STRESS INDUCED REORIENTATION OF VANADIUM HYDRIDE

Marcus Brad Beardsley

M.S. Thesis Submitted to Iowa State University

Ames Laboratory, ERDA
Iowa State University
Ames, Iowa 50011

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MASTER

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Stress induced reorientation of vanadium hydride

by

Marcus Brad Beardsley

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Stress induced reorientation of vanadium hydride

Marcus Brad Beardsley

The critical stress for the reorientation of vanadium hydride was determined for the temperature range 180 to 280 K using flat tensile samples containing 50 to 500 ppm hydrogen by weight. The critical stress was observed to vary from a half to a third of the macroscopic yield stress of pure vanadium over the temperature range. The vanadium hydride could not be stress induced to precipitate above its stress-free precipitation temperature by uniaxial tensile stresses or triaxial tensile stresses induced by a notch.

I. INTRODUCTION

Hydrogen embrittlement of vanadium, niobium, and tantalum at low temperatures is a well-documented fact (1-5). However, the mechanism of the embrittlement is still a point of disagreement among the investigators of this phenomenon. Specifically, it is uncertain whether hydrogen in solution or hydrogen in the form of hydrides is responsible for the embrittlement.

A. Review of Hydrogen Embrittlement of Vanadium

A schematic illustration of the ductility of hydrogen charged vanadium as a function of temperature is shown in Fig. 1 (1). The ductility, as measured by the percent reduction in area of tensile samples, is approximately equal to the ductility of the uncharged vanadium at point A. As the temperature is lowered, the ductility gradually decreases until at point B it rapidly drops to virtually zero. Some 10 to 15°K below this point the hydride is visually observed to precipitate and is present at all lower temperatures. At low hydrogen concentrations the ductility starts to increase again at point C until finally at point D the ductility has returned to around 40% reduction in area which is still less than the uncharged vanadium but enough that it can no longer be considered brittle.

Increasing the hydrogen concentration tends to shift the curve to the right on the temperature scale increasing the

Fig. 1. Schematic illustration of the ductility behavior of hydrogen charged vanadium depicting four temperature regions, A, B, C and D, of special interest. Ref. (1)

ductile-to-brittle transition temperature and decreasing the hydrogen concentration shifts the curve to the left decreasing the ductile-to-brittle transition temperature.

The ductile-to-brittle transition temperature occurs 10 to 15°K above the visual precipitation temperature of the hydrides. This would suggest that the hydrogen in solution is the cause of the embrittlement. However, it is possible that the hydride could be stress induced to precipitate above its stress-free precipitation temperature. Thus hydrogen in the form of hydride could cause the embrittlement. On the other hand, the return of ductility at low temperatures would support hydrogen in solution as the embrittling agent since as the temperature is lowered hydrogen would be removed from solution by continued hydride precipitation and growth.

Vanadium hydride is thought to be lenticular in shape and appears needle-like when viewed with a light microscope. It has been shown (1) that a tensile stress can cause the hydride to reorient such that its long axis becomes perpendicular to the stress axis. A knowledge of the affect that stress has upon vanadium hydride could lead to a better understanding of the hydrogen embrittlement mechanism.

B. Review of Previous Studies of Stress

Orientation of Precipitates

Stress induced orientation of precipitates has been reported in zirconium-hydrogen, titanium-hydrogen, and iron-

nitrogen alloys (6-10). There is also evidence to suggest that it occurs during creep in aluminum-lithium alloys (11).

Louthan and Marshall (6) reported that zirconium hydride would orient perpendicular to tensile stress and parallel to compressive stress in drawn Zircaloy tubing loaded circumferentially when the stress was greater than 34.5 MPa (5,000 psi) as shown in Fig. 2. The fraction of the hydride showing a preferred orientation was proportional to the stress with 73 percent of the hydrides being oriented at 103.4 MPa (15,000 psi). The critical stress below which no orientation took place was dependent upon the fabrication technique used to make the Zircaloy tubing. Roll formed tubing in the as-received condition showed no preferred orientation at 103.4 MPa (15,000 psi) and only a small amount at 153.7 MPa (22,000 psi). Fig. 3 illustrates the affect of several fabrication techniques upon the critical stress for the orientation of zirconium hydride in circumferentially loaded Zircaloy tubing. It was also noted that prior deformation of more than 8 percent plastic strain would cause the hydrides to align with the direction of the plastic flow with no applied stress.

