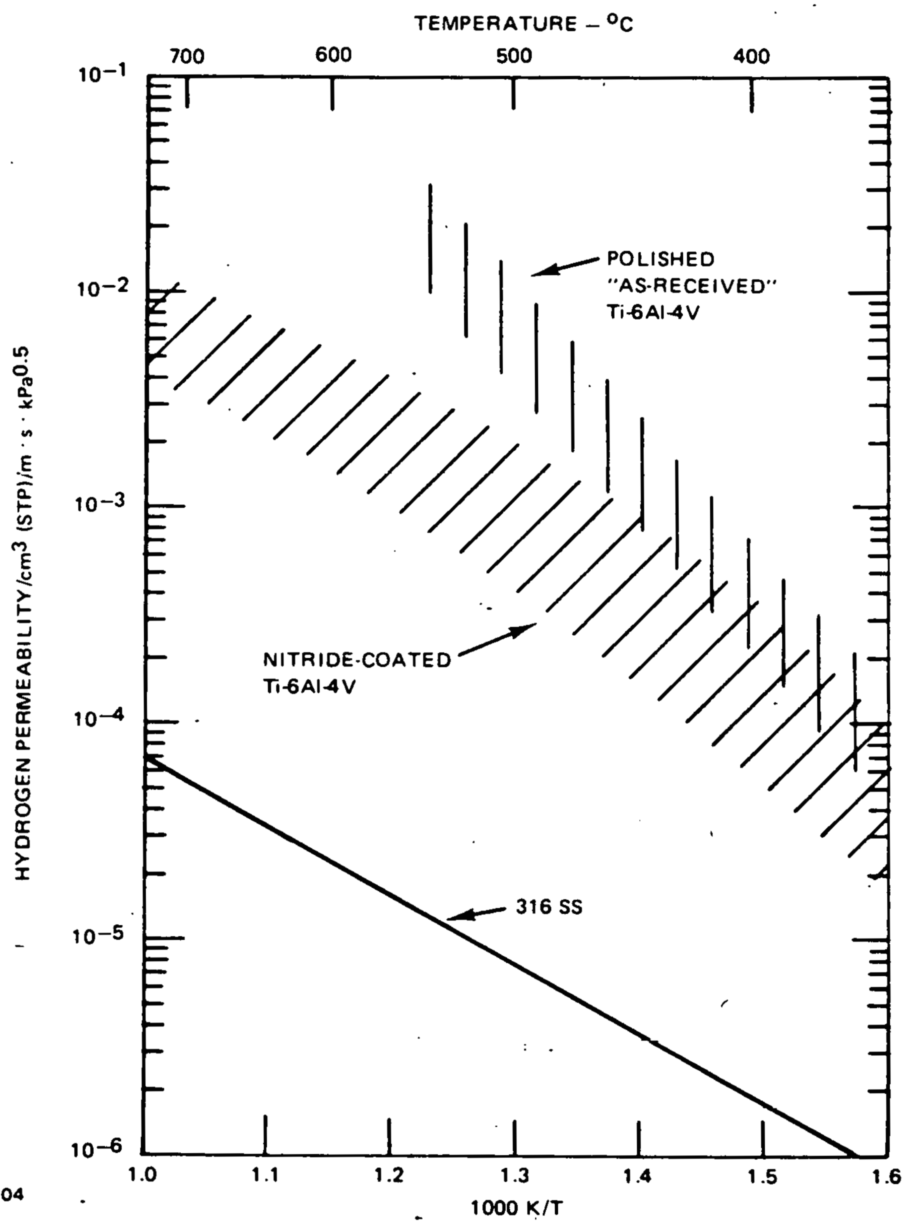


FIGURE 3–3 HYDROGEN PERMEABILITY VERSUS TEMPERATURE FOR "AS-RECEIVED" AND NITRIDE-COATED Ti-6Al-4V

4.0 MECHANICAL PROPERTIES EFFECTS OF HYDROGEN ON TITANIUM

The particular type effect that can develop in titanium because of hydrogen generally depends upon the relative phases in the microstructure. Alpha titanium is susceptible to impact embrittlement, thus properties that are effected are those which are notch and/or strain rate sensitive. Hydrogen may cause a decrease in the notched impact strength, but effects of hydrogen diminish as strain-rate is decreased; normal room temperature tensile properties are only affected at relatively high hydrogen concentrations.(6,10) The embrittlement of high purity alpha titanium occurs after the hydrogen content exceeds the solubility limit. For impure alpha, the characteristics are the same, however, the amount of hydrogen needed to cause embrittlement is less than that needed to cause embrittlement in pure alpha titanium.

The alpha-beta alloys are susceptible to slow-strain-rate embrittlement, thus normal tensile properties may adversely be affected. Under normal tensile testing conditions, the ductility decreases as strain-rate decreases.(6) The extent of slow-strain-rate embrittlement of these alloys is also dependent upon temperature.(6,34) Optimum conditions for susceptibility to embrittlement would appear to be slow-strain-rates applied at or near room temperature.

Beta titanium alloys appear to be more tolerant of hydrogen than the other alloy types because of higher hydrogen solubility in the beta phase. The beta alloys are susceptible to slow strain-rate embrittlement; however, higher hydrogen concentrations are generally necessary before severe degradation of properties occurs.

The following sections will elaborate on the hydrogen effects.

4.1 <u>MECHANICAL PROPERTY EFFECTS ON ALPHA TITANIUM</u> - High purity alpha titanium with hydrogen above the solubility limit shows an increased tendency for impact embrittlement with increasing strain rate, decreasing temperature of the test, and/or presence of a notch on the surface of the specimen.(6,10) Commercial purity alpha titanium is susceptible to detrimental hydrogen effects at lower hydrogen concentrations than high purity alpha titanium. Figure 4-1 shows the elongation and reduction in area vs. hydrogen content for both high purity and commercial purity alpha titanium. Even though solubility of hydrogen in alpha phase of commercially pure titanium is less than that in high purity titanium (6 vs. 8 atomic percent, respectively at 400°C), solution heat treatments

