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Report No. FAA-SS-72-07

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# SST Technology Follow-On Program - Phase I TITANIUM ALLOY 6AL-4V HYDROGEN EFFECTS

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FINAL REPORT  
TASK I



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Prepared for  
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16. Abstract This report summarizes the investigations for the Boeing SST program from 1966 to 1971 on the effects of hydrogen in Ti-6Al-4V. The tests conducted include the effect of hydrogen content on fracture toughness, stress-corrosion resistance, and delayed-failure cracking. Hydrogen contents of up to 750 ppm had little effect on the fracture toughness and stress corrosion of beta-annealed and beta-STA 1250° F Ti-6Al-4V. Delayed failures were observed in room temperature air in beta annealed, beta-STA 1250° F, and STA 1000° F with hydrogen contents from 150-275 ppm. Failure times were shorter with the STA 1000° F heat treatment and with increasing H <sub>2</sub> content.  Hydrogen pickup during chemical milling was studied and found to be generally low, although isolated high amounts (100-150 ppm) were observed. One instance of high hydrogen pickup was observed during a simple hot forming test. Hydrogen pickup appears to be a function of microstructure.  A practical manufacturing outgassing procedure was developed to reduce the hydrogen content to less than 150 ppm. The procedure involved a vacuum treatment at 1150° F for 1 hr in a vacuum of 50 torr.				14. Sponsoring Agency Code	
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## PREFACE

This is one of a series of final reports on titanium materials technology submitted in fulfillment of task 1-A of Department of Transportation contract DOT-FA-SS-71-12, dated June 30, 1971. The report was prepared by the Materials Technology organization of The Boeing Company, Commercial Airplane Group, Seattle, Washington.

The author acknowledges the many coworkers and supervisors who assisted with or directed parts of this program. Acknowledgment is also given to the Manufacturing Development organization of The Boeing Company, which conducted a major portion of the hydrogen outgassing studies.

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## 1.0 INTRODUCTION

This report describes the results of test programs conducted at The Boeing Company for the SST program from 1968 to 1971 on the effects of hydrogen in Ti-6Al-4V.

Since most of the structural components of the SST prototype were to be fabricated from titanium, control of hydrogen content in the final aircraft parts was of extreme importance. It was imperative to control the hydrogen content of the incoming raw material from the titanium supplier, and in this regard Boeing material specifications required maximum hydrogen limits of 125 ppm for most of the titanium mill products, although thin sheet material limits were 150 ppm. It was also necessary to have a full understanding of hydrogen pickup and outgassing during the various manufacturing operations. These include but are not limited to cleaning, descaling, chemical milling, hot forming, diffusion bonding, brazing, and heat treating. These process specifications were developed to specifically limit the amount of hydrogen pickup, with 15 ppm generally being the maximum allowable pickup. Much work has been conducted on the effects of hydrogen on the ductility and on the delayed cracking of titanium alloys (refs. 1 and 2). The data presented in this report concern the effects on Ti-6Al-4V of hydrogen levels of 100-750 ppm on the fracture toughness ( $K_{IE}$ ), stress-corrosion resistance ( $K_{ISCC}$ ), and resistance to delayed failure in room temperature air in the presence of a fatigue crack.

Chemical milling was used extensively for SST part fabrication, both for a sculpturing or configuration control and for a method of removing the oxygen-contaminated layer resulting from elevated-temperature processing in air. Hydrogen pickup was investigated during the chemical milling operation, and data were obtained for Ti-6Al-4V sheet and plate. Isolated instances of large amounts of hydrogen pickup were observed on some sheets and plates during chemical milling. This prompted a rather extensive development of practical manufacturing outgassing techniques for removing hydrogen on finished or partly finished parts after chemical milling. Many developments were in progress at the time of termination of the SST contract. These plans and potential solutions will be presented along with the firmer data developed.

## 2.0 PROCEDURES

This section describes the testing procedures used for both the evaluation of the effects of hydrogen on fracture properties and the hydrogen pickup and outgassing studies.

### 2.1 FRACTURE PROPERTY EVALUATION

#### 2.1.1 Hydrogenation

The fracture specimens were charged with hydrogen in a modified Sievert's apparatus by exposing them to a given partial pressure of hydrogen at elevated temperatures. Relatively reliable curves were developed which related the resulting hydrogen content in the titanium sample versus hydrogen pressure. The curves had to be modified for various sizes and shapes of test specimens, but once established, they were reasonably accurate in predicting the final hydrogen in the specimen. It was found that a surface pickling step prior to charging and a very clean vacuum system were both necessary for a successful charge. The pickling solution was 90%  $\text{HNO}_3$ , 10% HF at room temperature. The presence of an oxygen layer inhibited the transfer of molecular  $\text{H}_2$  to atomic H and into solution with the titanium. Because successful charging could not be accomplished at 1000° F, all hydrogenation was accomplished at 1250° F. This temperature was of course unacceptable for charging condition III (solution treated and aged at 1000° F) since overaging would occur. The charging of the condition III specimens was therefore accomplished by charging at 1250° F and then solution treating at 1725° F in air. The oxide layer which formed at 1725° F prevented the outgassing of hydrogen at this temperature. The samples were then aged at 1000° F.

A schematic diagram of the hydrogen charging apparatus is shown in figure 1. The procedure was to pass commercial hydrogen through the palladium-silver purifier into a holding tank after the system had been evacuated to approximately  $1 \times 10^{-5}$  torr. Hydrogen was then allowed to enter the vacuum chamber to a pressure on the dial gage based on the amount of hydrogen desired in the sample. Figure 2 shows the vacuum chamber gage pressure versus specimen hydrogen content for a Charpy specimen. After the chamber had stabilized it was closed, and then the hydrogen was allowed to enter the tube furnace. As the sample absorbed hydrogen, the vacuum chamber gage decreased to approximately 1 mm Hg. The system was then allowed to equilibrate for 24 hr at the charging temperature (usually 1250° F). After 24 hr it was cooled to room temperature, the specimen removed, and the hydrogen content of the specimen analyzed. The Charpy and notched bend specimens were analyzed using a vacuum fusion technique, and the single-edge-notched specimens were analyzed using the hot extraction method per ASTM E-146.

In one set of specimens hydrogen was introduced by chemical milling in a 3  $\text{HNO}_3$ /1 HF acid bath.

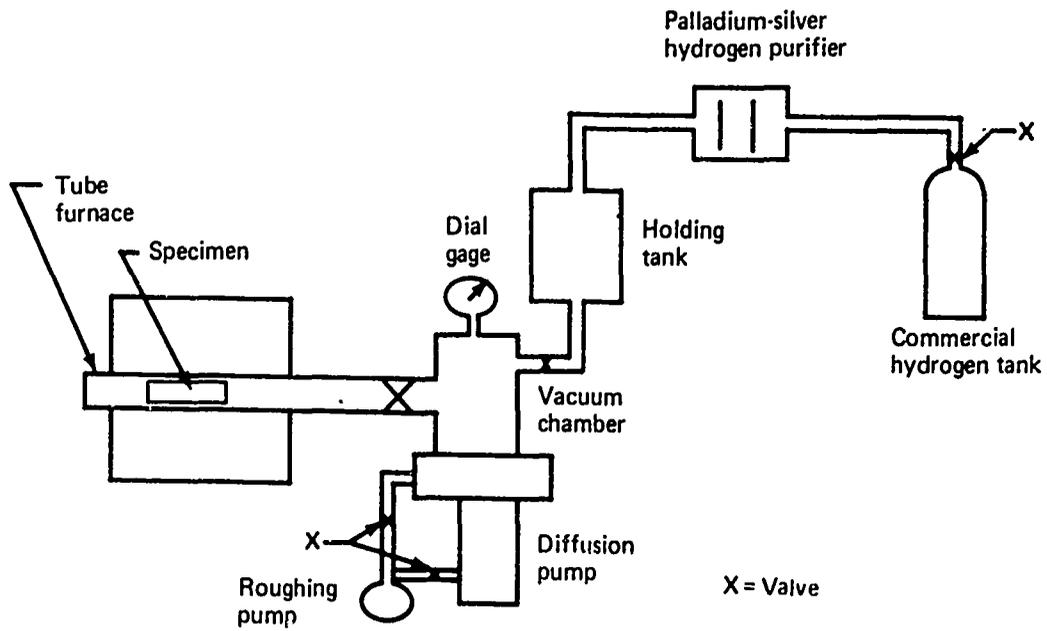


FIGURE 1.—SCHEMATIC DIAGRAM OF HYDROGEN CHARGING APPARATUS

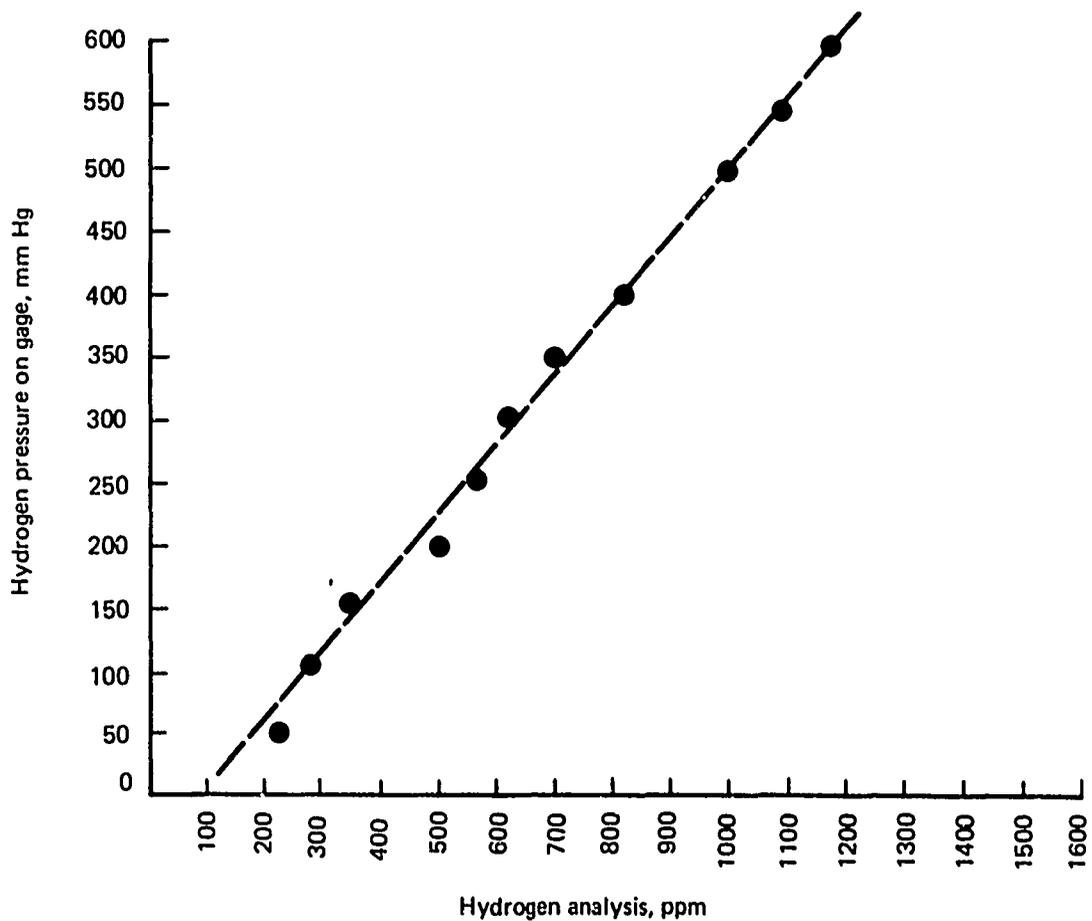


FIGURE 2.—EFFECT OF HYDROGEN CONTENT ON GAGE PRESSURE FOR A CHARPY SPECIMEN

## 2.1.2 Fracture Test Procedures

### 2.1.2.1 Fracture Toughness

The fracture toughness tests will be referred to as  $K_{Ic}$  tests, even though they fail to meet the ASTM validity requirements. This invalidity is true for this section, and particularly true for the precracked Charpy specimens in the delayed-failure section (2.1.2.3).

$K_{Ic}$  fracture toughness tests were conducted on one heat of 0.500-in.-thick Ti-6Al-4V plate having the following chemical composition (weight percent):

Heat	Sheet	Al	O <sub>2</sub>	V	Fe	C	N <sub>2</sub>	H <sub>2</sub>
G2205	8506	5.9	0.110	4.0	0.10	0.023	0.011	0.005

The heat treatments investigated were condition IV (STA 1250°F) and condition I (mill annealed), both with a prior beta anneal as follows:

#### Beta STA 1250°F

1900°F/30 min/air cool

1725°F/30 min/water quench

1250°F/4 hr/air cool

#### Beta mill annealed

1900 F/30 min/air cool

1350°F/2 hr/air cool

Four-point-loaded, notched bend specimens were used to determine  $K_{Ic}$  as shown in figure 3, which gives the specimen configuration and fracture toughness formulas used. The loading rate was 1000 psi/sec. The hydrogen content was varied from 200 to 750 ppm.

### 2.1.2.2 Stress Corrosion

Stress corrosion,  $K_{Isc}$ , tests were conducted using the same specimen configuration, material, and hydrogen content levels as those described in 2.1.2.1. To determine  $K_{Isc}$ , sustained loading was applied to the precracked, notched bend specimens in 3.5% NaCl solution either for 360 min or until failure at a stress intensity,  $K$ , level as calculated from figure 3. Except for series 750HT, which used only two specimens, three specimens were tested at various  $K$  levels and threshold curves were plotted as shown in figure 4. In some cases specimens that did not fail after 360 min were fatigue cracked again and sustained loading applied at higher  $K$  levels to obtain more data. From curves such as those shown in figure 4 the  $K_{Isc}$  threshold level was determined.

Stress intensity factor  $K_{Ic} = P_{DL} \alpha$

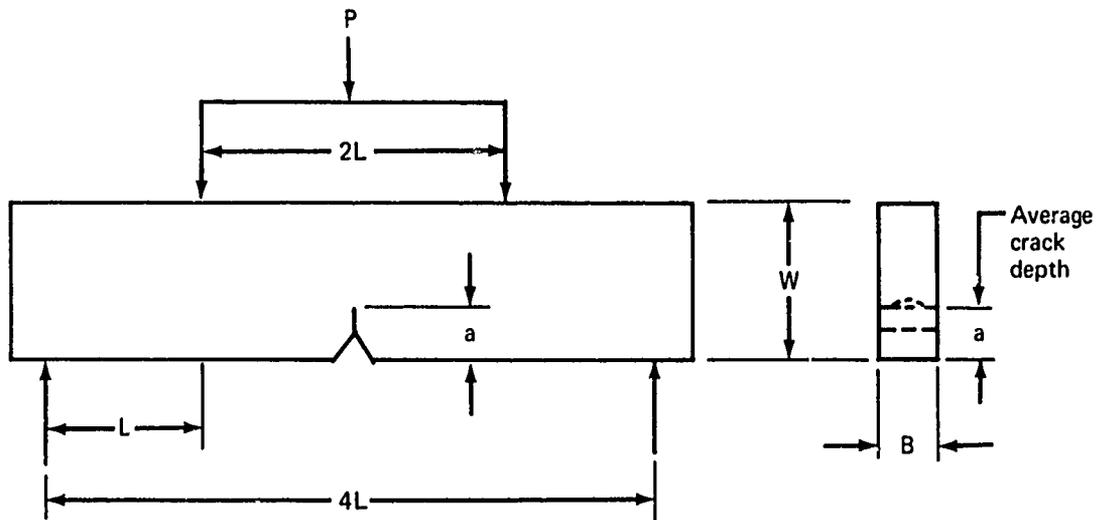
Stress intensity level (environmental)  $K_{Ii} = P$

$$\alpha = \frac{L}{BW^{3/2}} \left[ \left( \frac{1}{1-\mu^2} \right) \left( 34.7 \frac{a}{w} - 55.2 \left( \frac{a}{w} \right)^2 + 196 \left( \frac{a}{w} \right)^3 \right) \right]^{1/2}$$

$P_{DL}$  = load at deviation from linearity—for fracture toughness testing

$P$  = static load—for crack-growth-resistance testing

$$\sigma_N = \text{net area stress} = \frac{M_c}{I}, \text{ where } M = L \frac{P_{DL}}{2} \text{ and } I = \frac{B(w-a)^3}{12}$$



$L = 1.5$  in.  
 $B = 0.480$  in.  
 $w = 1.5$  in.