Marshall (7) distinguished between this "natural" preferred orientation due to prior deformation and the stress induced orientation. He also showed that the susceptibility for stress induced orientation was not dependent upon the crystallographic texture of the material but upon the fabrica-

Fig. 2. Dependence of zirconium hydride orientation on stress level in bend tests of circumferential sections of drawn tubing. Ref. (6)

Fig. 3. Dependence of zirconium hydride orientation on stress level in bend tests of circumferential sections of tubing formed in various ways. Ref. (6)

tion technique. Thus, two cold rolled samples with different textures would have the same critical stress for orientation while a cold rolled sample and a hot rolled sample having the same texture would have different critical stresses. Therefore the texture of the Zircaloy cannot be used to predict the susceptibility to stress induced orientation of the zirconium hydride.

Walters (8) observed a $\{10\bar{1}0\}$ habit plane for zirconium hydride in hydrogen charged zirconium with no stress applied. At stress levels above 69.0 MPa (10,000 psi) the hydrides were observed to preferentially orient on $\{10\bar{1}0\}$ planes normal to the stress axis. If no $\{10\bar{1}0\}$ plane was normal to the stress axis, it required a 89.6 MPa (13,000 psi) stress to orient the hydrides on $\{10\bar{1}0\}$ planes that were 60 degrees to the stress axis. No habit plane other than the $\{10\bar{1}0\}$ plane was observed.

Westlake (12) did not observe preferred orientation of hydrides in single crystal samples of zirconium at a stress of 11.7 MPa (1700 psi). This was attributed to the critical stress for orientation being higher than the yield stress of the single crystal samples. Westlake also observed only $\{10\bar{1}0\}$ habit planes for the zirconium hydride.

Therefore, to explain Marshall's observed independence of stress orientation susceptibility on texture in Zircaloy tubing, it was suggested by Louthan and Angerman (13) that

the habit plane of the zirconium hydride changes with alloying addition and the type of deformation prior to precipitation.

Titanium hydride was observed by Louthan (9) to be stress induced to orient perpendicular to the tensile stress axis and parallel to the compressive stress axis at 206.8 MPa (30,000 psi). No attempt was made to find the critical stress for the orientation since it would probably depend upon the fabrication technique as in the case of zirconium hydride.

Nakada et al. (10) showed that Fe_{16}N_2 precipitates in an iron-nitrogen alloy also oriented perpendicular to the tensile stress axis and parallel to the compressive stress axis. It was also shown that there was a critical stress for the orientation but it was not determined because residual stresses were present in the samples.

Stress induced orientation of precipitates can be explained simply as a demonstration of Le Chatelier's principle. Since the density of precipitates is significantly less than that of the metal, the growth of the precipitate in planes normal to the applied stress tends to relieve that stress.

Two theories have been proposed to explain the phenomena of stress induced orientation of precipitates. The first, proposed by Li (10, appendix of Li) and modified by Ells (14), is based upon the assumption that the orientation is due to preferential nucleation of the precipitates. This theory successfully explains many of the observed features for stress

induced orientation in the zirconium-hydrogen, titanium-hydrogen, and iron-nitrogen alloys.

For these alloys, the stress is applied at a temperature above the precipitation temperature of the precipitate, usually several hundred degrees Centigrade, then cooled to room temperature. The orientation would occur as the hydride or nitride precipitated. After precipitation, the stress could be removed and no change would be observed.

This theory was shown to fit the data of Louthan and Marshall (6) given in Fig. 2 very well as shown in Fig. 4. The existence of the critical stress reported by Louthan and Marshall was assumed to be due to the inability to detect the small amount of preferred orientation at the lower stresses.

The second theory, proposed by Ells and Simpson (15), assumes the orientation is due to preferred growth of existing precipitates. Thus it is actual reorientation of the precipitates. This is thought to be the mechanism for the reorientation of small zirconium hydrides precipitated within grains observed by Mishima et al. (16) and for the reorientation of vanadium hydrides observed by Sherman et al. (1).