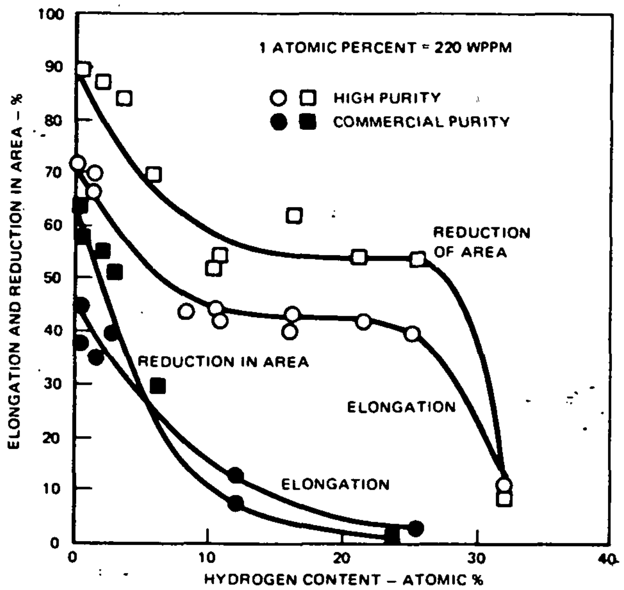


FIGURE 4–1 NORMAL TENSILE DUCTILITIES OF HIGH PURITY AND COMMERCIALLY PURE TITANIUM AS A FUNCTION OF HYDROGEN CONTENT AT ROOM-TEMPERATURE

followed by slow cooling or quenching did not lead to the formation of a hydride phase in a commercially pure titanium with 0.26 atomic percent hydrogen; a composition that could show a hydride in high purity alpha titanium.(6) These differences between solubility of hydrogen in the two examples above must be due to the presence of beta phase from small amounts of beta-stabilizing elements in the less pure metal and resulting higher solubility of hydrogen in the beta phase. Perhaps, nearly all of the hydrogen in the beta phase.

The notch-bend-impact-strength of titanium is affected by purity of the titanium, and also by the amount of beta present in the alloy as a result of alloying elements. Comparison of Figure 4-2 and 4-3 shows that the impact strength of high purity titanium is greater than commercial purity titanium; both show a decrease in impact strength after room temperature aging. The lower impact strength of the commerically pure titanium, even with low hydrogen content, may be explained by the presence of impurities and beta phase at the grain boundaries. The addition of hydrogen lowers the impact resistance of both high and commercial purity titanium, with the commercially pure titanium showing the largest percent degradation. Figure 4-4 shows the effect of small additions of alloying elements which affect the amount of beta phase present. This figure indicates that the impact resistance of high purity titanium with up to approximately 2200 appm (50 wppm) hydrogen is reduced by the addition of any alloying element. With hydrogen contents above 2200 wppm (50 wppm) the alloying elements tend to lessen the

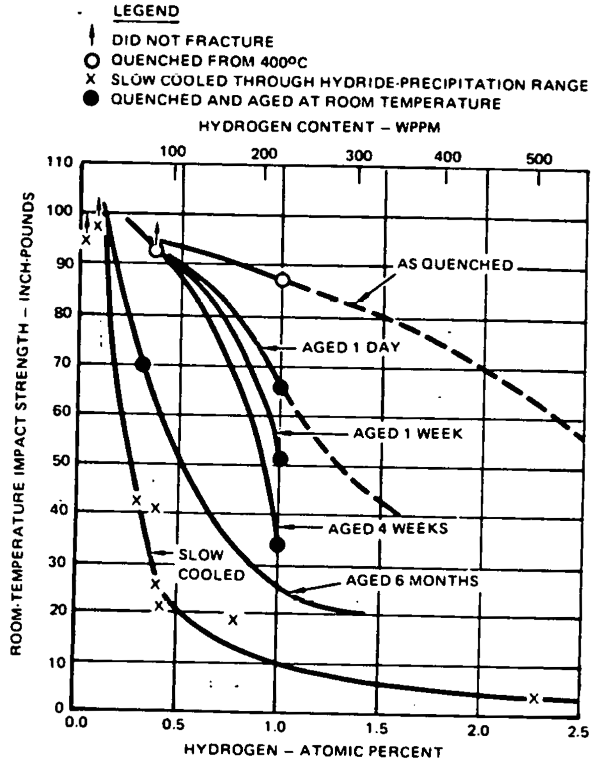


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FIGURE 4–2 EFFECT OF SOLUTION TREATMENT AND ROOM-TEMPERATURE AGING ON THE NOTCH-BEND IMPACT STRENGTH OF HIGH-PURITY TITANIUM

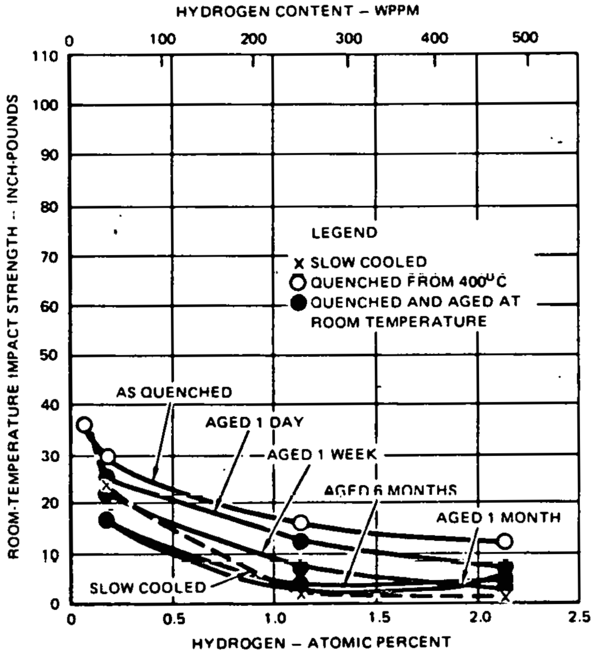

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FIGURE 4–3 EFFECT OF SOLUTION TREATMENT AND ROOM-TEMPERATURE AGING ON THE NOTCH-BEND IMPACT STRENGTH OF COMMERCIAL A-55 TITANIUM