FIGURE 3.—FOUR-POINT-LOADED, NOTCHED, BEND FRACTURE SPECIMEN FORMULAS

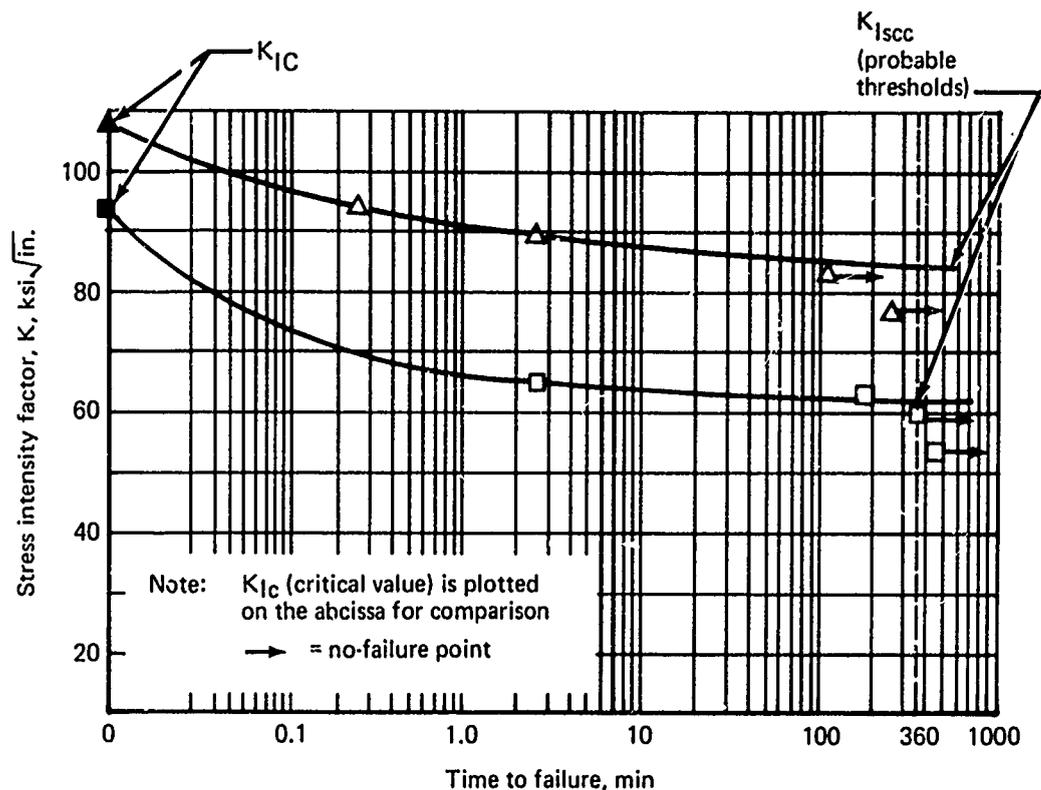


FIGURE 4.—STRESS-CORROSION ( $K_{Isc}$ ) THRESHOLD LEVEL CURVES

### 2.1.2.3 Delayed-Failure Tests

Delayed-failure tests were conducted by sustained loading in room temperature air of precracked specimens charged with various levels of hydrogen. The tests were conducted for either 2500 or 5000 hr or until failure. Two types of specimens were used: the precracked Charpy specimen for Ti-6Al-4V plate and the single-edge-cracked specimen for Ti-6Al-4V sheet. The specimen configuration and formulas are shown in figures 5 and 6, respectively (ref. 3.)

After the specimens were charged with hydrogen, either two or three specimens were failed in air at approximately 1000 psi/sec to obtain a relative fracture toughness value. The remaining specimens were then given sustained loading at either 50%, 75%, or 87% of this predetermined value.

## 2.2 HYDROGEN PICKUP AND OUTGASSING

This section presents the procedures used in evaluating the susceptibility of various mill product forms of Ti-6Al-4V to hydrogen pickup during chemical milling. Also presented are the preliminary general procedures for outgassing Ti-6Al-4V finished or semifinished parts to reduce the hydrogen content to lower levels. Much of the testing and procedure development was being conducted at the time of the SST contract termination and is therefore either preliminary or only partially complete. However, it was felt useful to include even the partially complete programs to emphasize the need and provide the basis for further work.

Stress intensity factor  $K_{Ic} = P_{max}\alpha$

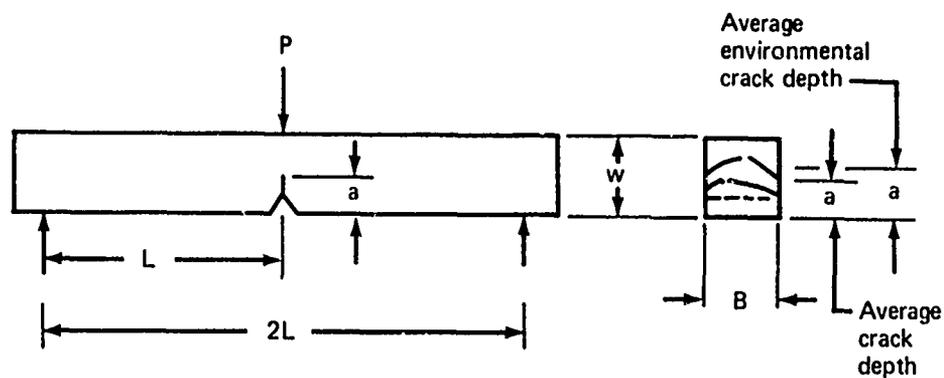
Initial stress intensity level (environmental)  $K_{II} = P\alpha$

$$\alpha = \frac{L}{BW^{3/2}} \left[ \left( \frac{1}{1-\mu^2} \right) \left( 31.7 \frac{a}{w} - 64.8 \left( \frac{a}{w} \right)^2 + 211 \left( \frac{a}{w} \right)^3 \right) \right]^{1/2}$$

$P_{max}$  = ultimate load

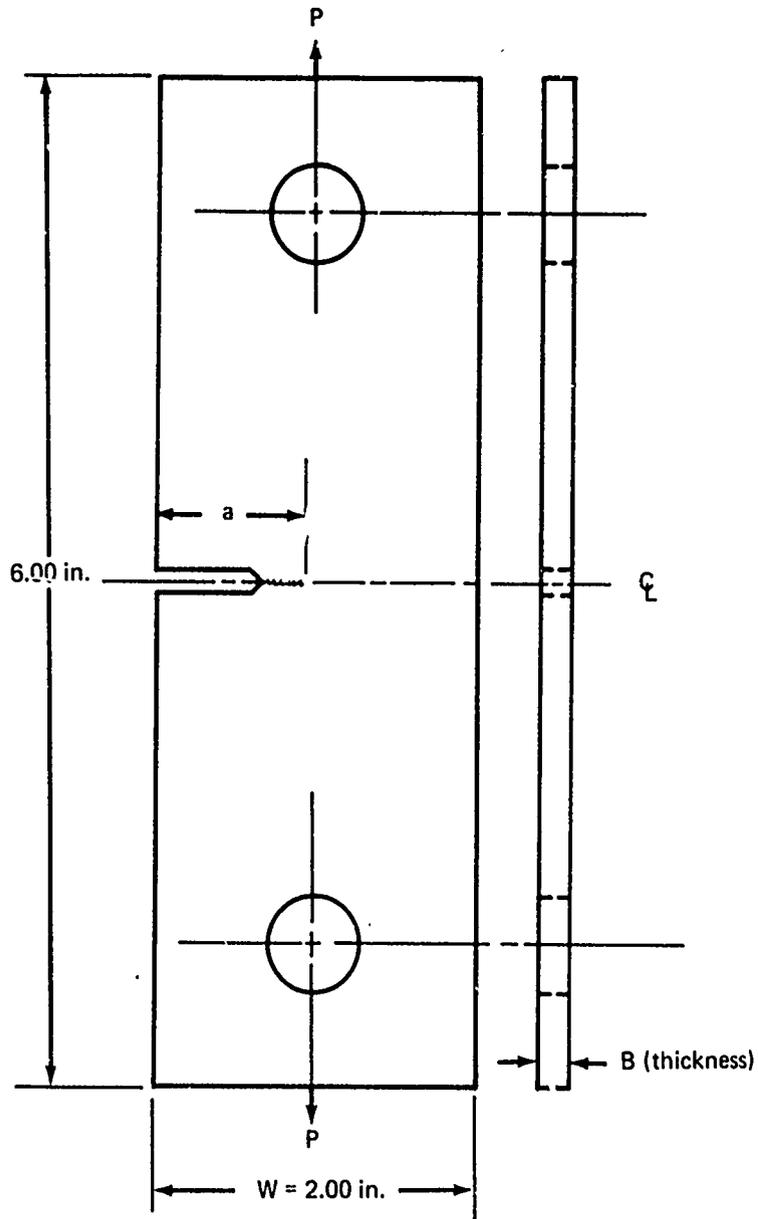
$P$  = static load—for crack-growth-resistance testing

$$\delta N = \text{net area stress} = \frac{M_c}{I}, \text{ where } M = \frac{LP_{max}}{2} \text{ and } I = \frac{(W-a)^3}{12}$$



$L = 0.82$  in.  
 $B = 0.394$  in.  
 $W = 0.394$  in.

FIGURE 5.—PRECRACKED CHARPY DELAYED-FAILURE TESTING SPECIMEN FORMULAS



$$k = \frac{Pa^{1/2}}{Bw} \gamma$$

$$\text{where } \gamma = 1.99 - 0.41\left(\frac{a}{W}\right) + 18.70\left(\frac{a}{W}\right)^2 - 38.48\left(\frac{a}{W}\right)^3 + 53.85\left(\frac{a}{W}\right)^4 \text{ (ref. 3)}$$

FIGURE 6.—SINGLE-EDGE-CRACKED SPECIMEN USED FOR DELAYED-FAILURE TESTING

### 2.2.1 Hydrogen Pickup

The procedures used to analyze the susceptibility of various heats and sheets of Ti-6Al-4V to hydrogen pickup were relatively straightforward. Several heats of material were analyzed for hydrogen using the hot extraction method described in ASTM E146 both after and before chemical milling, the difference being the amount of hydrogen pickup. Care was taken during sampling for hydrogen analysis to ensure that a representative cross section of the material was taken. Several heat treatments were evaluated to determine the effects of various thermal cycles on the hydrogen pickup susceptibility of Ti-6Al-4V. Specimens were heat treated in air for 30 min at various temperatures and either water quenched, furnace cooled at 150°-300° F/hr, or air cooled. The specimens were descaled per the Boeing process specification (ref. 4), and chemically milled 0.005 in. per side before and after hydrogen measurements were taken.

The chemical milling in all cases was accomplished in a low nitric acid-hydrofluoric acid bath. This solution was optimized for Ti-6Al-4V conditions I (mill annealed), III (STA 1000° F), IV (STA 1250° F), and V (duplex annealed) and produced very uniform milling. The details of the chemical milling process are described elsewhere (ref. 5). The detailed requirements of the solution used are listed in table 1.

TABLE 1.—CHEMICAL MILLING SOLUTION REQUIREMENTS

Ingredient or property	Makeup of 100 gal	Control range
Water (initial)	60 gal	—
Nitric acid	0.5 gal	0.060 x dissolved titanium plus 0.2-0.8 oz/gal as HNO <sub>3</sub>
Hydrofluoric acid	4 gal	As required to maintain etch rate
Ammonium bifluoride (optional)	(2 lb)	(0.1-4 oz/gal as NH <sub>4</sub> HF <sub>2</sub> )
Wetting agent	1.0 oz	30-40 dynes/cm at 67°-73° F (33 dynes/cm optimum)
Water	Balance required	—
Dissolved titanium	2 lb	0.3-12 oz/gal as Ti
Etch rate	—	0.0007-0.0011 in./side/min
Temperature	—	90°-130° F (115° F optimum)

### 2.2.2 Hydrogen Outgassing

The outgassing study was a combined manufacturing and engineering program involving the development of a feasible manufacturing process which would not impair the mechanical properties of the titanium being outgassed. The following is a description of the manufacturing procedures developed for outgassing (ref. 6).

The conventional method of reducing hydrogen content is by thermal cycling in a vacuum furnace. However, because Boeing did not have a vacuum furnace of sufficient size to process all flight hardware, alternate means of degassing were required for some items; for example, face skins for brazed panels that are machined, contoured, and chemically milled to final gage. These panels are then ready for brazing, except that they require further processing to remove excess hydrogen. Because brazing is performed in a vacuum within a retort at elevated temperature, it was believed that an assembly similar to the brazing layup could be used as a substitute for a vacuum furnace. A cost advantage could also be gained by using the existing brazing tools (retort, shims, and an integrally heated ceramic fixture) for hydrogen removal.

Degassing tests were performed on Ti-6Al-4V specimens in a vacuum furnace and in small retorts positioned between heated, matched ceramic platens to determine the time-temperature-vacuum relationships required to remove excessive hydrogen.

The small retort tests were intended to verify that hydrogen could be removed without causing indenting from honeycomb core or other physical damage to a thin part. Figure 7 compares the cross section of the retort layup used for degassing tests and the retort layup anticipated for production parts.

One contoured brazed panel face skin (part number 65A21548-7) rejected for excessive hydrogen (more than 500 ppm) was released by the Engineering organization to Manufacturing Research and Development for developmental use. A contoured retort and an integrally heated brazing tool were also available, and evaluation of the retort approach was made from full-scale tests with this face skin and its related brazing tooling.

Titanium specimens for testing in the vacuum furnace and the small retorts were prepared by chemically milling thick sheet to 0.020-0.040-in. to increase their hydrogen content.

Retorts were sealed by welding and leak checked prior to the degassing tests. Purging of the welded retort assembly (fig. 7) was performed during heatup in accordance with XBAC 5967 (ref. 7) and Product Manufacturing and Assembly Manual 6M 64-053 (ref. 8), "Brazing Titanium Honeycomb Sandwich Structure." This procedure consisted of a series of vacuum purges and argon backfills until 800° F was reached. A constant vacuum level of 50 torr was maintained at temperatures above 800° F and during cooldown to 300° F.