C. Purpose of the Present Investigation

The purpose of the present investigation was to determine whether a critical stress exists for the reorientation of vanadium hydride in single crystal and polycrystalline vanadium and, if it did exist, to determine its dependence upon

Fig. 4. Fit of theory (solid line) to data from Fig. 2 (dashed line). Ref. (14)

hydrogen concentration and temperature. Also, it was desired to determine whether vanadium hydride could be stress induced to precipitate above its stress-free precipitation temperature.

II. MATERIALS AND PROCEDURE

A. Preparation of Polycrystalline Tensile Samples

The vanadium used to make the polycrystalline tensile samples was produced by fused salt electrolysis (17). A chemical analysis of the metal is given in Table 1.

Table 1. Chemical analysis of vanadium

Element	Content, ppm	Element	Content, ppm
Cr	200	Ti	<50
Cu	200	O	115
Fe	<100	H	3
Ni	<50	N	8
Si	<50	C	10

The metal was arc melted into a button approximately 2 cm thick and 5 cm in diameter. It was then rolled into a sheet 0.191 cm thick then given a 2 hour anneal at 1000°C under a dynamic vacuum of 10^{-6} torr. The sheet was then rolled to 0.152 cm thick and flat tensile samples with the dimensions shown in Fig. 5 were cut from it. The samples were then given a 4 hour anneal at 1000°C under a dynamic vacuum of 10^{-6} torr.

After annealing, the samples were ground flat and electropolished for 4 minutes in a 6% perchloric acid-methanol solution at -70°C using 40 volts. Each sample was then individually charged with hydrogen by the method described by Owen and Scott (2). The samples were heated to 1000°C under a dynamic vacuum of 10^{-6} torr, held there for 5 minutes to

Fig. 5. Schematic illustration of polycrystalline tensile sample showing approximate dimensions before electropolishing the gauge length

"activate" the surface, then cooled to 850°C. The samples were then isolated from the pumping system and hydrogen from the thermal decomposition of uranium hydride was admitted to a predetermined pressure that would give the desired hydrogen concentration. The system was held at 850°C for 1/2 hour to insure homogenization and then allowed to furnace cool to room temperature.

It was found that to achieve some accuracy in the hydrogen concentration of each sample, scrap vanadium needed to be added with the sample so that a higher pressure of hydrogen could be used. This provided a greater driving force for the hydrogen to enter the sample.

The hydrogen concentration for each of the polycrystalline tensile samples is given in Table 2.

Table 2. Final gas content of polycrystalline samples in ppm by weight

Sample number	O	N	H
I	180	91	500
II	210	85	380
III	210	84	310
IV	210	110	160
V	200	93	55
VI	62	2	180
VII	81	6	145

During the charging process, several samples developed a bluish film on the surface. This was thought to be due to thermal etching caused by a variation in grain size across

the sample. It was removed by polishing the samples in a 20% sulfuric acid-methanol solution for 5 minutes at room temperature, using 10 volts.

B. Preparation of Single Crystal Tensile and Compressive Samples

Single crystals of vanadium were prepared by arc melting the metal into a finger then passing the arc along the length of the finger creating a moving molten section. After several passes of the arc, the vanadium was transformed into a large single crystal by the unique conditions of the process. Samples of the desired crystallographic orientation and size were then spark cut from the large single crystal finger.

Single crystal tensile samples were made by arc welding polycrystalline tensile ends to slabs of single crystals as shown in Fig. 6. The two sides of the samples were ground parallel then both the tensile and compressive samples were electropolished in a 6% perchloric acid-methanol solution at -70°C and 40 volts.

The tensile samples were given a 1 hour anneal at 1000°C under a dynamic vacuum of 10^{-6} torr to relieve any residual stresses caused by the welding process after which both the tensile and compressive samples were charged with hydrogen in the manner already described for the polycrystalline samples. The concentration for each sample is given in Table 3.