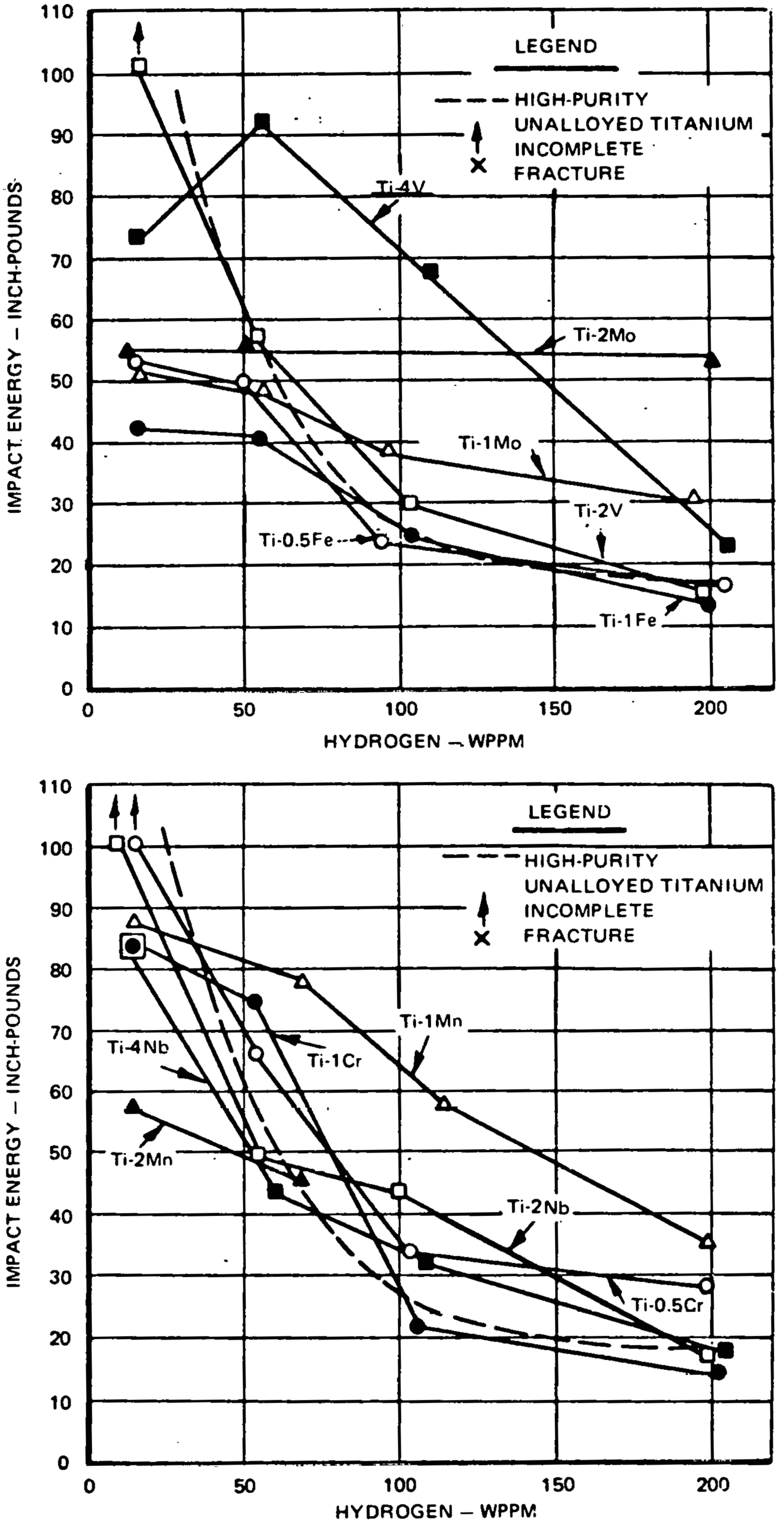

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FIGURE 4–4 EFFECT OF SMALL AMOUNTS OF BETA ON HYDROGEN EMBRITTLEMENT OF HIGH-PURITY TITANIUM IN THE NOTCH-BEND IMPACT TEST AT ROOM TEMPERATURE effects of hydrogen on the impact resistance as compared to pure titanium. The addition of 1% manganese, 2% molybdenum, or 4% vanadium individually to titanium showed the greatest positive effect on minimizing the decrease in impact resistance due to the presence of hydrogen.

Investigation on the effects of hydrogen on titanium with alpha-stabilizer element additions indicate that room temperature impact strengths of Ti-Al alloys is not necessarily proportional to the amount of aluminum as is shown in Figure 4-5(10). It does indicate that 5 wt. percent or more aluminum provides for higher hydrogen contents (200 to 300 wppm) before a rapid decrease in impact strength occurs.

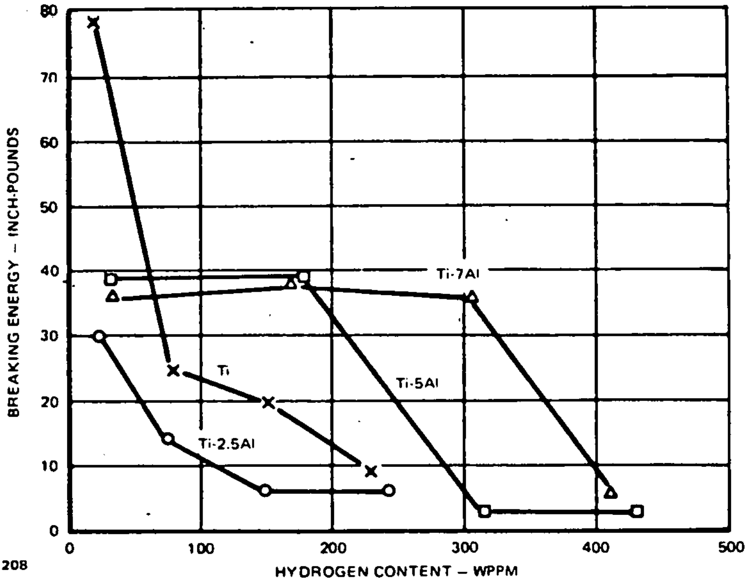


FIGURE 4–5 THE EFFECT OF HYDROGEN CONTENT ON THE ROOM-TEMPERATURE IMPACT STRENGTH OF TITANIUM-ALUMINUM ALLOYS

Van Deventer and Maroni(28) have stated that the surface condition and mechanical integrity of a near-alpha alloy Ti-5Al-6Sn-2Zr-1Mo-Si membrane used for permeation studies appeared to be unaffected by approximately 2600 hours of hydrogen infiltration under typical power reactor plasma-chamber conditions with respect to temperature, 537 to 625°C; hydrogen pressure, 10^{-1} to 10^{2} Pa; and gas composition. Although no physical tests were conducted to measure properties, it does indicate that the material was not catastrophically affected.

4.2 EFFECTS ON ALPHA-BETA TITANIUM - The alpha-beta alloys are susceptible to slow strain rate embrittlement, therefore normal tensile properties may be affected by hydrogen.