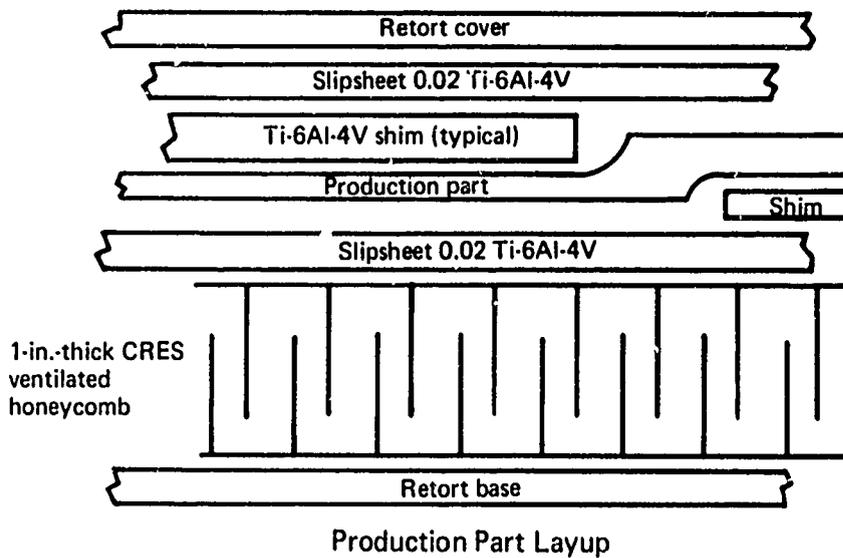
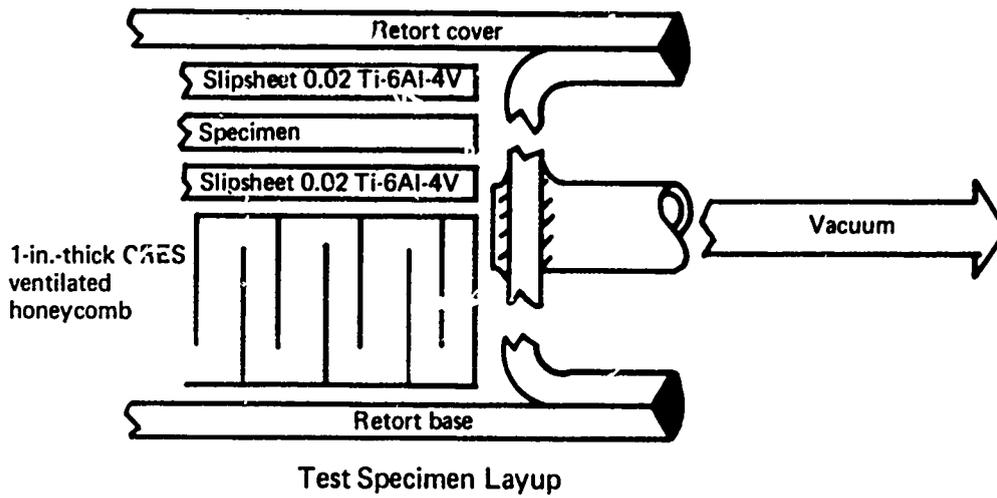


FIGURE 7.—TYPICAL VACUUM RETORT ASSEMBLY FOR ELEVATED-TEMPERATURE HYDROGEN REMOVAL

### 3.0 RESULTS AND DISCUSSION

#### 3.1 FRACTURE PROPERTY EVALUATION

##### 3.1.1 Fracture Toughness and Stress Corrosion

The fracture toughness results are shown in table 2 for hydrogen contents of 200-750 ppm for both beta-mill-annealed and beta-STA 1250°F Ti-6Al-4V. These results are plotted in figures 8 and 9. In general, hydrogen has little effect on the  $K_{Ic}$  of Ti-6Al-4V for either of these heat treatments. There appears to be a slight downward trend with increasing hydrogen content. This trend is somewhat more pronounced for beta-STA 1250°F than for beta-mill-annealed Ti-6Al-4V. However, considering the rather unusual scatter in the data this trend is probably not statistically significant. It is remarkable that even at very high hydrogen contents of 300-750 ppm the  $K_{Ic}$  for Ti-6Al-4V is still greater than 92 ksi√in. for both heat treatments.

TABLE 2.—FRACTURE TOUGHNESS RESULTS FOR Ti-6Al-4V WITH HYDROGEN CONTENTS OF 200 TO 750 PPM

Specimen	Hydrogen content, ppm	$K_{Ic}$ , ksi in.	
		Data	Average
Beta mill annealed			
200-HT 1-1 200-HT 1-2	200	103.7 115.9	109.8
250-HT 1-1 250-HT 1-2	250	108.0 108.2	108.1
300-HT 1-1 300-HT 1-2	300	120.0 108.8	114.4
400-HT 1-1 400-HT 1-2	400	101.8 93.5	97.6
500-HT 1-1 500-HT 1-2	500	99.0 100.8	99.9
750-HT 1-1 750-HT 1-2	750	94.3 109.3	101.8
Beta STA 1250° F			
200-HT 3-1 200-HT 3-2	200	109.5 103.3	106.4
250-HT 3-1 250-HT 3-2	250	109.5 111.2	110.3
300-HT 3-1 300-HT 3-2	300	118.2 105.1	111.6
400-HT 3-2	400	95.4	95.4
500-HT 3-1 500-HT 3-2	500	104.8 102.2	103.5
750-HT 3-1 750-HT 3-2	750	97.9 94.5	96.2

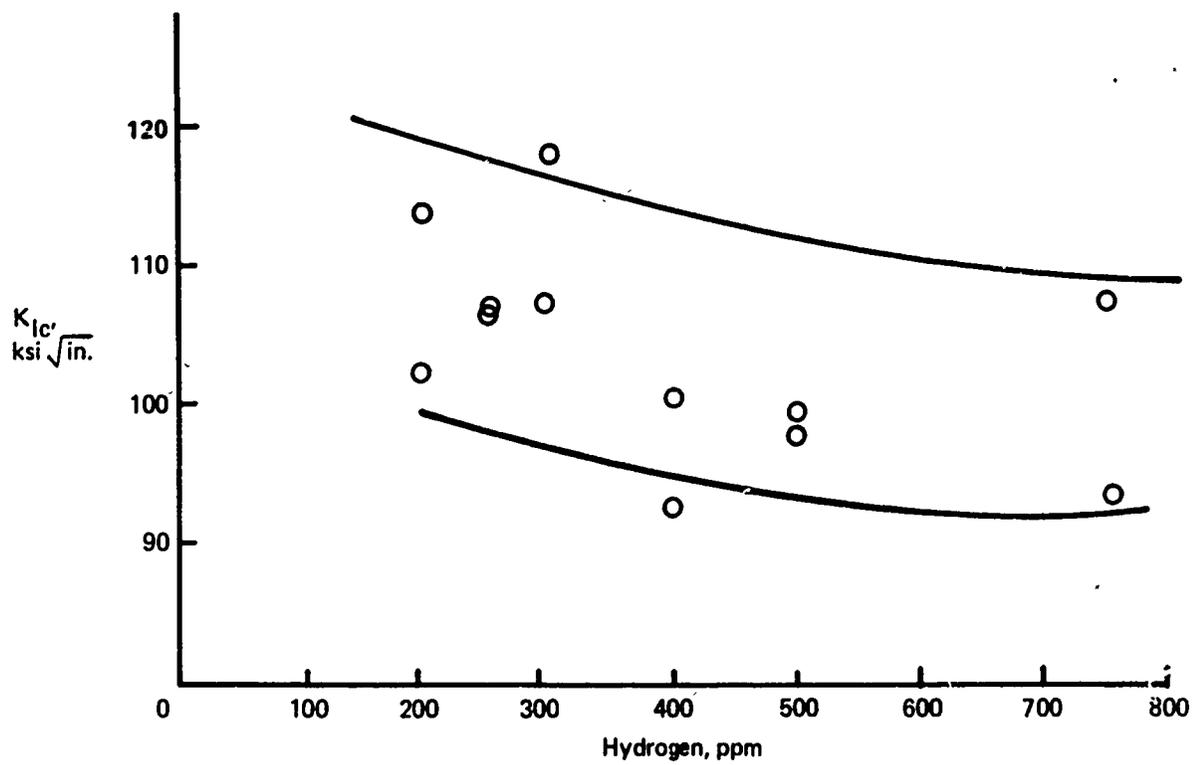


FIGURE 8.—EFFECT OF HYDROGEN ON  $K_{Ic}$  OF BETA-MILL-ANNEALED Ti-6Al-4V

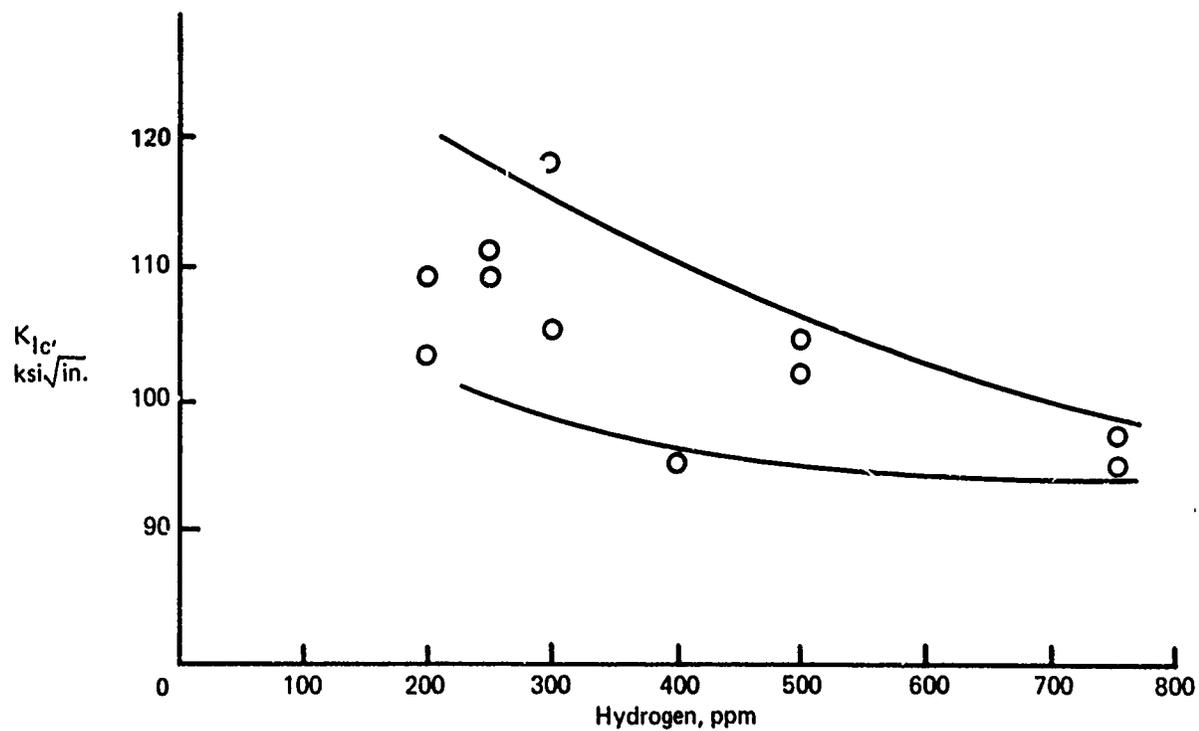


FIGURE 9.—EFFECT OF HYDROGEN ON  $K_{Ic}$  OF BETA-SOLUTION-TREATED AND AGED 1250°F Ti-6Al-4V

The stress-corrosion test results are shown in figures 10 and 11 for beta-mill-annealed and beta-STA 1250° F Ti-6Al-4V, respectively. These data are summarized in table 3 for both these conditions. As with  $K_{IC}$ , hydrogen contents of 200-750 ppm have little effect on  $K_{ISCC}$ . The  $K_{ISCC}$  values are virtually identical for hydrogen levels of 200 ppm and 750 ppm. The relatively high  $K_{ISCC}$  values for all the levels tested is a direct result of the good microstructure (acicular or Widmanstätten) and low oxygen (0.11%) and aluminum (5.9%) contents. Much lower  $K_{ISCC}$  values have been obtained for higher oxygen and aluminum contents and for poorer microstructure (ref. 9), even though the hydrogen contents were less than 125 ppm. There was no difference in hydrogen effects between the two different heat treatments used, since the average ratio of  $K_{ISCC}/K_{IC}$  was 0.75 for both heat treatments.

### 3.1.2 Delayed-Failure Tests

The results of the first series of delayed-failure tests of the Ti-6Al-4V beta-STA 1250° F precracked Charpy specimens are shown in table 4. The hydrogen levels investigated were 125, 135, 190, and 260 ppm, and the time to failure is given as a function of percent of average  $K_{IC}$  baseline. Data are for tests conducted either until failure or until 2500 or 5000 hr had elapsed with no failure. The data are plotted in figure 12 as the effect of hydrogen on delayed-failure times for various K levels expressed as a percent of  $K_{IC}$ . No failures occurred after 2500 or 5000 hr for hydrogen contents of 125 or 135 ppm, at levels of 50% and 75% of baseline  $K_{IC}$ . No failure was observed even at 85% of baseline after 2500 hr. Failures were observed, however, after relatively short times for hydrogen contents of 190 ppm and 265 ppm. The failure time was a direct function of hydrogen content and stress intensity level. For the high hydrogen contents (260 ppm), failures were observed after 80 hr, when specimens were given sustained loading to only 50% of  $K_{IC}$ . For a comparable failure time in the specimens with 190-ppm hydrogen, K levels of 85% of  $K_{IC}$  were required.

It must be recognized that the hydrogen contents reported were those measured on the specimen and are subject to some error. Boeing experience indicates that the accuracy of hydrogen measurement is approximately  $\pm 10\%$ . In this regard, twenty hydrogen measurements were made on the specimens at the end face, the core, the edges of the fracture surface, and the center of the fracture face. The test report is given in appendix A; average values are listed in table 5.

As the measurements show, the correlation was quite good with most of the measurements within  $\pm 10\%$ . The hydrogen content was evenly distributed as expected from charging in the Sievert's apparatus (sec. 2.1.1). The delayed-failure data can be summarized by grouping the hydrogen results into general ranges rather than specific hydrogen values, as shown in table 6.

A second series of delayed-failure tests were conducted using both precracked Charpy and single-edge-cracked specimens. Hydrogen was charged into the specimen using the Sievert's apparatus, as well as in a few specimens by chemical milling. Sustained loading was applied to most of the specimens in room temperature air at either 50% or 75% of baseline  $K_{IC}$ . Four specimens were loaded at 450° F and four other specimens were exposed to 450° F for 2 hr prior to loading at room temperatures. If no failure occurred after 2500 hr the test was discontinued. The material and heat treatment conditions used are listed in table 7.