Fig. 6. Schematic illustration of single crystal tensile sample showing weld zones between single crystal and polycrystalline ends

Table 3. Final gas content of single crystal samples in ppm by weight

Sample number	Type of sample	O	N	H
VIII	Tensile	460	74	160
IX	Tensile	380	89	270
X	Compressive	190	15	170

C. Equipment

Since the vanadium hydrides precipitate below room temperatures for the concentrations of interest, a vacuum stage was built for the microscope to keep moisture in the atmosphere from condensing on the sample and objective lens of the microscope. Within the vacuum stage was placed a screw loading jig which was used to stress the samples. Strain gauges attached to two stainless steel cylinders were placed in the loading jig to determine the load on the samples. The output of the strain gauges was calibrated using an Instron tensile testing machine. A load versus strain output curve was derived and used in determining the load on all samples.

A schematic illustration of the vacuum stage and loading jig is given in Fig. 7. Viewing of the entire gauge length of the samples was accomplished by moving the entire loading jig in the longitudinal direction and by rotation of the cap through which the objective lens projected. The hole for the objective lens was off center and therefore swung in an arc to transverse the width of the sample.

1. SCREW FOR LOADING
2. THERMOCOUPLE
3. STATIONARY COPPER BLOCK
4. SAMPLE
5. ATTACHED COPPER BLOCK
6. MICROSCOPE OBJECTIVE
7. CYLINDERS WITH STRAIN GAGES
8. STRAIN GAGE LEADS

Fig. 7. Schematic illustration of loading jig showing placement of strain gages and cooling blocks. Enclosing box and cooling bath are omitted for clarity

Cooling of the samples was through a copper block that was clamped to the samples by one of the screws holding the sample in the loading jig. This copper block moved as the loading jig was moved and was in contact with the stationary copper block that projected upward into the part of the lid of the vacuum stage that was surrounded by methanol. The temperature of the methanol bath was lowered by liquid nitrogen which was circulated through a copper coil in the bath. The flow of liquid nitrogen, and therefore the temperature, was automatically controlled such that the sample temperature was held to within $\pm 1^\circ\text{K}$ for the temperature range from 220°K to room temperature and $\pm 3^\circ\text{K}$ for the range 180°C to 220°K .

D. Procedure

After a sample had been charged with hydrogen and a good surface for metallographic examination prepared, it was placed in the vacuum stage. The stage was then evacuated to a pressure of approximately 25 microns. It was then back filled with air dried by two Drierite columns and a liquid nitrogen cold trap. The sample was then cooled to the desired temperature.

Since the reorientation of the vanadium hydride could be observed as it took place the critical stress for the reorientation was determined for individual hydrides rather than determining the percent of hydrides that was oriented at various stresses as was done for zirconium hydride.

The critical stress was then defined as the minimum stress that would cause any hydride in the sample to begin to reorient. In the tensile samples this was indicated by a reduction in size of a hydride parallel to the stress axis. A magnification of 40X was used so that several hydrides could be observed at the same time. Thus usually only one hydride out of several observed would begin to reorient at the critical stress.

To actually determine the critical stress several hydrides parallel to the stress axis were brought into view. A picture at 0 load was taken for reference. The load was then increased in 50 pound increments with pictures taken at each load until reorientation of one of the hydrides was noted. The loads were applied for 10 minutes to permit equilibrium to be attained but changes were usually observed within the first 3 minutes. Once reorientation was noted, the sample was unloaded and allowed to sit for 10 minutes before it was again loaded. This was done because it had been observed that applying a load which had not caused changes previously would cause reorientation if applied within 5 minutes after the first load was released. A halving method was used to determine the next load to be applied. The method was repeated until the critical stress was determined. It is felt that the load was accurate to 5 pounds, therefore, 5 pounds above the stress for which no change was observed was taken as the

critical stress since the smallest increment of stress used was 10 pounds.

Stress induced precipitation of hydrides above their stress-free precipitation temperature was tried using samples II, IV, V, and VI. Samples V and VI were notched to provide stress concentrations to enhance stress induced precipitation. The notches were cut using a 6 mil diamond saw blade.

III. RESULTS

A. Hydride Reorientation in Polycrystalline Tensile Samples

The critical stress for the reorientation of vanadium hydride in tension was determined for five hydrogen concentrations over the temperature range 180 to 280°K. The data are presented in Fig. 8 along with yield stress data for vanadium of similar concentrations. The stress plotted is the lowest stress to cause reorientation of any hydride in the field of view hereafter known as the sample critical stress. Thus, the sample critical stress for reorientation at each temperature for a given hydrogen concentration represents a different hydride in every case.