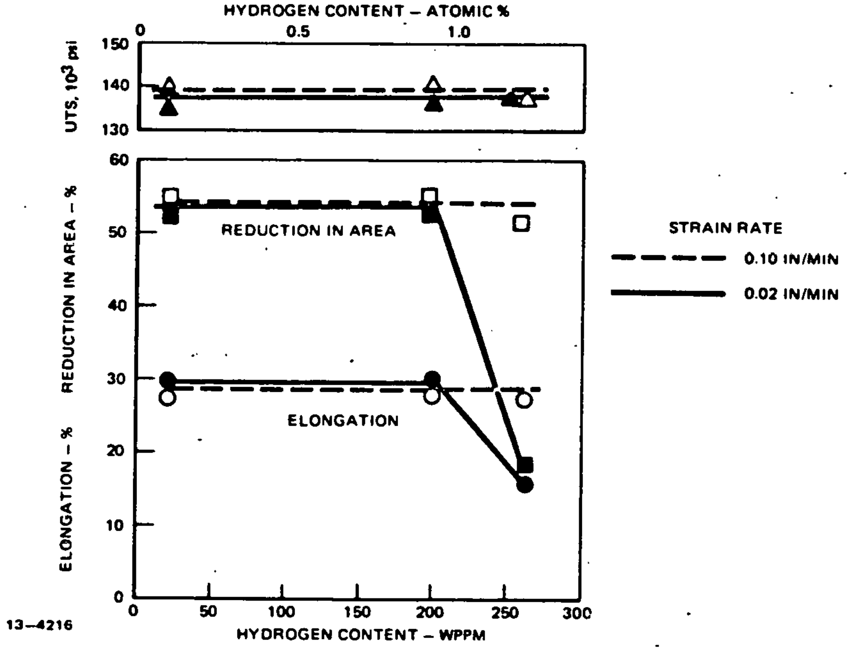


FIGURE 4–6 THE EFFECT OF HYDROGEN ON THE ROOM TEMPERATURE TENSILE PROPERTIES OF A Ti-140A ALLOY AT A SLOW AND A FAST STRAIN-RATE

Figure 4-6 shows the effect of strain rate on the room temperature tensile properties of Ti-140A alloy (Ti-2Mo-2Fe-2Cr).(6) The effect of strain-rate and temperature on the embrittlement of Ti-140A is also shown in Figure 4-7. At a loading rate of 1 inch per minute no decrease in reduction in area was noted, whereas an 80 percent decrease in reduction in area occurred at lower loading rates. For Ti-140A the embrittlement effect disappears above about 90°C and below -50 to -100°C. Thus, if Ti-140A is representative, it appears that conditions for

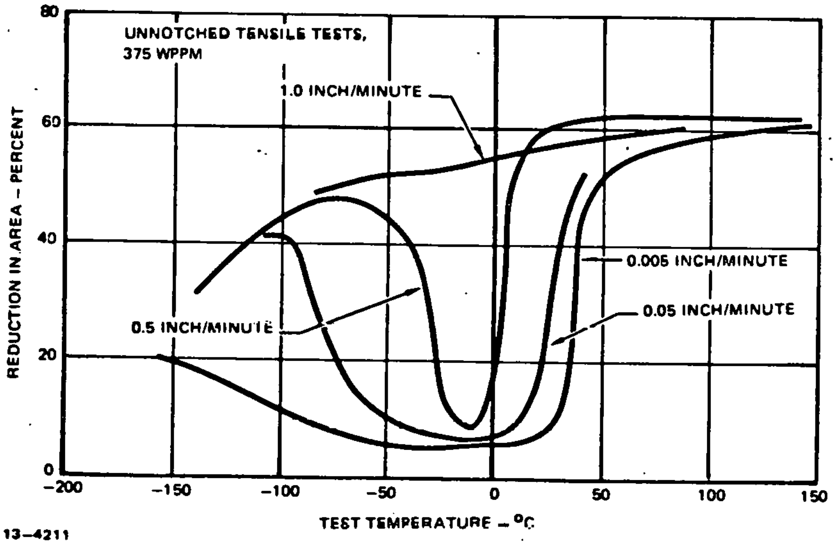


FIGURE 4–7 EFFECT OF LOADING RATE AND TEMPERATURE ON Ti-2Mo-2Fe-2Cr WITH 375 WPPM HYDROGEN

susceptibility to hydrogen embrittlement of alpha-beta alloys would be optimum at or near room temperature when slow strain rates are applied.

Research at McDonnell Douglas Research Laboratory (35) has been conducted on sustained load cracking of wedge opening loading specimens from Ti-6Al-6V-2Sn in three microstructural forms. Figure 4-8 shows the effect of hydrogen on crack growth in a dry argon atmosphere for beta annealed, recrystallization annealed, and solution treated and aged materials. This figure indicates a change in crack growth rate not only due to hydrogen but also due to different microstructures. It is interesting to note that the changes indicated for the beta and recrystallization annealed material occur at hydrogen contents allowed by all titanium specifications. Yoder, et al (36) have observed similar phenomena and a 50 fold difference in crack growth resistance in titanium depending upon the grain size.

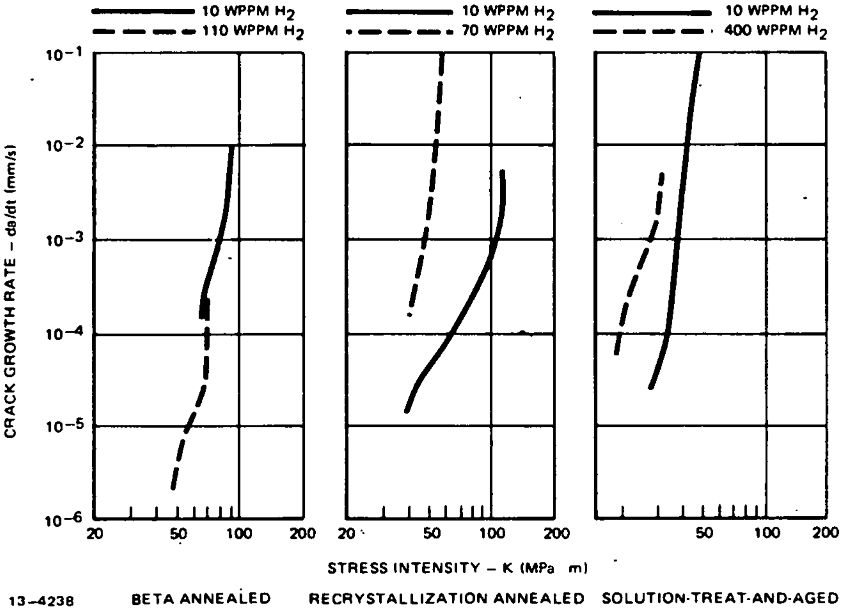


FIGURE 4–8 EFFECT OF HYDROGEN CONCENTRATION ON CRACK GROWTH IN Ti-6Al-6V-2Sn IN DRY ARGON ATMOSPHERE

Figure 4-9 shows the effect of hydrogen on the room temperature reduction in area of several alpha-beta alloys.(6) The Mo containing alloys are less affected by hydrogen than the Mn containing alloys because Mo is a much stronger beta stabilizer. The Mn containing alloys show a loss in ductility at approximately 200 wppm, however the presence of Al in Ti-4Mn-4Al increases significantly (1000 wppm) the hydrogen necessary to cause a decrease in ductility.