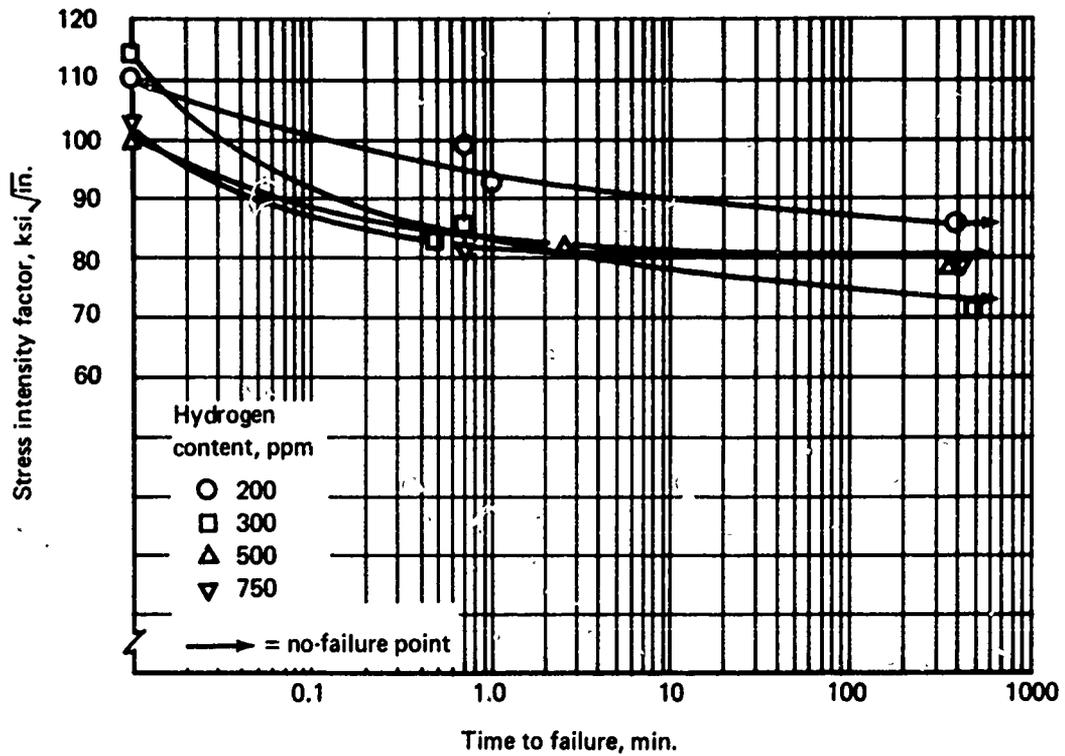


FIGURE 10.—EFFECT OF HYDROGEN ON  $K_{Isc}$  OF BETA-MILL-ANNEALED Ti-6Al-4V

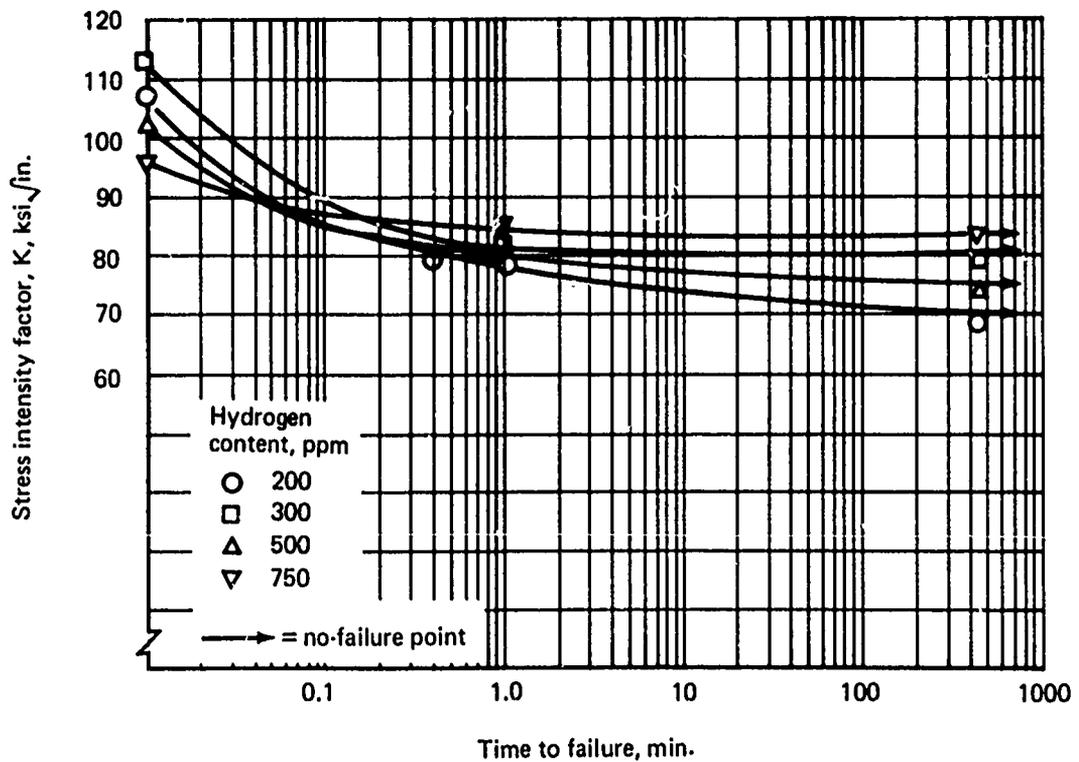


TABLE 3.—EFFECT OF HYDROGEN ON  $K_{Isc}$  OF Ti-6Al-4V

Hydrogen content, ppm	$K_{Isc}$ ksi√in.	Ratio, $\frac{K_{Isc}}{K_{Ic}}$
Beta mill annealed		
200	85	0.78
300	73	0.64
500	80	0.80
750	80	0.79
		Avg 0.75
Beta STA 1250 F		
200	70	0.66
300	80	0.72
500	74	0.72
750	83	0.86
		Avg 0.74

TABLE 4.—HYDROGEN DELAYED-FAILURE TEST RESULTS ON Ti-6Al-4V BETA STA 1250° F

Specimen	Hydrogen content, ppm	Baseline $K_{Ic}$ ksi in.		Delayed failure		
		Data	Avg	K level	K/ $K_{Ic}$	Time to failure, hr <sup>a</sup>
DH-1-1	125	86.2		—	—	—
DH-1-2	125	78.6	82.3	—	—	—
DH-1-3	125	82.3		—	—	—
DH-1-4	125			61.8	0.75	2500 NF
DH-1-5	125			61.8	0.75	2500 NF
DH-1-6	125			61.8	0.75	5000 NF
DH-1-7	125			61.8	0.75	5000 NF
<sup>b</sup> DH-1-4	125			70.8	0.87	2000 NF
<sup>b</sup> DH-1-5	125			70.8	0.87	2300 NF
DH-6-1	135	88.6		—	—	—
DH-6-2	135	83.6	84.6	—	—	—
DH-6-3	135	81.7		—	—	—
DH-6-4	135			63.5	0.75	2500 NF
DH-6-5	135			63.5	0.75	2500 NF
DH-6-6	135			63.5	0.75	5000 NF
DH-6-7	135			63.5	0.75	5000 NF
<sup>b</sup> DH-6-4	135			73.6	0.87	2400 NF
<sup>b</sup> DH-6-5	135			73.6	0.87	2300 NF
<sup>b</sup> DH-6-6	135			73.6	0.87	2800 NF
<sup>b</sup> DH-6-7	135			73.6	0.87	2100 NF
CH-1-1	190	90.4		—	—	—
CH-1-2	190	81.8	87.2	—	—	—
CH-1-3	190	89.5		—	—	—
CH-1-4	190			65.4	0.75	139
CH-1-5	190			43.6	0.50	2360
CH-1-6	190			65.4	0.75	2860 NF
CH-1-7	190			65.4	0.75	188
<sup>b</sup> CH-1-6	190			75.9	0.87	72
DH-7-1	260	83.0		—	—	—
DH-7-2	260	88.9	85.3	—	—	—
DH-7-3	260	83.2		—	—	—
DH-7-4	260			64.0	0.73	30
DH-7-5	260			42.7	0.50	82
DH-7-6	260			64.0	0.75	35
DH-7-7	260			64.0	0.75	40

<sup>a</sup>NF = no failure; test terminated

<sup>b</sup>Retest

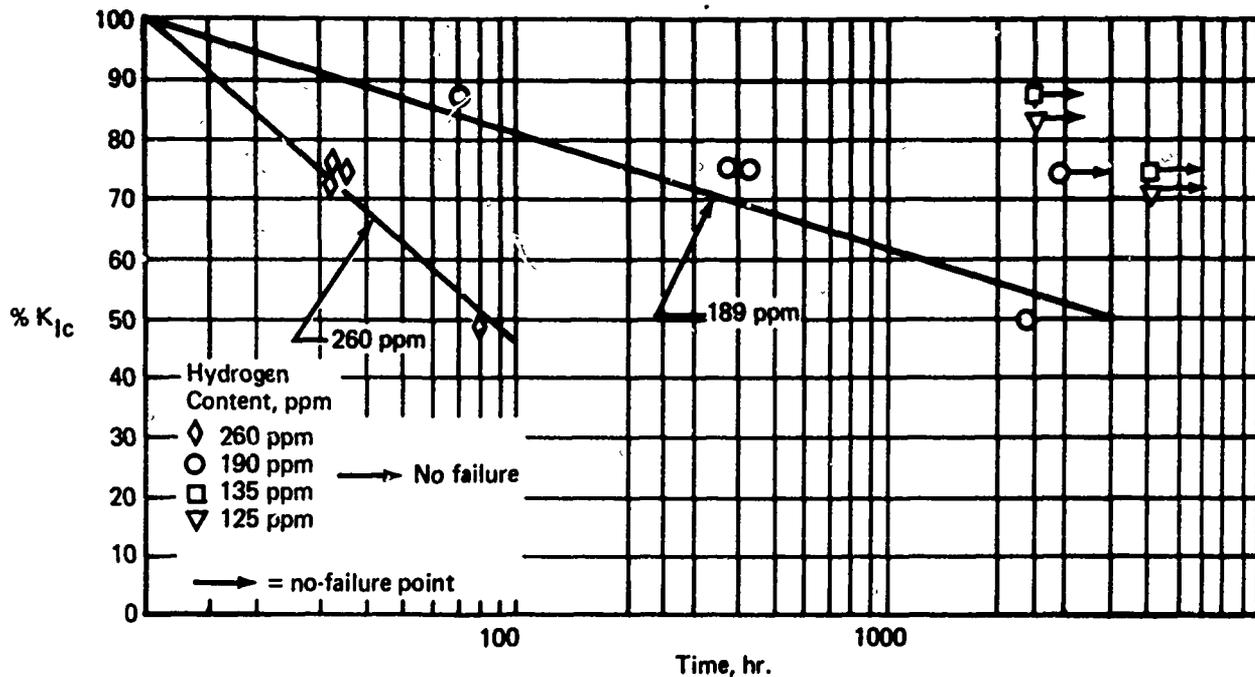


FIGURE 12.—EFFECT OF HYDROGEN ON SUSTAINED-LOAD  $K_{Ic}$  (PRECRACKED CHARPY) OF Ti-6Al-4V BETA STA 1250°F

TABLE 5.—AVERAGE HYDROGEN DELAYED FAILURE TEST VALUES

Sample	Hydrogen content, ppm	
	Content	Range
DH-7	285	276-301
DH-1	113	105-119
DH-6	154	150-157
CH-1	214	211-217

TABLE 6.—DELAYED-FAILURE TEST SUMMARY

Hydrogen content, ppm	Results of delayed failure
110-125	No failure after 2500-5000 hr up to 87% $K_{Ic}$
135-155	No failure after 2500-5000 hr up to 87% $K_{Ic}$
190-215	Failure after 100 hr at 80% $K_{Ic}$
190-215	Failure after 1000 hr at 60% $K_{Ic}$
260-285	Failure after 50 hr at 60% $K_{Ic}$
260-285	Failure after 100 hr at 45% $K_{Ic}$

**TABLE 7.—DELAYED-FAILURE TEST MATERIALS  
AND HEAT TREATMENT CONDITIONS**

Sheet	Specimen	Heat treatment	
13706	Single-edge notched	IC	(continuously annealed) 1800° F/5 min/AC plus 1100° F/5 min/AC
10011	Single-edge notched	I	(mill annealed) 1350° F/4 hr/AC
8506	Charpy	Beta I	(beta mill annealed) 1900° F/30 min/AC plus 1350° F/2 hr/AC
8506	Charpy	III	(STA 1000° F) 1725° F/30 min/WQ plus 1000° F/4 hr/AC

The results of these tests are given in table 8 for the continuously rolled and annealed (condition IC) and mill-annealed (hand mill) sheet material using the single-edge-cracked specimen, and in table 9 for the STA 1000° F and beta-mill-annealed plate material using the pre-cracked Charpy specimen.

There were no failures in any of the single-edge-cracked specimens for either the continuously rolled and annealed or the mill-annealed sheet. This was true for all hydrogen levels from 110 to 250 ppm. In this regard there was no difference between the mill-annealed sheet, which has a nondirectional texture, and the continuously rolled sheet, which has a highly transverse texture. Typical basal plane (0002) pole figures for mill-annealed and continuously rolled Ti-6Al-4V sheet are shown in figures 13 and 14, respectively. Stress corrosion and other fracture properties have been shown (ref. 10) to be related to the preferred orientation of Ti-6Al-4V sheet. However, the transverse nature of the basal planes in relationship to the applied stress on the single-edge-cracked specimens did not result in delayed failure, even with hydrogen levels of 250 ppm. There was also no effect of loading the specimens at 450° F with hydrogen levels of 239-272 ppm, and no failures when the hydrogen was introduced due to chemical milling either with or without a prior 2-hr exposure at 450° F. Although time did not permit the analysis of the actual hydrogen content in the chemically milled specimens, it is estimated that the average or bulk content was 100-150 ppm. The hydrogen due to chemical milling is nonuniform with surface levels much higher than the bulk content.

Failures were obtained in the precracked Charpy specimens for the beta-mill-annealed and the STA 1000° F Ti-6Al-4V plate. For the beta-mill-annealed specimens no failures were observed after 2500 hr at 75% baseline fracture value for 170 ppm hydrogen levels. However, at levels of 205 and 270 ppm H<sub>2</sub>, failures occurred after approximately 250 hr at 75% baseline K level. At 50% of baseline sustained K level, no failures were observed with 205 and 250 ppm H<sub>2</sub>. However, one of the specimens with 250 ppm H<sub>2</sub> (actual measured value of 255 ppm) did fail at 53.7% of baseline after 882 hr. In view of the type of test conducted and the insufficiency of specimens for each test condition, the difference between 50% and 53.7% of baseline is not significant. Hence, it appears that delayed failures do occur under the conditions of 250 ppm and 50% baseline K loading.