No definite trend can be seen other than reorientation begins to occur at stresses that are approximately half the yield stress of hydrogen free vanadium at room temperature and a third of the yield stress at lower temperatures.

The yield stresses for samples I through V were determined at several temperatures and are given in Table 4. The data were determined by pulling the samples at the given temperatures until yielding occurred then unloading them. The highest temperatures were done first with only 2% plastic strain occurring at each temperature. Since very little work-hardening accrues during small strain increments in vanadium, the yield stress increase at lower temperatures is a reflection, primarily, of the temperature dependence of the yield

Fig. 8. Critical hydride reorientation stress of samples as a function of temperature. Numbers given indicate concentration of hydrogen in ppm by weight. Yield stress (Y.S.) data for pure vanadium and vanadium with 85 ppm hydrogen given for reference

stress. Fracture of the samples occurred after yielding at temperatures below the ductile-to-brittle transition temperature of each sample.

Table 4. Yield stress data for samples I through V in MPa (psi)

Temp.	I	II	III	IV	V
280°K	266.6 (38,660)				
260°K	290.3 (42,100)	265.2 ^a (38,460)	271.4 (39,360)		
240°K	284.3 (41,240)		293.4 (42,550)	289.4 (41,980)	
230°K	325.8 ^a (47,250)		322.8 ^a (46,810)	308.8 ^a (44,780)	
200°K					340.3 (49,360)
180°K					351.4 (50,960)

^aSamples broke after yielding at these temperatures.

The average of the sample critical reorientation stresses for each concentration over all temperatures, assuming no significant temperature dependence for the reorientation stress, are plotted in Fig. 9. The average of the sample critical stresses at each temperature for all hydrogen concentrations are plotted in Fig. 10. An increase of the sample critical reorientation stress with increased hydrogen concen-

Fig. 9. The averages of the critical hydride reorientation stresses for each sample over all temperatures plotted as a function of hydrogen content of the sample. Precipitation temperature at the given concentration is given in parentheses

Fig. 10. The averages of the critical hydride reorientation stresses for each temperature over all concentrations of hydrogen plotted versus temperature

tration is indicated in Fig. 9. The trend shown in Fig. 10 may not be significant since the two points for the higher temperatures represent only one data point each.

When a stress larger than the sample critical stress is applied, hydrides oriented parallel to the stress axis become smaller. Hydrides oriented perpendicular to the stress axis become larger and new hydrides precipitate perpendicular to the stress axis. When the stress is released, the originally random distribution of the hydrides returns. The hydrides perpendicular to the stress become smaller, the newly precipitated hydrides disappear, and the hydrides parallel to the stress axis return to their original size.

The critical stress to cause the reorientation of an individual hydride that is parallel to the stress axis (which may not necessarily be the sample critical stress for the entire specimen) is shown as a function of temperature in Fig. 11. The data correspond to five different hydrides; four hydrides at one concentration and one at a higher concentration. Two of the four hydrides at the lower concentration were in the same grain. These plots show a definite increase of the critical stress, for an individual hydride, with decreasing temperature.

The sample critical stress, based on the lowest stress for any hydride to reorient, and the critical stress for an individual hydride to reorient are not controlled by kinetic

Fig. 11. Plot showing the affect of temperature on the critical stress for the reorientation of individual hydrides at two different concentrations. Precipitation temperatures (PPTT) of each hydride are given in order to reveal the degree of undercooling

affects. This may be inferred from the fact that reorientation occurred within three minutes at stresses 6.9 MPa (1000 psi) above the critical stress even at the lowest temperature and no reorientation was observed at stresses 6.9 MPa (1000 psi) below the critical stress after twenty minutes, even at the highest temperature.

B. Results of Single Crystal Tensile and Compressive Test

Single crystal tensile samples VIII and IX were oriented with the $\langle \bar{5}31 \rangle$ direction parallel to the stress axis and the $\{112\}$ plane parallel to the plane of view. For sample VIII, at 240°K, reorientation was observed at a stress of 201.3 MPa (29,200 psi). For sample IX, at 240°K, reorientation was observed at a stress of 198.2 MPa (28,740 psi).