VanDeventer and Maroni(28) have stated that the surface condition and mechanical integrity of a Ti-6Al-4V membrane used for permeation studies appeared

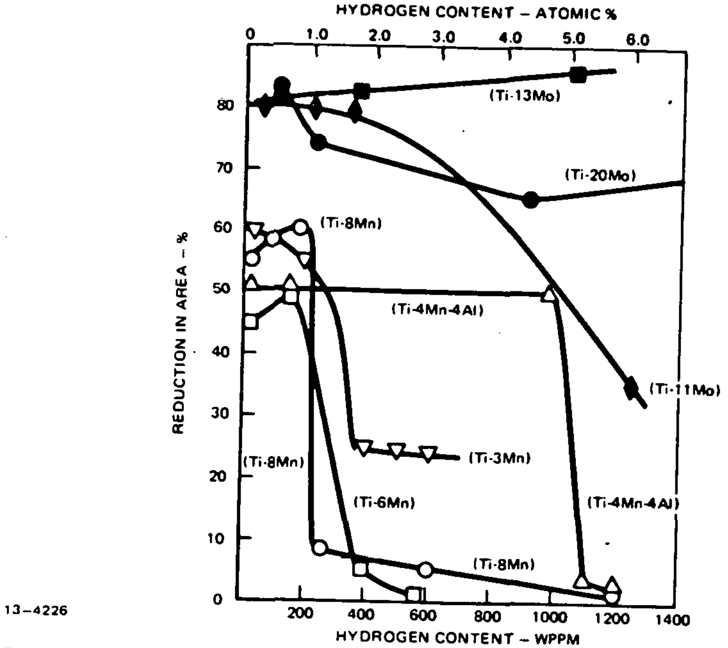


FIGURE 4–9 EFFECT OF HYDROGEN ON THE REDUCTION OF AREA OF A SERIES OF ALPHA - BETA TITANIUM ALLOYS TESTED AT A SLOW STRAIN-RATE AT 25°C ~~ALPHA-BETA~~

to be unaffected by approximately 1400 hours of hydrogen infiltration under typical power reactor plasma-chamber conditions with respect to temperature, 377°C to 547°C; hydrogen pressure, 0.4 to 4 Pa; and gas composition. No physical tests were conducted to measure properties.

Rhodes, et.al.(37) have investigated the influence of hydrogen on the tensile properties of Ti-6Al-4V at room temperature and 350°C. The results are shown in Table 4-1. At room temperature the higher hydrogen content (1000 vs. 10 wppm) increased the ultimate strength and elongation with no significant effect on the yield strength; this was typical at both the 0.05 and 0.005 strain rate. At 350°C the higher hydrogen content increased the ultimate strength and had no effect on the elongation at either strain rate. The yield strength at 350°C was apparently increased by the 1000 ppm hydrogen when tested at 0.05 strain rate whereas it decreased when tested at 0.005 strain rate. The results of these tests are encouraging for fusion applications, as they show no significant degradation of titanium mechanical properties due to the presence of 10 to 10^{-1} Pa hydrogen pressure at 300 to 600°C temperature conditions expected in the reactor.

Hoeg, et al(38) have hydrogen charged Ti-6Al-4V to various concentrations and subjected it to fracture toughness and conventional tensile testing. The results indicate that the properties were not unduly influenced by hydrogen contents of up to 499 wppm. Transmission electron microscopy revealed that at hydrogen concentrations higher than 225 wppm, strain induced hydride precipitation

TABLE 4-1 INFLUENCE OF HYDROGEN ON TENSILE PROPERTIES OF Ti-6Al-4V

Yield Strength (ksi)

Hydrogen Content	Room Temperature Strain Rate .005	Room Temperature Strain Rate .05	350°C Strain Rate .005	350°C Strain Rate .05
0	126.8	129.5	95.6	93.6
1000 wppm	126.8	132.7	87.4	101.5

Ultimate Tensile Strength (ksi)

Hydrogen Content	Room Temperature Strain Rate .005	Room Temperature Strain Rate .05	350°C Strain Rate .005	350°C Strain Rate .05
0	138.0	139.1	104.9	100.5
1000 wppm	154.0	155.1	114.6	112.7

Total Elongation (percent)

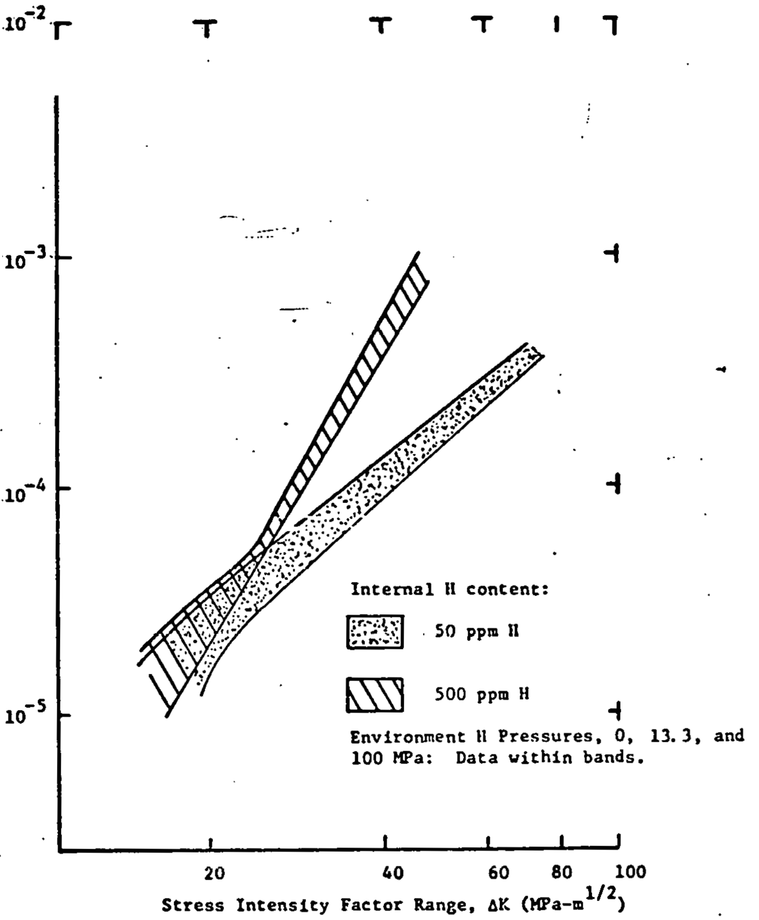
Hydrogen Content	Room Temperature Strain Rate .005	Room Temperature Strain Rate .05	350°C Strain Rate .005	350°C Strain Rate .05
0	11.1	12.1	9.9	9.9
1000 wppm	16.5	16.2	10.2	9.4

occurred ahead of the crack tip. The detection of strain-induced precipitation in the plastic zone at the crack tip indicates that other properties involving longer times under load, such as creep, stress corrosion, and sustained load cracking resistance could be impaired.