**TABLE 8.—DELAYED-FAILURE TEST RESULTS FOR CONTINUOUSLY ANNEALED AND MILL-ANNEALED Ti-6Al-4V SHEET—SINGLE-EDGE-CRACKED SPECIMEN, TRANSVERSE DIRECTION**

Specimen	Hydrogen content, ppm	Heat treatment condition	Baseline, ksi $\sqrt{\text{in.}}$	% of baseline	K level, ksi $\sqrt{\text{in.}}$	Time to failure, hr <sup>a</sup>
1A	Base	IC ↓	101.2	—	—	—
1B	Base		102.6	—	—	—
1C	111		75	76.9	2595 NF	
1D	131		75	76.9	2595 NF	
1E	174		75	76.9	2595 NF	
1F	160		75	76.9	74.5 AF	
1G	223		75	76.9	2595 NF	
1H	220		75	76.9	2596 NF	
1I	216		50	51.3	2596 NF	
1J	195		50	51.3	2596 NF	
1K	270		75	76.9	2596 NF	
1L	243		75	76.9	2596 NF	
1M	256		50	51.3	2688 NF	
1N	230		50	51.3	2688 NF	
1Ob	262		75	76.9	2640 NF	
1Pb	239		75	76.9	2640 NF	
1Ob	270		50	51.3	2640 NF	
1Rb	252		50	51.3	2639 NF	
1S	(c)		75	76.9	2664 NF	
1T	(c)		75	76.9	2424 NF	
1U	(c)		50	51.3	2544 NF	
1V	(c)		50	51.3	2544 NF	
1Wd	(c)		75	76.9	2568 NF	
1Xd	(c)		75	76.9	2568 NF	
1Yd	(c)	50	51.3	2568 NF		
1Zd	(c)	50	51.3	2568 NF		
2A	Base	↓	100.8	—	—	—
2B	Base		100.9	—	—	—
2C	155		75	75.6	2660 NF	
2D	157		75	75.6	2660 NF	
2E	204		75	75.6	2660 NF	
2F	193		75	75.6	2660 NF	
2G	204		50	50.4	2688 NF	
2H	203		50	50.4	2688 NF	
2I	253		75	75.6	2660 NF	
2J	240		75	75.6	2660 NF	
2K	253		50	50.4	2688 NF	
2L	230		50	50.4	2688 NF	

<sup>a</sup>NF = no failure; test terminated

AF = accidental failure

<sup>b</sup>Loaded at 450° F

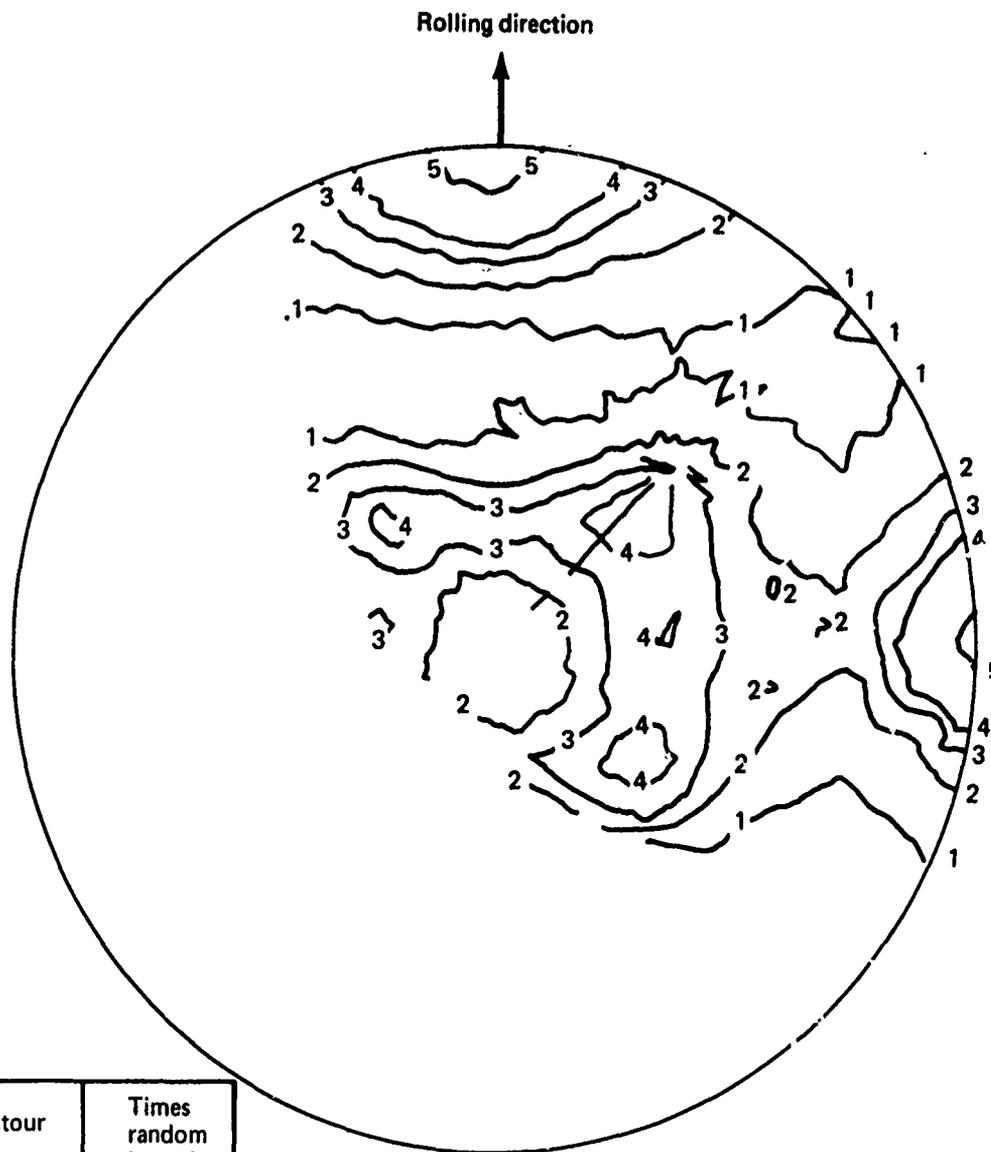
<sup>c</sup>Hydrogen introduced by chemical milling

<sup>d</sup>Exposed at 450° F for 2 hr before loading

**TABLE 9.—DELAYED-FAILURE TEST RESULTS FOR STA 1000° F AND BETA-MILL-ANNEALED Ti-6Al-4V PLATE-PRECRACKED CHARPY SPECIMEN, TRANSVERSE DIRECTION**

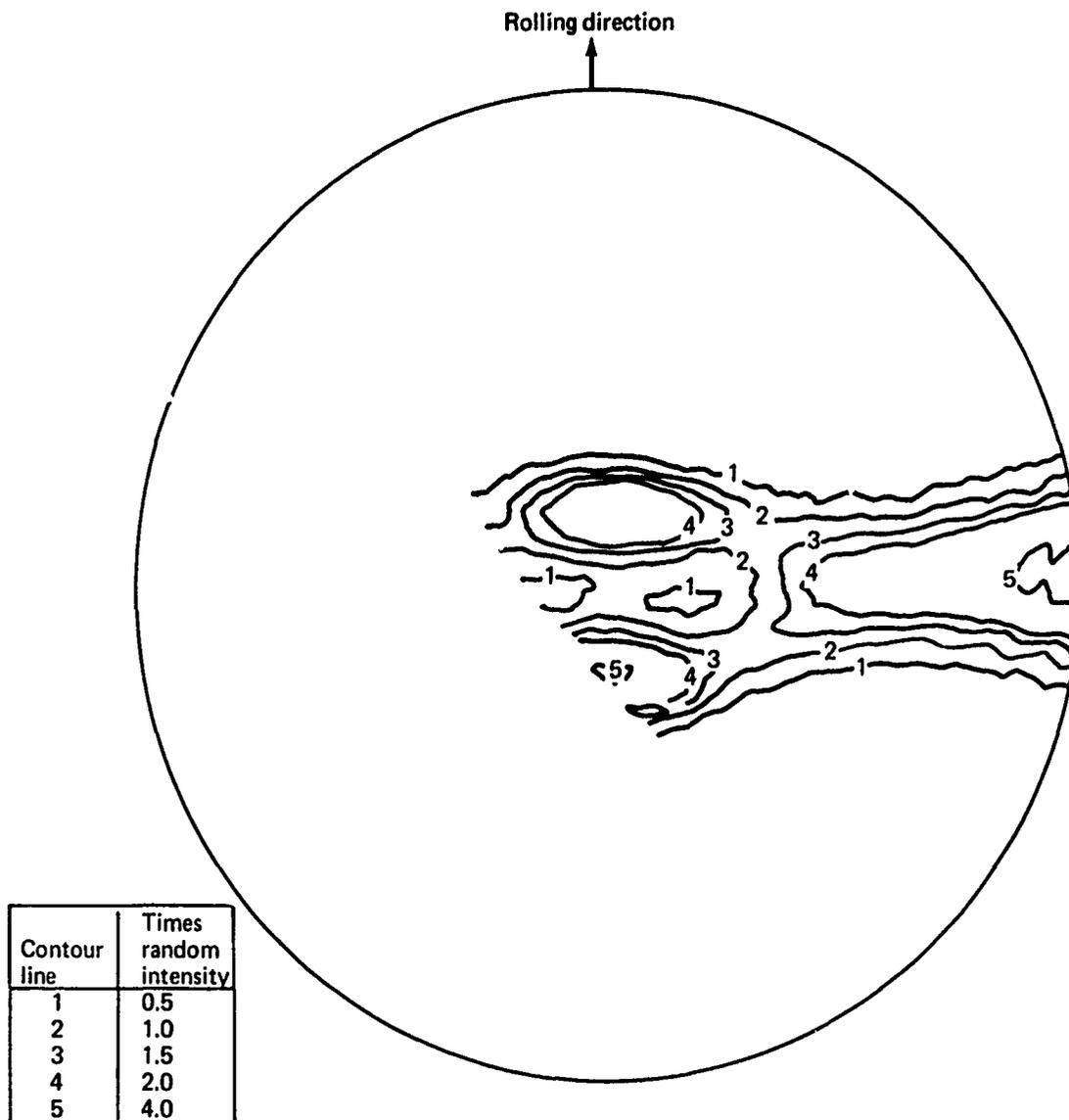
Specimen	Hydrogen treatment condition	Heat content, ppm	Baseline ksi in.	% of base-line	K level, ksi $\sqrt{in.}$	Time to failure, hr <sup>a</sup>
3A	Beta I ↑ ↓	Base	80.39	—	—	—
3B		Base	78.54	—	—	—
3C		174	75	59.6	2570 NF	
3D		163	75	59.6	2570 NF	
3E		205	77.5	61.6	258.5	
3F		205	75	59.6	259	
3G		207	50	39.7	2570 NF	
3H		210	50	39.7	2570 NF	
3I		275	77.5	61.6	402	
3J		263	77.5	61.6	258.3	
3K		254	50	39.7	2570 NF	
3L		255	53.7	42.7	882	
4A	III ↑ ↓	Base	51.0	—	—	—
4B		Base	55.6	—	—	—
4E		158	80	42.6	213.7	
4F		154	78.5	41.8	141.5	
4G		205	82.6	44.1	93	
4H		212	83.1	44.4	93	
4K		245	86.1	45.9	21.5	
4L		250	85.7	45.7	21.5	
4M		274	52.1	27.8	93	
4N		248	52.1	27.8	93	

<sup>a</sup>NF = no failure; test terminated



Contour line	Times random intensity
1	0.5
2	1.0
3	1.5
4	2.0
5	4.0

FIGURE 13.—TYPICAL BASAL PLANE POLE FIGURE FOR MILL-ANNEALED HAND MILL Ti-6Al-4V SHEET



**FIGURE 14.—TYPICAL BASAL PLANE POLE FIGURE FOR CONTINUOUSLY ROLLED AND ANNEALED Ti-6Al-4V SHEET**

In the case of the more notch-sensitive, lower fracture toughness heat treatment condition, STA 1000°F, failures occurred in all specimens with hydrogen contents from 150-275 ppm. At 155 ppm H<sub>2</sub>, failures occurred in an average time of 177 hr at a K level of 80% of baseline and the failure time decreased sharply to 21 hr when the hydrogen was increased to 250 ppm. Figure 15 shows a graph of the effect of hydrogen content on the time to failure for STA 1000°F specimens loaded at approximately 80% baseline K. The actual K level at which the specimens were loaded increased slightly from 79.2% to 85.9% baseline as the hydrogen content increased from 156 to 250 ppm. This K level increase in itself would undoubtedly account for part of the decrease shown in figure 15. However, since the data in the beta-mill-annealed specimen showed this trend, they tend to substantiate that the delayed-failure resistance is reduced as the hydrogen content is increased from 150 to 250 ppm. More data would be required to provide a quantitative relationship.

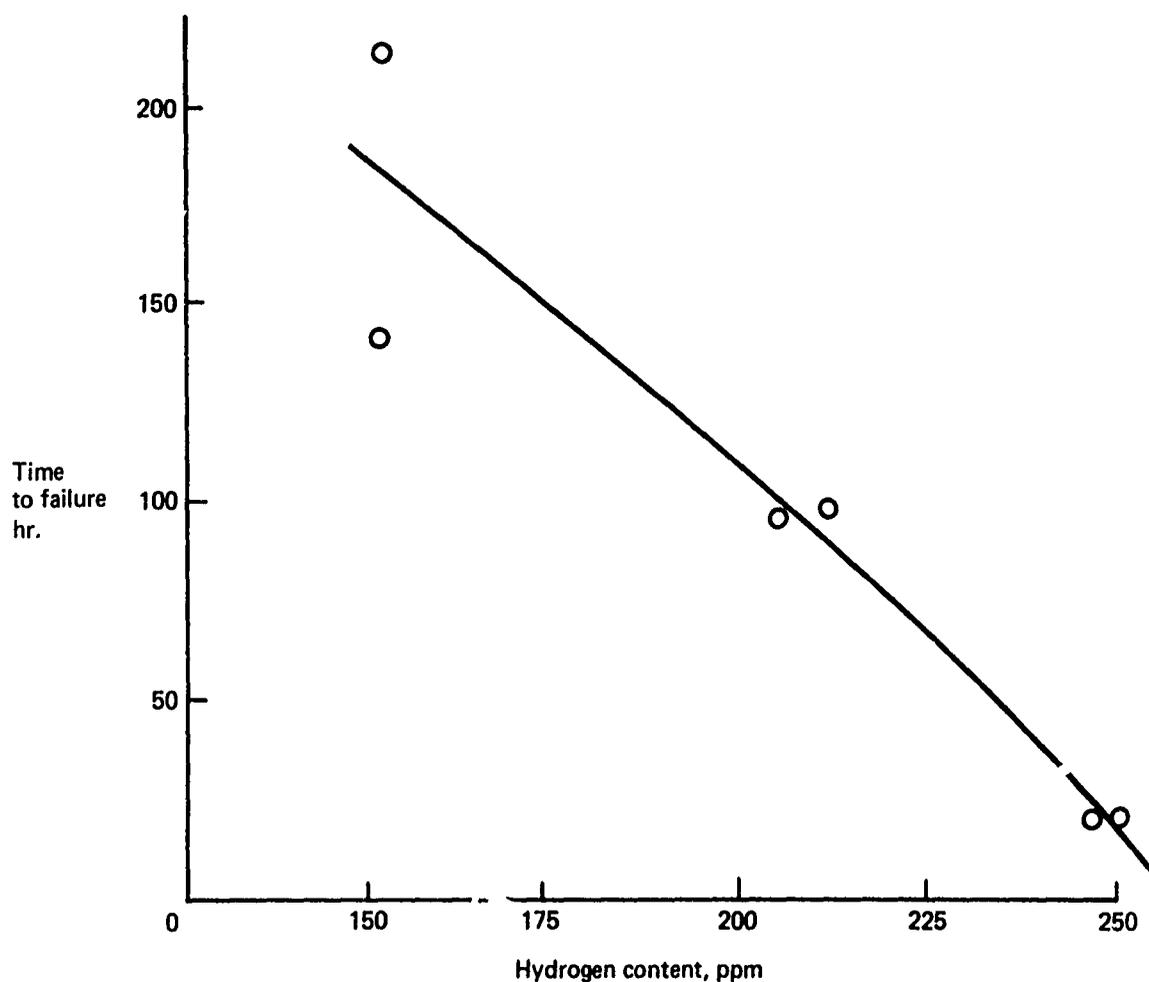


FIGURE 15.—EFFECT OF HYDROGEN CONTENT ON DELAYED FAILURE OF STA 1000°F Ti-6Al-4V PLATE LOADED AT 80% OF BASELINE  $K_{IC}$ —PRECRACKED CHARPY SPECIMEN