The critical stress for these samples could not be determined because the hydrides did not return to their original orientations upon release of the load as they did for polycrystalline samples. Hydrides which had reoriented perpendicular to the stress axis persisted in that orientation when the load was removed and the hydrides that were parallel to the stress axis originally did not reappear. The permanent change in the distribution of the hydrides in the stress-free state was probably due to plastic deformation which accompanied hydride formation and the lower yield stress of the single crystal compared to the polycrystalline samples which exhibited no observable plastic accommodation. Plastic accommoda-

tion was indicated by the presence of surface relief after heating the sample to room temperature which was above the solubility limit. A critical stress is known to exist since no reorientation was observed at a stress of 151.0 MPa (21,900 psi) for sample VIII or at a stress of 99.1 MPa (14,370 psi) for sample IX while, as indicated above, these samples showed reorientation at 201.3 and 198.2 MPa respectively. In all cases the samples were at 240°K.

A compressive stress of 27.8 MPa (4,000 psi) applied to sample X at 230°K caused hydrides parallel and perpendicular to the stress axis to shrink indicating that the solubility limit with respect to vanadium hydride at that temperature was raised. However, sample X was incorrectly placed in the compression jig. The length of the sample was approximately 1/4 of the width instead of the reverse. The state of stress in sample X cannot be known for certain because interface friction probably altered the stress state through a significant portion of the thickness. The results noted would therefore be due to a complex stress state approaching hydrostatic compression, instead of a uniaxial compression.

C. Results of Stress Inducement Studies with Polycrystalline Tensile Samples

Samples II, IV, and V were held at the stresses given in Table 5 at temperatures 5 to 10°C above their respective stress-free hydride precipitation temperatures. No hydrides

were observed to be stress induced and, upon cooling each stressed sample, hydrides always precipitated at the normal stress-free precipitation temperature. The applied stress was near the yield stress as revealed by slip line formation in each sample.

Table 5. Data for stress inducement of hydrides

Sample number	Stress-free precipitation temperature	Applied stress
II	283°K	337.4 (48,940)
IV	243°K	373.0 (54,100)
V	205°K	351.4 (50,960)
V notched	205°K	138.0 (20,000)
IV notched	245°K	172.0 (25,000)

Sample V subsequently was notched and a nominal stress of approximately 138.0 MPa (20,000 psi) was applied at a temperature 10°C above the stress-free precipitation temperature. The stress at the base of the notch was unknown but was probably 2 to 3 times the nominal stress. The stress was held for ten minutes and no hydrides were observed to precipitate. Upon cooling, with the stress applied, hydrides precipitated at the stress-free precipitation temperature along either edge of the notch. The sample was then heated to remove the hydrides and again cooled to 10°C above the stress-free precipitation temperature. Upon increasing the nominal stress above 138.0 MPa, a crack began to propagate; it continued to

propagate in stages across the sample as the nominal stress was increased incrementally. The stress was increased until the crack started to move and, if an artifact resembling a hydride was observed, the stress was released and the sample heated slightly. If the artifact remained it was assumed to be a slip line. During crack propagation across the sample no hydrides were observed to precipitate. The same procedure was used for sample VI at a temperature 5°C above its stress-free precipitation temperature and, again, no stress induced hydrides were observed at the crack front or elsewhere. In addition, while determining the stress-free precipitation temperature for sample VI, a hydride precipitated at the crack tip 5°C below the stress-free precipitation temperature with no stress applied. The hydride was oriented parallel to the crack and perpendicular to the nominal stress axis. When stress was applied the hydride disappeared. This important observation will be cited again in the Discussion.

D. Summary of Results

- 1) There is a sample critical stress for the reorientation of vanadium hydride in tensile specimens. The sample critical stress is in the range 28.3 MPa (4,100 psi) to 172.4 MPa (25,000 psi) for the temperature range 180° to 280°K and for hydrogen concentrations of 50 to 500 ppm by weight.