Wille and Pao(20) are currently investigating the effects of both internal and external hydrogen on fatigue crack growth of Ti-6242S at temperatures and pressures of interest for fusion. Results of room temperature tensile teats at a strain rate of 7×10^{-5} sec $^{-1}$ on Ti-6Al-2Sn-4Zr-2Mo-0.8 Si with 2400 appm (53 wppm) and 24,100 appm (530 wppm) hydrogen are shown in Table 4-2 and reveal that the tensile strengths of the hydrogen charged specimens were slightly higher than those of the as-received alloy. The ductilities of the two groups were equivalent. Scanning electron microscopy of the failed surfaces indicated a ductile nature of fracture. Initial fatigue crack growth rate tests have been conducted at room and elevated temperatures with environment hydrogen pressures from 0 to 100 Pa (0.75 torr) on Ti-6242S samples containing 50 and 500 wppm internal hydrogen. These tests indicate that at room temperature there is an increase in the crack growth rate with the 500 wppm hydrogen content, as shown in Figure 4-10; no effect of environment hydrogen pressure was noted. Tests conducted at elevated temperatures indicate a decrease in crack growth rate with higher temperatures, as shown in Figure 4-11.

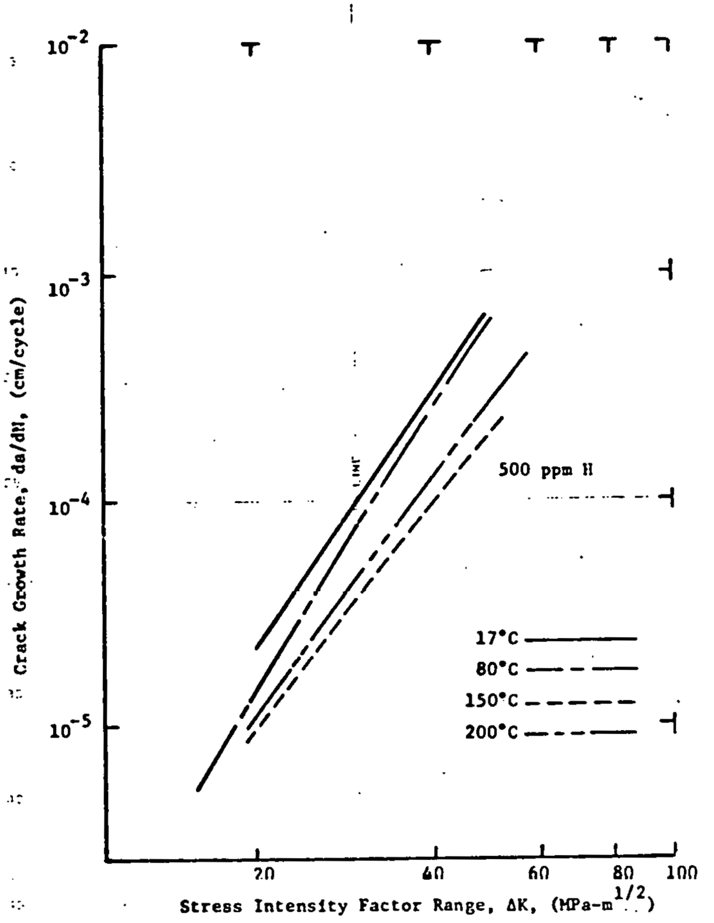
TABLE 4-2. TENSILE PROPERTIES OF Ti-6242S

Material	Ultimate Tensile Strength		Yield Strength		Elongation, Percent
	MPa	ksi	MPa	ksi	
As-Received Ti-6242S - 2400 appm H (53 wppm H)	1089	158	1027	149	13.4
Charged Ti-6242S 24,100 appm H (530 wppm H)	1130	164	1054	153	13.8



4-10.

Figure ~~5.3.[illegible]~~ Effect of Internal and Environment Hydrogen on the Fatigue-Crack-Growth Rate of Ti-6Al-2Sn-4Zr-2Mo-Si at Room Temperature



4-11.

Figure ~~5.3.[illegible]~~ The Effect of Temperature on the Fatigue Crack Growth Rate of Ti-6242S with 500 wppm Internal Hydrogen

4.3 EFFECTS ON BETA TITANIUM - Craighead, et al,(6) reported that impact and tensile properties of a series of beta alloys were unaffected by hydrogen in high proportions. For example, an all-beta alloy containing 13.1 percent Mo had a ductility on the order of 90 percent at a hydrogen content of approximately 9 atomic percent (1900 wppm).

Paton, et al,(37)(39) have investigated tensile properties of beta alloys Ti-18Mo,Ti-30V, and Ti-3Al-8V-6Cr-4Mo-4Zr over the temperature range -123°C to room temperature. The initial strain rate was 1.3 x $10^{-4}/sec^{-1}$. This work showed that both yield strength and Young's modulus decrease with increasing hydrogen content, while the lattice parameter increases. See Figure 4-12, which shows that proportional limit and 0.2% offset yield strength decrease linearly when plotted as a function of square root hydrogen concentration. When Young's modulus was plotted versus square root hydrogen concentration as in Figure 4-13, the modulus increased at -173°C and decreased at temperatures of -73 and 27°C. Figure 4-14 shows the effect of temperatures and hydrogen content on Young's modulus of Ti-18Mo. In contrast to the decrease in yield strength and proportional limit of Ti-18Mo with respect to hydrogen content (Figure 4-12), the Ti-3Al-8V-6Cr-4Mo-4Zr alloy shows an increase in these properties as is shown in Figure 4-15. The authors postulated that this difference in properties was due to lesser stability of Ti-3Al-8V-6Cr-4Mo-4Zr alloy in comparison to Ti-18Mo alloy.