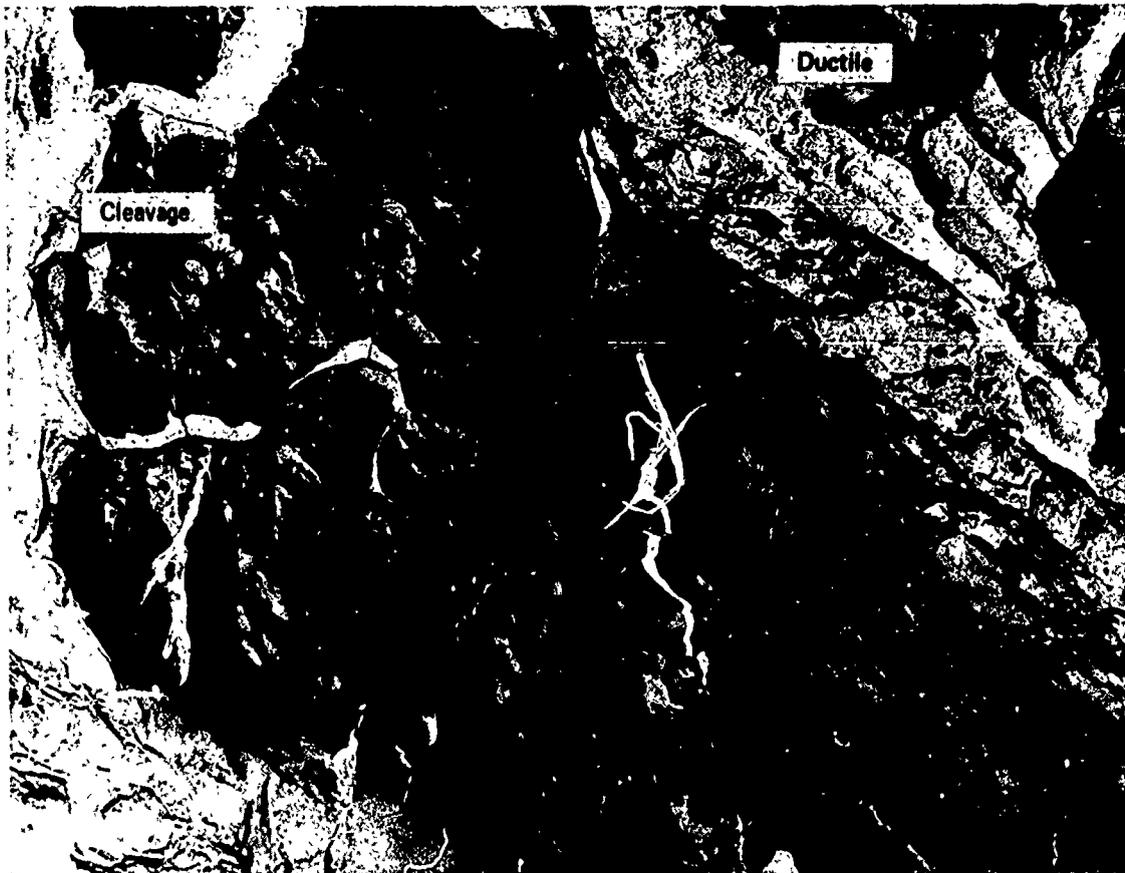
Electron fractographic analysis was conducted on the failed specimens. In general, there seemed to be a weak indication that the fracture appearance was more brittle (more cleavage) as the hydrogen content was increased. However, this was complicated by the fact that as the stress intensity level was increased from 50% to 82% of baseline  $K$ , the fracture appearance was less brittle with more evidence of dimple rupture. Figures 16 through 20 show results of the fractographic investigation for the failed precracked Charpy specimens. Areas of brittle appearance were always present on all failed specimens.

It must be pointed out that all the failures observed were in precracked Charpy specimens in which plane strain is approached. In any case, triaxiality of the stress field is much more severe in these cases than for the thinner sheet, single-edge-cracked specimens where no failures were observed. Although no tests were conducted using the two different specimens and the same material heat treatment condition, it is safe to conclude that the tolerance for hydrogen is much higher in thin material (0.050 in.) than in thicker material (0.400 in.)



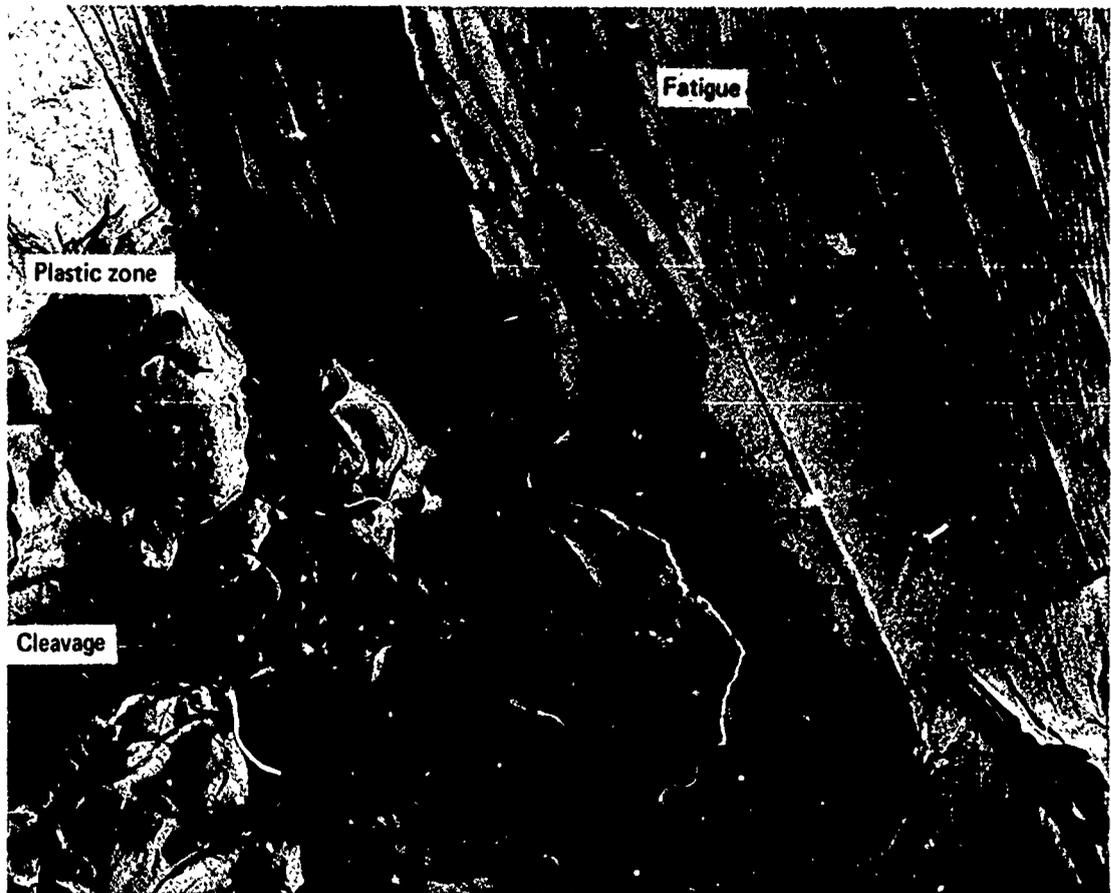
Magnification	X 3500
Specimen	CH-7
Hydrogen content	190 ppm
K level	75% $K_{Ic}$
Failure time	188 hr

**FIGURE 16.—FRACTURE SURFACE OF BETA STA 1250°F Ti-6Al-4V SHOWING CLEAVAGE AREAS**



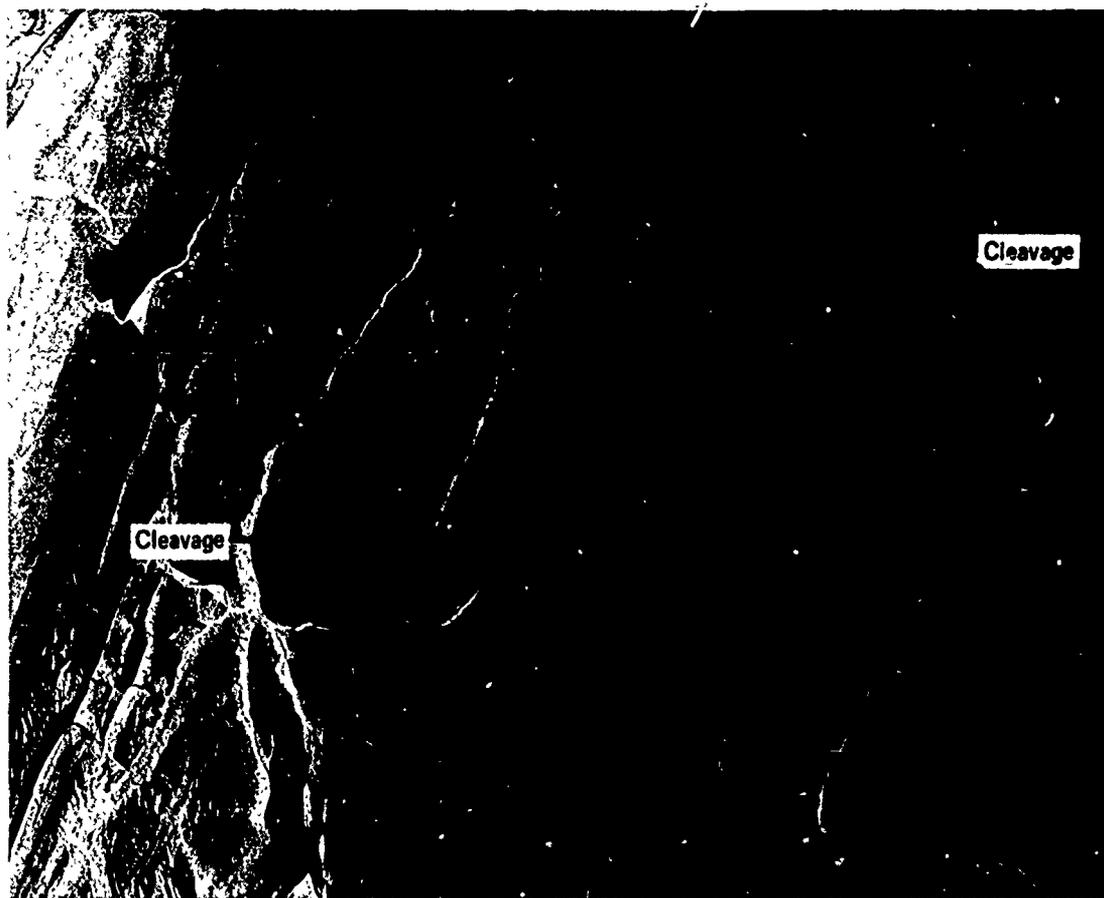
Magnification	X 3950
Specimen	DH 7-7
Hydrogen content	260 ppm
K level	75% baseline
Failure time	40 hr

**FIGURE 17.—FRACTURE SURFACE OF BETA STA 1250°F Ti-6Al-4V SHOWING MIXED CLEAVAGE AND DUCTILE AREAS**



Magnification	X 4830
Specimen	3I
Hydrogen content	275 ppm
K level	77% $K_{Ic}$
Failure time	402 hr

**FIGURE 18.—FRACTURE SURFACE OF BETA-MILL-ANNEALED Ti-6Al-4V SHOWING FATIGUE PRECRACKING, PLASTIC ZONE, AND CLEAVAGE AREAS**



Magnification X 4830  
Specimen 3I  
Hydrogen content 275 ppm  
K level 77%  $K_{Ic}$   
Failure time 402 hr

**FIGURE 19.—FRACTURE SURFACES OF BETA-MILL-ANNEALED Ti-6Al-4V SHOWING LARGE CLEAVAGE AREAS**



Magnification	X 4830
Specimen	3J
Hydrogen content	263 ppm
K <sub>I</sub> level	77% K <sub>Ic</sub>
Failure time	258 hr

**FIGURE 20.—FRACTURE SURFACE OF BETA-MILL-ANNEALED Ti-6Al-4V SHOWING MASSIVE CLEAVAGE AREAS**

### 3.2 HYDROGEN PICKUP AND OUTGASSING

Many of the hydrogen pickup studies were conducted in 1971 just prior to the SST contract termination date and some were not completed. However, it is felt that it would be useful to document all of the programs under way at contract cancellation even though in some cases more problems than solutions are presented.

#### 3.2.1 Hydrogen Pickup

Most of the earlier work at Boeing was conducted on the effect of chemical milling procedures on hydrogen pickup in titanium. This centered around chemical milling solution variables such as composition, temperature, presence of agitation, etc. The procedure developed as described in section 2.2.1 resulted in an optimum combination of low hydrogen pickup and excellent milling properties such as rapid consistent etch rate, equal rates for horizontal and vertical surfaces, and dimensional tolerances of approximately  $\pm 0.002$  in. This procedure also resulted in a maximum pickup of 20 ppm of hydrogen or less during chemical milling. In fact, one of the required tests for qualifying to produce chemically milled parts per this procedure was that the maximum hydrogen pickup be 20 ppm.

Jacobson (ref. 11) evaluated the effect of various thermal cycles on the susceptibility of Ti-6Al-4V to hydrogen pickup during chemical milling. Ti-6Al-4V mill-annealed sheet 0.040 in. thick was exposed to temperatures from 1350°-1900° F and either air cooled, water quenched, or furnace cooled at 150°-300° F/hr. The material used is described in table 10.

The specimens were heated in air for 30 min, cooled, descaled (ref. 4), and chemically milled (ref. 5) to remove 0.005 in. per side. The hydrogen pickup was measured as the difference between the as-heat-treated and the as-chemically-milled values. The data are presented in figure 21. The hydrogen pickup values were adjusted by multiplying the actual values obtained by dividing the final gage in inches by 0.040 inch to compensate for the thickness effect in measuring hydrogen. Since most final thicknesses were approximately 0.030 in., this amounted to a 25% reduction in the actual values obtained.