- 2) The sample stress, which was defined as the lowest stress to cause any hydride in the specimen to reorient, appears to increase with increasing hydrogen concentration.
- 3) The critical stress for individual hydrides in a specimen increases with decreasing temperature while no definite trend was evident for the sample stress.
- 4) A complex stress state approaching a hydrostatic pressure, produced by an incorrectly applied compressive load, caused all orientations of hydrides to shrink. This indicates that the solubility limit with respect to the vanadium hydride increased.
- 5) Vanadium hydride cannot be stress induced to precipitate above its stress-free precipitation temperature by uniaxial tensile stresses or triaxial tensile stresses produced by a notch or crack.
- 6) At temperatures below the stress-free precipitation temperature, a tensile stress caused hydride at the tip of a notch or crack to shrink by dissolution even when it was orientated normal to the direction of applied tensile stress; this orientation was stable in uniaxially loaded samples, i.e., samples without notches or cracks.

IV. DISCUSSION

A critical stress for stress induced reorientation of vanadium hydride in tension does exist as attested to by the results shown in Fig. 8. However it is unclear why a critical stress should exist or why the sample critical stress appears to be a function of concentration, indicated by Fig. 9, and independent of temperature, indicated by Figs. 8 and 10, while the critical stress for individual hydrides is a function of both temperature and hydrogen concentration as shown in Fig. 11. Furthermore, if the compression test which was done incorrectly did apply a hydrostatic pressure which then caused hydrides to disappear by dissolution, why did not the reverse occur at the base of a notch in tension, where triaxial tensile stresses exist? These are but a few of the questions and observations which any model for the reorientation phenomenon must attempt to explain.

The theories of Li (10, appendix by Li) and Ells and Simpson (15) do not apply in the case of vanadium hydride formation and reorientation. The theory by Li is based upon the applied stress increasing the nucleation frequency of a particular orientation. In this study the hydride was already precipitated before reorientation occurred and a uniaxial tensile stress had no affect on the nucleation of vanadium hydride since it did not raise the precipitation temperature. The theory by Ells and Simpson does not explain the presence

of a critical stress since they assume any stress will cause reorientation. They use a kinetic argument to show why reorientation of zirconium hydride was not observed at certain stress levels. Since the critical stress observed for the reorientation of vanadium hydride is not a kinetic affect as indicated by the short times for reorientation to occur at stresses of only 6.9 MPa (1000 psi) above the critical stress, the theory of Ells and Simpson does not apply.

Understanding the stress induced reorientation of vanadium hydride probably involves a stability problem in thermodynamics. The stability of the hydride will depend upon its free energy of formation. Contributing to the free energy of formation of vanadium hydride are the chemical free energy per unit volume of hydride, the surface energy of the hydride, and the strain energy per unit volume of hydride due to the expansion accompanying its formation. An applied stress provides strain energy to change the free energy of the system composed of the vanadium solid solution and the vanadium hydride.

A tensile stress will decrease the strain energy of hydrides oriented perpendicular to the stress axis by expanding the lattice in the stress direction. The tensile stress will cause an increase in the strain energy of hydrides oriented parallel to the stress axis due to the lateral contraction which is characterized by Poisson's ratio. This pro-

motes the growth of perpendicular hydrides and the shrinkage of parallel hydrides. However, when the hydrides change size their volumes and surface areas change. The change in the total free energy of the system will depend on how the changes in the strain energy, volume free energy, and surface energy are related. To formulate an exact relationship between these variables is too complex to treat here. However, the existence of a critical stress for reorientation suggests that a certain quantity of strain energy is needed before reorientation can take place. Another observation which any model of the reorientation phenomenon must explain is the dependence of the amount of hydride that reorients upon the applied stress, and therefore the amount of strain energy supplied to the system. The sample critical stress was defined as the stress at which any hydride in the specimen began to reorient. At only 6.9 MPa (1000 psi) above the sample critical stress the hydride that eventually was the first to reorient decreased in size slightly; it continued to decrease in size as the stress was increased further until it had completely disappeared, i.e., reoriented. In addition, the number of reorienting hydrides increased with increasing stress and new hydrides precipitated perpendicular to the stress axis. When the stress was released the original random distribution of the hydrides returned.