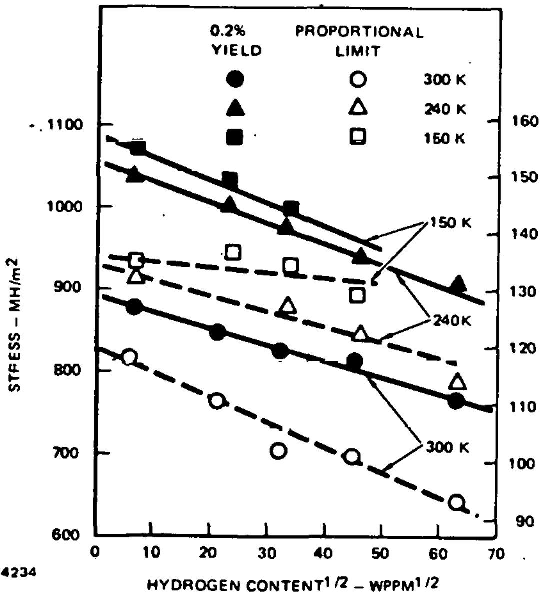


FIGURE 4–12 YIELD STRESS AND PROPORTIONAL LIMIT OF Ti-18Mo-H ALLOYS PLOTTED VERSUS SQUARE ROOT HYDROGEN CONCENTRATION

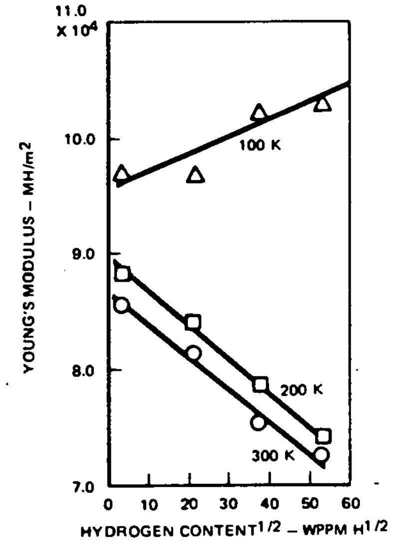


FIGURE 4–13 YOUNG'S MODULUS DATA FROM FIG. 2 REPLOTTED VERSUS SQUARE ROOT HYDROGEN CONCENTRATION

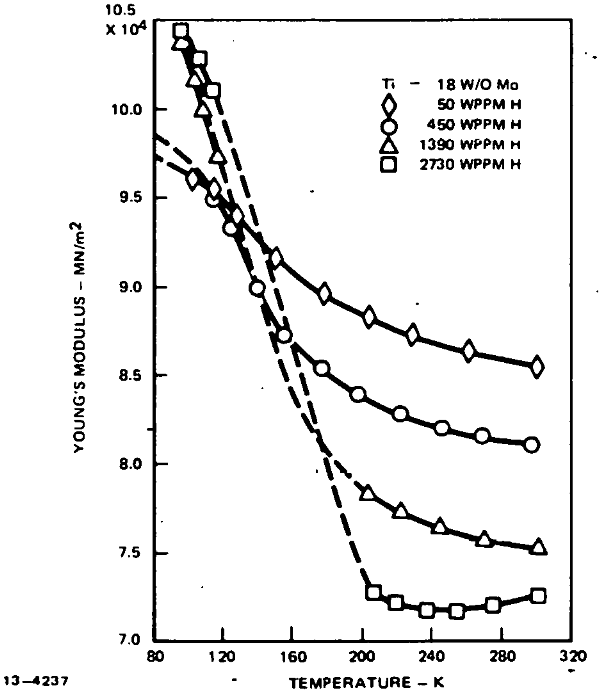


FIGURE 4–14 YOUNG'S MODULUS OF Ti-18Mo-H ALLOYS PLOTTED VERSUS TEMPERATURE

Criqui, et al,(40) have investigated the effects of internal and external hydrogen on mechanical properties of Beta I, VT15 and Beta III (Ti-11Mo-7Zr-5Sn) titanium alloy sheet. Figure 4-16 shows that the elongation of tensile specimens hydrogen charged at the solution treating temperature (850°C) and pulled at strain

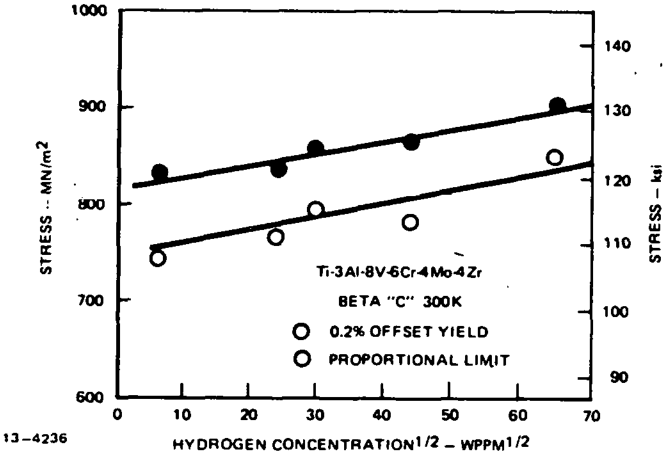


FIGURE 4–15 YIELD STRESS AND PROPORTIONAL LIMIT OF BETA "C" AT 300K PLOTTED VERSUS SQUARE ROOT HYDROGEN CONCENTRATION

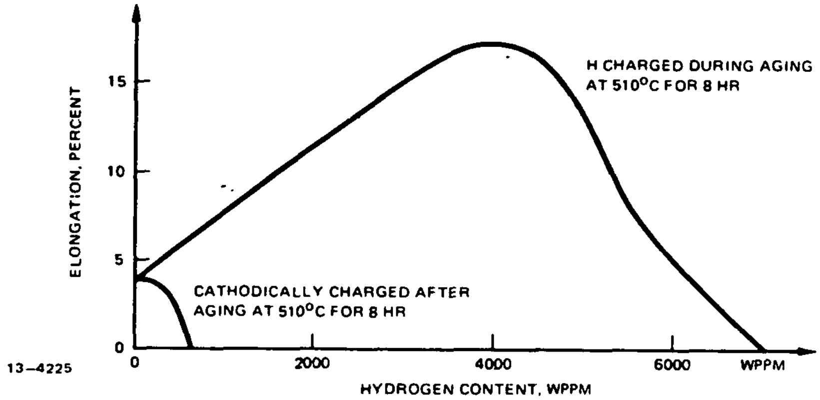


FIGURE 4–16 INFLUENCE OF H CONTENT ON PERCENT ELONGATION OF BETA III SOLUTION HEAT TREATED AT 850°C FOR 15 MIN., THEN CHARGED AS INDICATED ON CHART

rates of 10^4/sec $^{-1}$ decreased with increasing hydrogen content; the amount necessary to embrittle the material depended upon the alloy composition.