TABLE 10.—THERMAL CYCLE TEST MATERIALS

Heat	Sheet	Chemical composition, %						
		Al	V	O <sub>2</sub>	H <sub>2</sub>	Fe	C	N
G1768	8096	6.0	4.1	0.11	0.007	0.09	0.025	0.011
Grain direction		TUS, ksi		TYS, ksi			Elong, %	
Transverse		141.9 ksi		134.6 ksi			13	

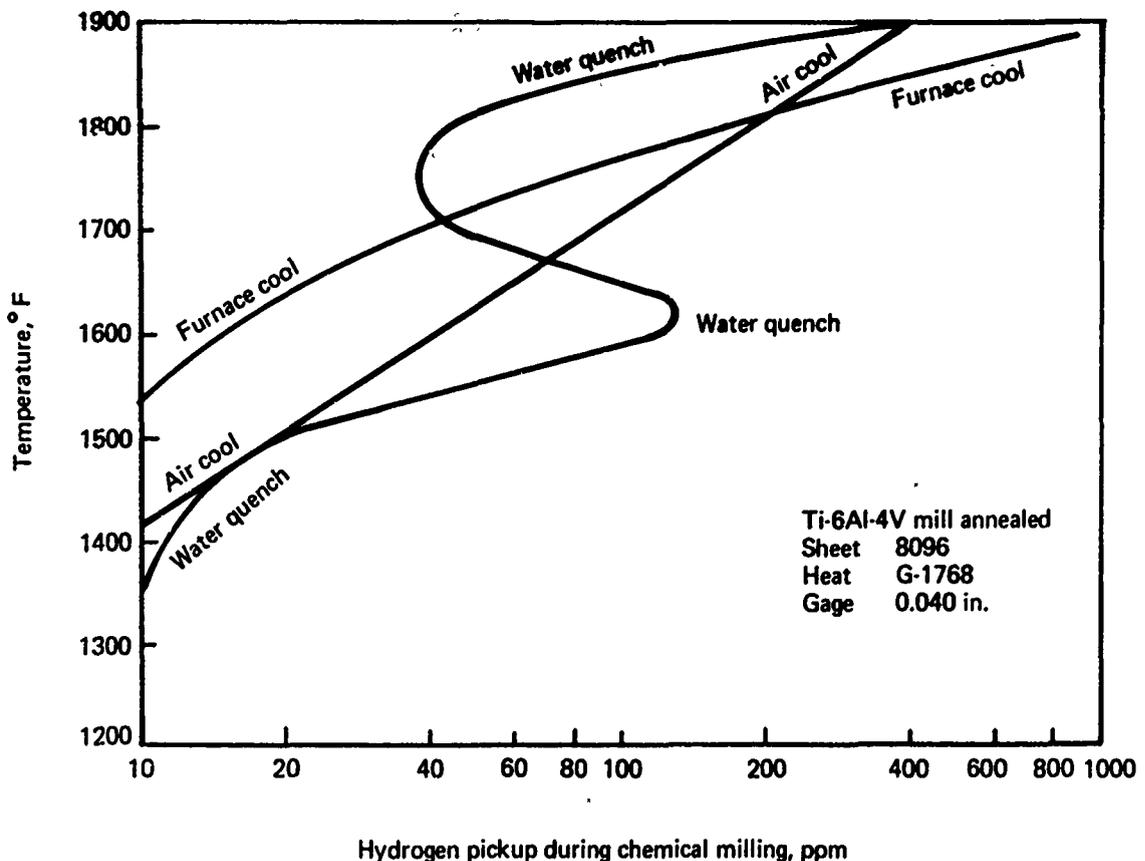


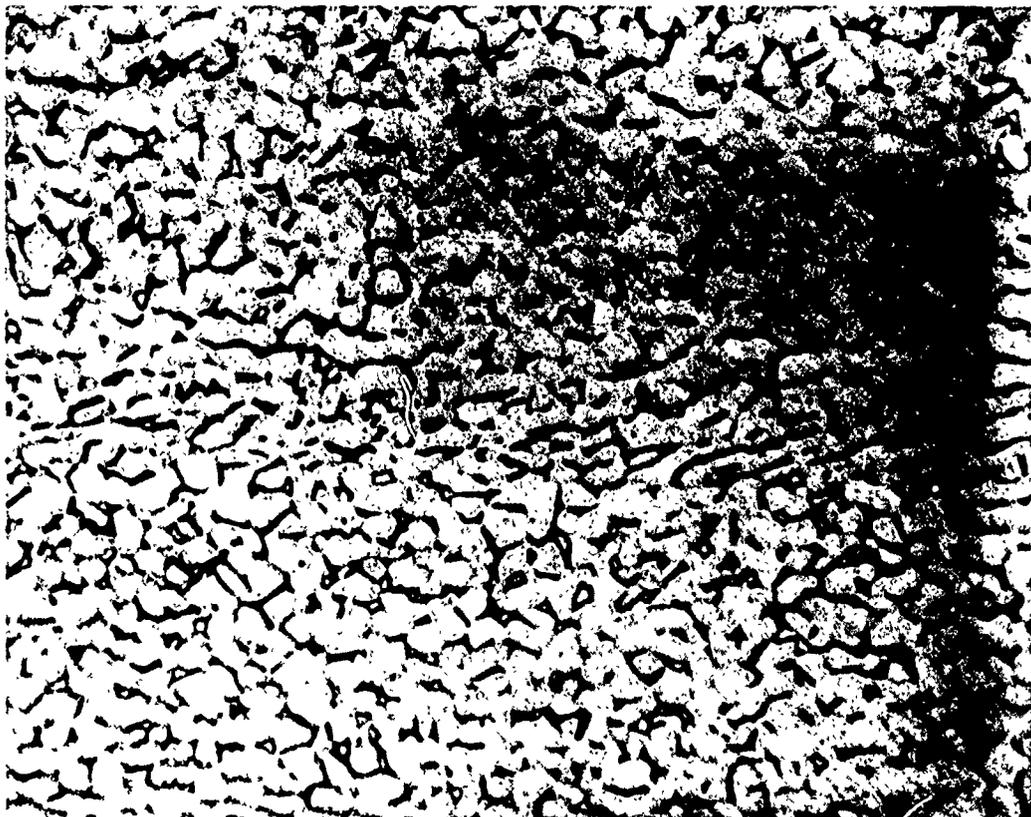
FIGURE 21.—EFFECT OF PRIOR THERMAL CYCLES ON THE SUSCEPTIBILITY OF Ti-6Al-4V TO HYDROGEN PICKUP DUE TO CHEMICAL MILLING (REF. 10)

The curves shown in figure 21 can be explained microstructurally. Since the diffusion rates and solubility of hydrogen in beta titanium (body-centered cubic, bcc) are much larger than those of alpha (hexagonal close-packed, hcp) titanium, the amount of hydrogen pickup during chemical milling will be related to the distribution of retained beta (beta phase at room temperature) in the Ti-6Al-4V being chemically milled. The distribution of retained beta in a transformed beta or Widmanstatten microstructure is very continuous with the beta phase outlining the alpha platelets (fig. 22a). This microstructure would allow hydrogen solution into the beta phase and diffusion throughout the material along the continuous beta network. Figure 22b shows an equiaxed alpha-plus-beta morphology obtained either by working the material below the beta transus to temperatures of approximately 1300°-1400° F or by alpha-beta working at higher temperatures (1600°-1700° F) and slow cooling. During the slow cooling (i.e., furnace cooling) the beta at temperature (50% beta at 1650° F) transforms as the material cools, but rather than forming a Widmanstatten structure as in figure 22a the equiaxed alpha particles grow as the percentage of beta decreases. As a result, the beta phase is concentrated at isolated triple points between equiaxed alpha grain boundaries and does not allow a continuous hydrogen diffusion path. If material is air cooled from 1650°-1750° F, the



*(a) Air Cooled From Above the Beta Transus (1900°F)*

500x



*(b) Slow Cooled From Below the Beta Transus (1725°F)*

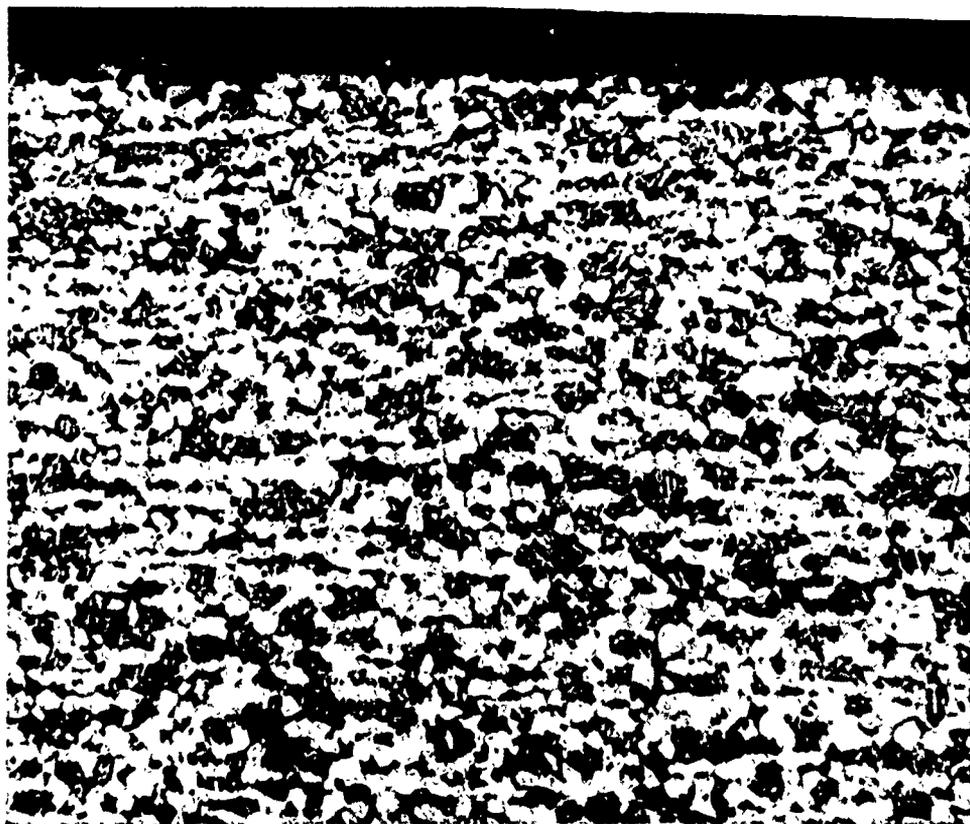
500x

**FIGURE 22.—MICROSTRUCTURES OF Ti-6Al-4V AIR COOLED AND SLOW COOLED FROM ABOVE AND BELOW THE BETA TRANSUS (X 500)**



*(c) Slow Cooled From Above the Beta Transus (1900°F)*

500x



*(d) Air Cooled From Below the Beta Transus (1725°F)*

500x

**FIGURE 22.—Concluded**

50%-70% beta at temperature transforms rapidly to a Widmanstatten structure since the equiaxed alpha does not have time to grow. A mixed or duplex structure results as shown in figure 22d. Figure 22c shows the microstructure of a material furnace cooled from 1900°F. Here the unworked alpha platelets retain their acicular shape but are much larger than material air cooled from above the beta transus. This explains the tendency for the air cooled material to pick up more hydrogen than the furnace-cooled material for a given temperature as shown in figure 21. In the former the beta phase is much more continuous, allowing for more rapid hydrogen diffusion along these beta paths. Also, the tendency for the totally transformed structures (figs. 22a and 22c) to pick up more hydrogen is explained in this manner. This totally transformed structure is present in any of the materials with a prior beta cycle (1900°F/30 min/air cool).

The water-quenched data in figure 21 appear to have an anomalous peak at approximately 1625°F where much more hydrogen (125 ppm) is picked up compared to both lower and higher temperatures (40-60 ppm). Originally it was felt that quenching from approximately this temperature would result in the maximum retention of the beta phase at room temperature. Below this temperature there is less beta phase at temperature and as a result less beta is retained at room temperature. Above this temperature alpha prime or martensite forms upon quenching and less beta is retained. The alpha prime has a hexagonal-type crystal structure, and although no data for the solubility of hydrogen in this phase have been found, it is likely that the solubility would be similar to the hexagonal alpha phase. At least it is probable that its solubility for hydrogen is less than that of the bcc beta phase. If so, this explains the reduced hydrogen pickup in material water quenched from above 1625°F. Recent preliminary tests have indicated that the amount of retained beta at room temperature is only slightly higher at this temperature, approximately 5% compared to approximately 4% at other temperatures. More work is required in this area, especially with respect to hydrogen content.

There is some question as to the applicability of the data at the very high temperatures. The specimens were heat treated in air with 0.005 in. chemically milled from each surface. This amount, however, is not sufficient to remove all of the contaminated layer. Figure 23 shows an oxygen gradient for Ti-6Al-4V after exposure to 1900°F. The data were developed using an electron microprobe with a special light element attachment (ref. 12) and show the probability of oxygen contamination of 0.15%-0.50% on the outer 0.005 in. of the specimens. Preliminary work (ref. 13) has indicated that oxygen contamination has tended to increase the hydrogen pickup and thus could exaggerate the hydrogen pickup effect at these temperatures. The 0.005-in. removal will be sufficient for all temperatures below 1750°F.

Table 11 shows the comprehensive results of a hydrogen pickup evaluation (ref. 14) on Ti-6Al-4V for conditions I (mill annealed), V (duplex annealed), and IC (continuously annealed) sheet. Beta processed plate (either beta rolled or beta annealed) is also shown. The basic evaluations are given elsewhere for the plate (ref. 9) and the sheet (ref. 10). The results are given for a HNO<sub>3</sub> etch as well as for chemical milling (ref. 5). The sheet data are quite consistent with past data listed in table 12 indicating the average hydrogen pickup due to chemical milling.

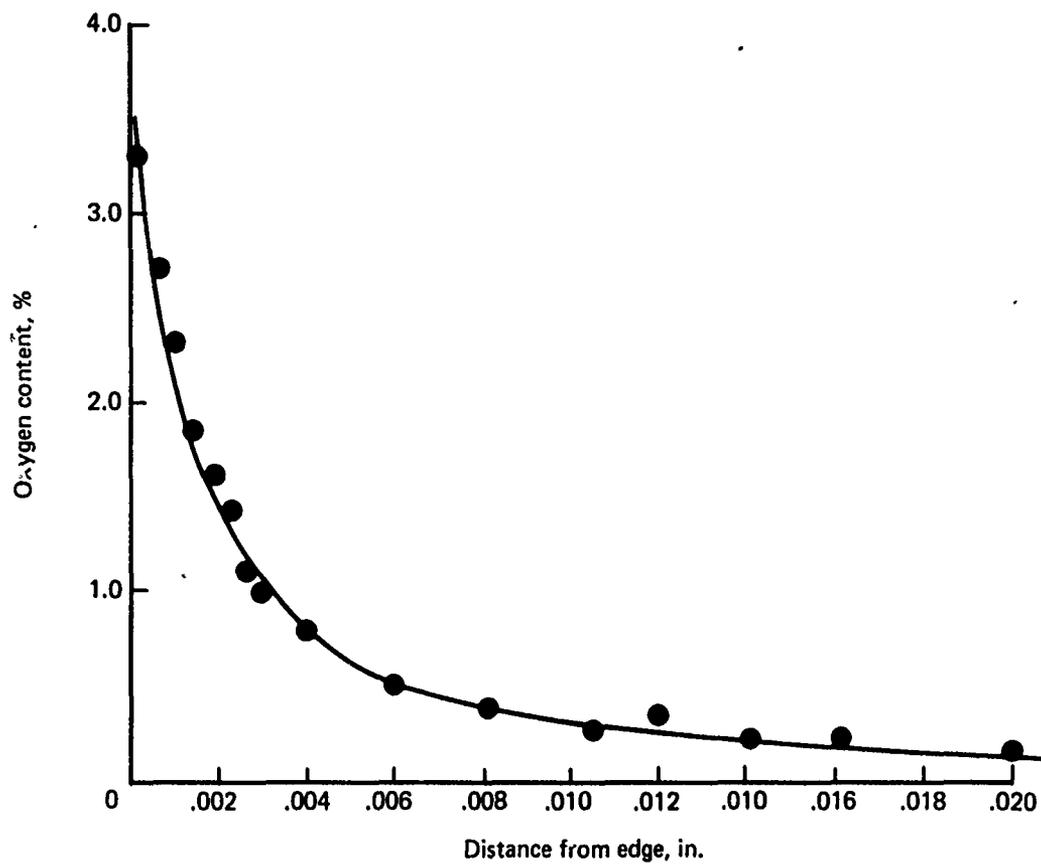


FIGURE 23.—OXYGEN GRADIENT IN Ti-6Al-4V AFTER EXPOSURE TO AIR AT 1800°F FOR 2 HR

TABLE 11.—HYDROGEN PICKUP OF Ti-6Al-4V SHEET AND PLATE DURING ETCH CLEANING AND CHEMICAL MILLING (REF. 14)