It may be possible to gain a better understanding of the reorientation phenomenon by looking at the affect of tempera-

ture on the critical stress for the reorientation of individual hydrides in specimens of different concentrations. As shown in Fig. 11, the critical stress increased with decreasing temperature for individual hydrides. At the same temperature, the hydride from the sample with higher hydrogen concentration had a higher critical stress. The amount of undercooling below the precipitation temperature of the hydride obviously increases with decreasing temperature. This increased undercooling would cause an increase in the chemical free energy per unit volume of the hydride. It would therefore take a larger change in the strain energy, hence a higher stress, to cause the hydride to become unstable and reorient. An increased hydrogen concentration produces a similar affect because it is another way to increase the degree of undercooling.

Also affecting the critical stress for individual hydrides in a specimen will be the response of individual grains to the applied stress due to orientation differences of the grains in the polycrystalline aggregate. This is probably the reason the four hydrides that are in the same specimen lie on different curves in Fig. 11. Two of the hydrides that were in the same grain, and therefore probably experienced the same effective stress, fall on the same curve.

These observations for individual hydrides give some understanding about the sample critical stress. Due to the

way in which the sample critical stress was defined, no temperature dependence of the critical stress would be observed. This follows from the fact that the sample critical stress at a given temperature was defined as the stress to cause any hydride in the sample to reorient. Thus, the sample critical stress would depend on the undercooling of the hydride and the effective stress which it would experience. Since the temperatures for determining the sample critical stresses were fixed, the first hydride to reorient at a higher temperature could have been undercooled more than the first hydride to reorient at a lower temperature. The amount of undercooling for each hydride would depend on its precipitation temperature relative to the observation temperature. Since the precipitation temperatures of the particular hydrides followed in the sample critical stress determinations were not recorded, their degree of undercooling is unknown. Consequently, the uncertainty in the amount of undercooling could lead to an apparent temperature independence of the sample critical stress.

The affects of undercooling and effective stress probably caused the fluctuations in sample critical stress shown in Fig. 8. In Fig. 9, the affects of undercooling and effective stress appear to average out and indicate increased sample critical stress with increased hydrogen concentration. Due to the smaller sampling, no temperature dependence is seen in Fig. 10.

Another observation which any model must accommodate is the inability to stress induce the precipitation of vanadium hydride above its stress-free precipitation temperature. A uniaxial tensile stress had no affect on the precipitation of vanadium hydride and the triaxial tensile stresses induced by a notch caused hydrides that were normal to the applied stress and parallel to the notch to shrink by dissolution. This contradicts the theory of Ells and Simpson (15) which stated that a balanced triaxial tensile stress would increase the precipitation temperature of zirconium hydride and hydrostatic pressure would decrease the precipitation temperature. If the compression test, which was done incorrectly, did produce hydrostatic pressure on the sample then the apparent raising of the solubility limit of hydrogen with respect to the hydride would agree with the theory by Ells and Simpson.

Since uniaxial stresses did not induce hydride precipitation above the stress-free solvus temperature and triaxial stresses produced by a notch caused existing hydrides which were stable under uniaxial tension, i.e. oriented normal to the applied stress, to shrink by dissolution, it can be concluded that the ductile-to-brittle transition of hydrogen charged vanadium tensile samples is due to hydrogen in solution and not stress induced hydrides. The return of ductility at low temperatures would be due to the combined affects of slower hydrogen diffusion and the saturation of nucleation

sites for the hydride which would stop the precipitation of new hydrides and cause only growth of the existing hydrides. This would lead to an increase in the free energy of the existing hydrides which would increase both the critical hydride reorientation stress and the stress needed to cause dissolution of the hydride at the tip of cracks.

V. CONCLUSION

There exists a critical stress for the stress induced reorientation of vanadium hydride in tension. The sample critical stress appears to be independent of temperature and only slightly dependent on hydrogen concentration with a magnitude of a half to a third of the yield stress of hydrogen free vanadium for the temperature range 180 to 280°K and hydrogen concentrations of 50 to 500 ppm. No evidence of stress induced precipitation of hydrides was observed even at the tip of a notch in tension. Therefore the ductile-to-brittle transition of hydrogen charged vanadium is due to hydrogen in solution not stress induced hydrides.

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