They also noted that the influence of the hydrogen was different on material hydrogen charged during aging than cathodically charged after aging. Figure 4-17 shows that there is a great difference between the room temperature percent elongation for Beta III titanium solution treated at 850°C for 15 minutes, then either a) hydrogen charged in a Sieverts apparatus during aging for 8 hours at 510°C or b) aged for 8 hours at 510°C followed by cathodically hydrogen charging. The softening or increase in elongation resulting from treatment (a),

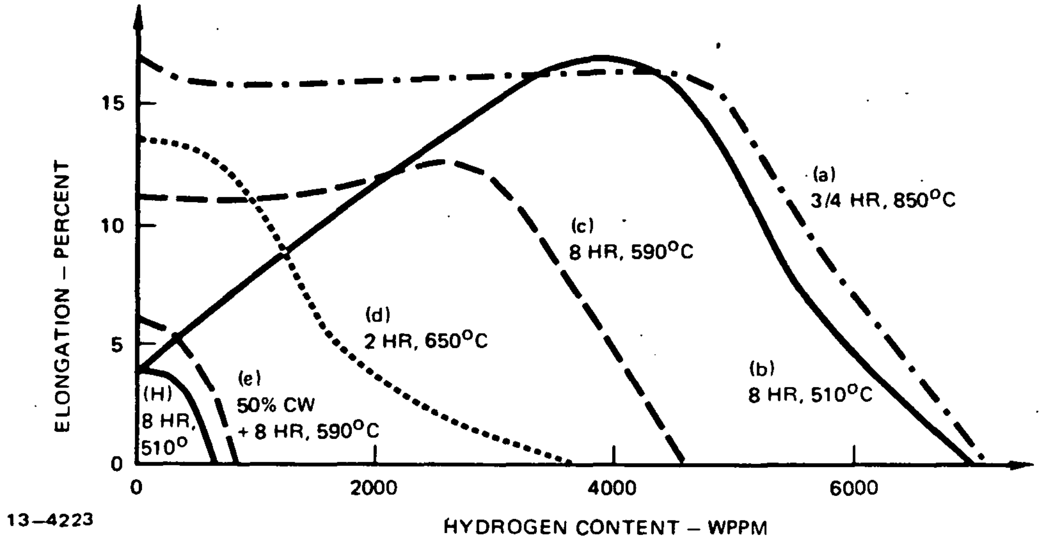


FIGURE 4–17 INFLUENCE OF H CONTENT ON E% OF BETA III ST 1/4 HR, 850°C H CHARGED DURING HEAT TREATMENT (a-e) OR CATHODICALLY CHARGED AFTER AGING 8 HR AT 510°C (H)

was credited to a hydrogen induced beta stabilization which causes a decrease in the alpha phase precipitation during aging. Charging during aging, treatment (a), promoted increased elongation to hydrogen contents up to 4000 wppm H. The introduction of hydrogen into titanium at elevated temperatures would represent the situation present in reactor, therefore embrittlement of Beta III would not appear to be a problem in reactor environment.

Rhodes et al(37) have investigated the tensile properties of Beta III in high pressure hydrogen and helium. Table 4-3 presents the data that shows severe degradation of tensile strength when tested in high pressure (5000 psi) hydrogen. This indicates that the tolerance for hydrogen is limited, however, these pressures are not being considered for fusion reactor environments.

4.4 SUMMARY - The data presented in this section shows the complexity of the hydrogen-titanium interactions upon the mechanical properties. The data generally indicates that the beta alloys are more tolerant of hydrogen that the alpha-beta alloys before tensile properties are degraded. The alpha alloys exhibit little degradation of tensile properties due to hydrogen; they are susceptible to impact embrittlement at hydrogen contents exceeding the solubility.

The near-alpha titanium alloys are presently considered the preferred alloys due to their superior elevated temperature creep strength. Both Ti-6242S and Ti-5621S are considered near-alpha alloys but technically are alpha-beta alloys with

TABLE 4-3 TENSILE PROPERTIES OF BETA III IN 34 MPa (5000 psi) HELIUM AND HYDROGEN

Specimen No.	Gas	Test Pressure PSIA	Yield Strength ksi	Ultimate Tensile Strength ksi	R.A. %	Elong. %
		ST 745°C /5 min/W.Q.				
1	H_2	5000	78.8	97.5	13.1	4.0
2	He	5000	79.8	113.7	63.4	22.0
		ST 745°C /5 min/W.Q. + Age 540°C/8 hrs				
4	H_2	5000	143.4	154.0	6.7	4.0
5	He	5000	143.1	152.3	16.6	7.2
		ST 815°C /5 min/W.Q.				
1	H_2	5000	80.5	96.8	6.3	3.8
2	He	5000	85.4	110.7	72.9	31.6
		ST 815°C /5 min/W.Q. + Age 540°C/8 hrs				
4	H_2	5000	143.4	150.4	7.1	6.6
5	He	5000	137.6	147.2	13.8	8.8

ST - Solution Treat
W.Q. - Water Quench

predominantly alpha phase. These alloys would respond to hydrogen as alpha-beta alloys and therefore be susceptible to slow-strain rate embrittlement if sufficient hydrogen concentrations are obtained. It is significant to note that hydrides tend to dissolve in the microstructure at temperatures above 100 to 150°C and also hydrogen diffusion rates are increased at elevated temperatures allowing for modest hydrogen concentration (500 wppm) within the material. Because of these conditions one could expect no deleterious effects will be experienced with these titanium alloys at the elevated reactor temperatures.

Because of the lack of directly applicable data, a sufficient data base must be generated to provide quantitative data to determine the effects of both internal and external hydrogen on the most favorable titanium alloys at temperatures nd pressures of interest for fusion reactors.

5.0 CONCLUSION

A thorough review of available information on hydrogen effects in titanium alloys under reactor conditions revealed little directly applicable information.

The titanium alloys that offer properties worthy of consideration for fusion reactors are Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-Si (Ti 6242S) and Ti-5Al-6Sn-2Zr-1Mo-Si (Ti-5621S). The Ti-6242S and Ti-5621S are being considered because of their high creep resistance at elevated temperatures of 500°C. Also, irradiation tests on these alloys have shown irradiation creep properties comparable to 20% cold worked 316 stainless steel. These alloys would be susceptible to slow strain rate embrittlement if sufficient hydrogen concentrations are obtained. Concentrations greater than 250 to 500 wppm hydrogen and temperatures lower than 100 to 150°C are approximate threshold conditions for detrimental effects on tensile properties. Indications are that at the elevated temperature - low hydrogen pressure conditions of the reactors, there would be negligible hydrogen embrittlement.

Because of the lack of directly applicable data, a sufficient data base must be generated to provide quantitative data to determine the effects of both internal and environmental hydrogen on the most favorable titanium alloys at temperatures and pressures of interest for fusion reactors. Ideally, this data base will also combine the effects of radiation damage as well as any hydrogen effects.

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