Sample	Vendor	Form	Condi- tion	Heat	Initial gage, in.	As received H <sub>2</sub>	Method 2 clean/etch		Solution 2 chemical mill	
							Total H <sub>2</sub>	ΔH <sub>2</sub>	Total H <sub>2</sub>	ΔH <sub>2</sub>
20017	RMI	Sheet	V	295393	0.095	77	69	-10	107	+30
20276	RMI	Sheet	V	295414	0.10	61	58	0	82	+20
20370	RMI	Sheet	V	295429	0.108	52	51	0	52	0
20458	RMI	Sheet	V	295451	0.18	56	78	+20	82	+20
20491	RMI	Sheet	V	295440	0.06	35	39	0	47	+10
69364	RMI	Sheet	V	295372	0.09	41	40	0	50	+10
69884	RMI	Sheet	V	295394	0.053	56	51	0	58	0
69956	RMI	Sheet	V	295407	0.18	36	34	0	52	+20
FM939	RMI	Sheet	V	310487	0.15/0.16	3114	96	-20	215/188	+100
FM935	RMI	Sheet	3Al-2.5V annealed	295456	0.040	—	65	—	73	+10
955563	Lawrence Aviation	Sheet	V	303752	0.048	—	78	—	74	0
20930	RMI	Sheet	V	295429	0.057	—	31	—	30	0
69954	RMI	Sheet	V	295407	0.12	—	74	—	85	+10
20293	RMI	Sheet	V	295429	0.12	—	39	—	51	+10
20240	TMCA	Sheet	V	K6835	0.18	—	66	—	66	0
20068	TMCA	Sheet	V	K6011	0.18	—	68	—	88	+20
20032	TMCA	Sheet	V	K6036	0.18	—	69	—	75	+10
12042	TMCA	Sheet	IC	G7637	0.051	—	41	—	100	+60
G7445	TMCA	Sheet	IC	G7445	0.063	—	32	—	64	+30
G6265	TMCA	Sheet	IC	G6265	0.051	—	44	—	85	+40
20471	RMI	Sheet	I	295406	0.14	—	40	—	40	0
FM591	RMI	Sheet	I	301755	0.045	—	52	—	49	0
FM963	RMI	Sheet	I	295364	0.07	—	22	—	28	+10
20471V	RMI	Sheet	I → V	295406	0.14	40	43	0	77	+30
FM591V	RMI	Sheet	I → V	301755	0.07	52	59	+10	78	+20
FM963V	RMI	Sheet	I → V	295364	0.14	22	28	+10	58	+30
A4	RMI	Plate	Beta rolled	295304	1.25	44	43	0	97	+50
A4B	RMI	Plate	Beta annealed	295304	1.25	52	60	+10	129	+80
A3B	RMI	Plate	Beta annealed	295304	1.25	56	58	0	132	+80
E4	RMI	Plate	Beta rolled	295074	1.15	82	82/80	0	213/217	+130
E4B	RMI	Plate	Beta annealed	295074	1.15	84	73/74	-10	286/229	+170
E3B	RMI	Plate	Beta annealed	295074	1.15	63	69	+10	192	+130
G4	RMI	Plate	Beta rolled	295291	0.45	86	88/83	0	159/155	+70
G4B	RMI	Plate	Beta annealed	295291	0.45	95	87/91	-10	112/122	+20
K3	RMI	Plate	Beta rolled	303963	0.27	58	57	0	82	+20
K3B	RMI	Plate	Beta annealed	303963	0.27	57	61	0	86	+30
Q4	TMCA	Plate	Beta rolled	K3236	0.65	90	92	0	121	+30
R3	TMCA	Plate	Beta rolled	K7335	0.65	82	83	0	116	+30
R3B	TMCA	Plate	Beta annealed	K7335	0.65	80	88	+10	126	+50
R4B	TMCA	Plate	Beta annealed	K7335	0.65	88	91	0	138	+50

TABLE 11.—Concluded

Sample	Vendor	Form	Condi- tion	Heat	Initial gage, in.	As received H <sub>2</sub>	Method 2 clean/etch		Solution 2 chemical mill	
							Total H <sub>2</sub>	H <sub>2</sub>	Total H <sub>2</sub>	H <sub>2</sub>
T4	TMCA	Plate	Beta rolled	K6020	0.35	93	96/99	0	119/123	+30
T4B	TMCA	Plate	Beta annealed	K6020	0.35	100	108/97	0	131/117	+20
U4	TMCA	Plate	Beta rolled	K5940	0.34	89	108/93	+10	114/99	+20
U4B	TMCA	Plate	Beta annealed	K5940	0.34	103	100/113	0	126/137	+30
V4	TMCA	Plate	Beta rolled	K6029	0.30	110	109/96	-10	110/102	0
V4B	TMCA	Plate	Beta annealed	K6029	0.30	91	100/109	+10	150/153	+60
X4	TMCA	Plate	Beta rolled	K5816	1.00	96	87/94	-10	111/118	+20
X4B	TMCA	Plate	Beta annealed	K5816	1.00	77	83/73	0	164/156	+60

TABLE 12.—CHEMICAL MILLING HYDROGEN PICKUP

Heat treatment condition	Heat treatment	Microstructure	Hydrogen pickup, ppm
I (sheet)	Mill annealed 1350°-1450° F/2-4 hr/air cooled	Equiaxed primary alpha plus isolated beta	10
V (sheet)	Duplex annealed 1725° F/15 min/air cooled plus 1250° F/4 hr/air cooled	Equiaxed primary alpha plus equal amounts of transformed beta	30
IC (sheet)	Continuously annealed 1600° F/5 min/air cooled 1100° F/5 min/air cooled	Equiaxed and elongated primary alpha plus equal amounts of transformed beta	50

The lower incidence of hydrogen pickup in condition I Ti-6Al-4V appears to be related to the lack of continuity of the beta phase in this condition. It has been stated previously that concentrated beta at the grain boundary triple points results in a lack of a diffusion path for the hydrogen and a low amount of hydrogen pickup during chemical milling. Both conditions V and IC have a 50% transformed beta or acicular alpha-plus-beta and provide diffusion paths for hydrogen. This also explains the high (average 84 ppm) hydrogen pickup for Ti-6Al-4V beta-annealed plate. There may also be a texture effect, since continuously rolled sheet has a

more transverse texture (fig. 14) than mill-annealed sheet conditions I or V (fig. 13). This effect is also noted in sheet specimen FM 939, heat 310487 in table 11 where an extremely large amount of hydrogen pickup (100 ppm) was observed. This, coupled with the nominally high hydrogen content in the as-received condition, resulted in a very high and unsatisfactory level of 200 ppm after chemical milling. Very recent work has shown that the percentage of retained beta on this sheet (heat 310487) was 10%. This is twice as much as has normally been found in a wide variety of Ti-6Al-4V heat-treat conditions and forms and would markedly increase the susceptibility of the sheet to absorb hydrogen. Also, the texture of this sheet was very highly transverse, much like that observed in continuously rolled sheet (fig. 14). If the diffusion rate of hydrogen in alpha titanium is greater in a direction parallel to the basal plane than in a direction perpendicular to the basal plane, then hydrogen pickup during chemical milling would be expected to be higher with a transverse texture (fig. 14) than with a less directional texture (fig. 13). More work needs to be done in the areas of texture, microstructure, chemical composition, and retained beta effects with respect to hydrogen diffusion and pickup in commercial titanium alloys using commercial feasible chemical milling solutions.

Table 13 shows the combined evaluation of hydrogen pickup due to both chemical milling and an elevated temperature forming cycle. Twenty-five Ti-6Al-4V condition V sheet samples were chemically milled down to 0.008-0.039 in. from the original thickness. After this the samples were cleaned in HNO<sub>3</sub>, coated with a hot forming lubricant, and exposed to the hot forming cycle, which consisted of 1350° F exposure for 15 min followed by air cooling to room temperature. The specimens were then descaled (ref. 4) and chemically milled to 0.016-0.025 in. (ref. 5). The hydrogen pickup was measured after the first chemical milling procedure and after all operations were completed, giving a value of the hydrogen pickup due to chemical milling and the complete hot forming cycle. The average pickup for the 25 condition V (duplex annealed) Ti-6Al-4V samples was 31 ppm, which compares favorably with past data and those presented in table 11.

However, one sample (G) again had an extremely high amount of hydrogen pickup (152 ppm), resulting in a total content after chemical milling of 206 ppm. This high hydrogen pickup was due to the fact that the sample was chemically milled to a very thin gage (0.008 in.). Since hydrogen is absorbed at the surface and diffusion is not sufficiently rapid at the temperature of the chemical milling bath (90°-130° F), a hydrogen gradient exists. Although the magnitude of this gradient is unknown, some measure can be obtained from specimen G where, at 0.008 in., the bulk hydrogen was found to be 206 ppm. A conservative estimate of the surface hydrogen (say, the outer 0.001 in.) is probably at least 400 ppm. SST contract cancellation prevented an investigation into the cause of this high pickup, but it does not appear to be solely the chemical composition since several other samples used were from the same heat (295414) and would have had virtually the same composition. The amount of retained beta and/or preferred orientation might have been the cause. The hydrogen pickup due to the entire manufacturing cycle was significantly large. The average pickup was 85 ppm, with 13 out of 22 samples resulting in total hydrogen content of more than 150 ppm. Two samples picked up 198 ppm of hydrogen. Clearly, the hot-forming cycle was responsible for this extreme hydrogen pickup. The actual source of the hydrogen was not determined but the dissociation of water vapor or thermal decomposition of hydrocarbons could have been the cause. More work is certainly needed in this area.



At the SST contract termination date 20 specific tasks had been defined and initiated to help quantitatively evaluate the hydrogen pickup problem. To demonstrate the technical approaches taken, table 14 lists these tasks.

### 3.2.2 Hydrogen Outgassing

The vacuum furnace tests showed that temperatures as low as 1050°F are effective in removing hydrogen. The results from 24 tests are summarized in figure 24.

The small retort test results are summarized in figure 25, which shows 1150°F to be the lowest temperature, for 1 hr at 50 torr vacuum, that will effectively remove hydrogen with the layup shown in figure 7. It was also demonstrated that an 0.020-in. Ti-6Al-4V separator was adequate to prevent the stainless steel honeycomb from indenting the test specimen.

For the large face skin, control specimens removed from the center and edges were used to determine the hydrogen level prior to the degassing cycle (fig. 26). The part was assembled and sealed into a retort as shown in figure 7, with an integrally heated ceramic tool used as a heat source. After heating and purging a degassing cycle of 1150°F for 1 hr and 50 torr (or greater) vacuum was maintained in the retort.

A leak developed in the retort during the run. However, the hydrogen content in half of the test areas was reduced to levels below 150 ppm (fig. 26). Because of the successful reduction of hydrogen content in some areas, the layup was reassembled in the retort, sealed, purged, and rerun at the same cycle in anticipation that a successfully sealed retort would yield consistent and significantly better results.

The second degassing test on the skin panel was made without any leaks developing in the retort. However, no consistent lowering of hydrogen content occurred. The edge samples did not show significant lowering of content, whereas the center samples generally did (fig. 26). The retort layup for this test was made without the part being chemically cleaned, because the large cleaning facility at the Boeing Developmental Center was not operating at that time. The surfaces near the edges of the panel were noticeably oxidized during the first test. It is believed that because the panel was not cleaned residual oxidation retarded hydrogen removal along the edges.

Because of the termination of the SST contract, testing under this program was not continued.

In summary, a vacuum furnace provides a consistent means of reducing hydrogen content in Ti-6Al-4V. This approach is recommended for raw material (plate and extrusions) and for finished parts where a slight change in shape or contour that might result from the thermal cycle would not affect their function. The recommended minimum furnace schedule is: (a) vacuum,  $10^{-4}$  torr, (b) temperature, 1050°F, (c) time, 2 hr.

**TABLE 14.—HYDROGEN PROBLEM TASKS**

1. Determine that the chemical milling (C/M) tanks are consistent in their hydrogen contamination proclivity—sheet and plate.
2. Determine if hydrogen contamination propensity is consistent over a single sheet and a single plate.
3. Determine why the hot-size cycle influenced hydrogen pickup in the quality control condition V experiment.
4. Determine if the hydrogen pickup observed in the quality control tests came from steps prior to C/M.
5. Determine if more than normal hydrogen is acceptable on aluminum brazed honeycomb panels if the hydrogen is only in the C/M areas.
6. Determine how much hydrogen is removed from C/M area during brazing, on both sheet and plate.
7. Determine the effect of microstructure and material condition on outgassing.
8. Determine the effect of material thickness on outgassing.
9. Determine the effect of a slipsheet on outgassing.
10. Determine the effect of vacuum pressure level on outgassing and the effect of temperature and time effects combined with pressure—sheet and plate.
11. Determine if oxide film impedes outgassing.
12. Review all available literature on hydrogen in titanium.
13. Determine if flowing argon or cycled argon purging is effective in outgassing sheet and plate.
14. Determine proper degassing treatment to remove excessive hydrogen from titanium (release operating controls in the form of a processing specification).
15. Determine if oxidation additives to the C/M bath can alleviate hydrogen pickup propensity.
16. Determine what the hydrogen distribution is through the thickness of C/M titanium sheet and plate.
17. Determine how much hydrogen can be handled in skins to be aluminum brazed, i.e., will too much H<sub>2</sub> ruin the braze.
18. Determine if the coupons available on annealed plates can be annealed and used to certify the plates in stock without taking new coupons.
19. Determine the status of hydrogen pickup on extrusions.
20. Determine the status of hydrogen pickup on bar and forgings.

All specimens chemically milled to final gage to raise hydrogen content.  
 Data derived from four specimens (two gages, two sheets)  
 at each temperature shown (900°, 950°, 1050°, 1150°, 1250°, 1350°F)  
 Vacuum:  $10^{-4}$  torr, minimum

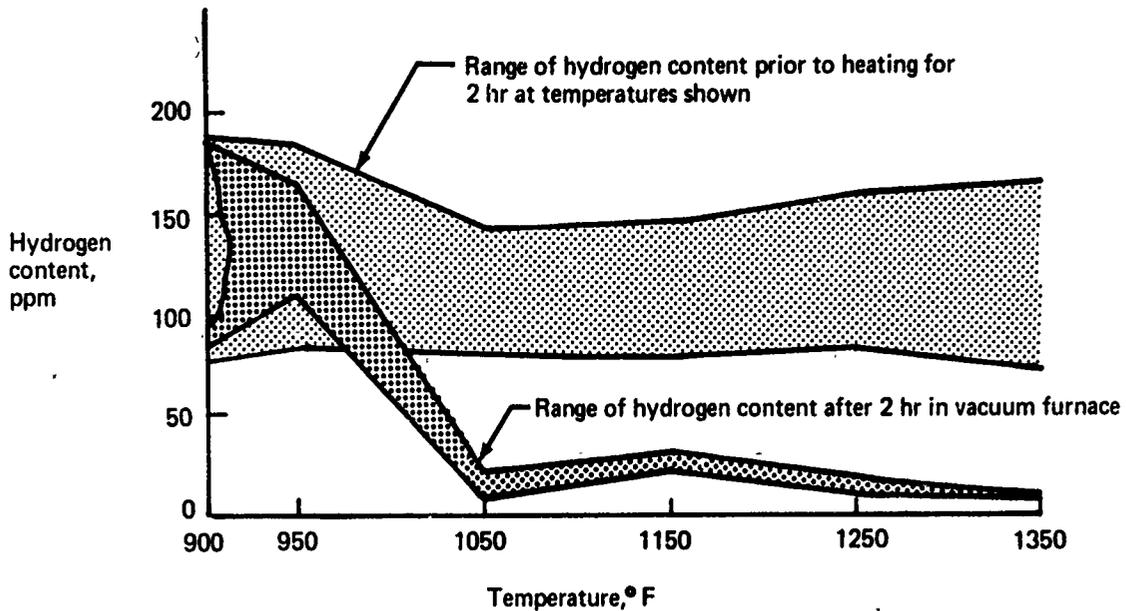


FIGURE 24.—HYDROGEN DEGASSING TESTS IN VACUUM FURNACE

Cycle: 50 torr vacuum for 1 hr at temperatures 950°, 1050°, 1150°, 1250°, 1350°F

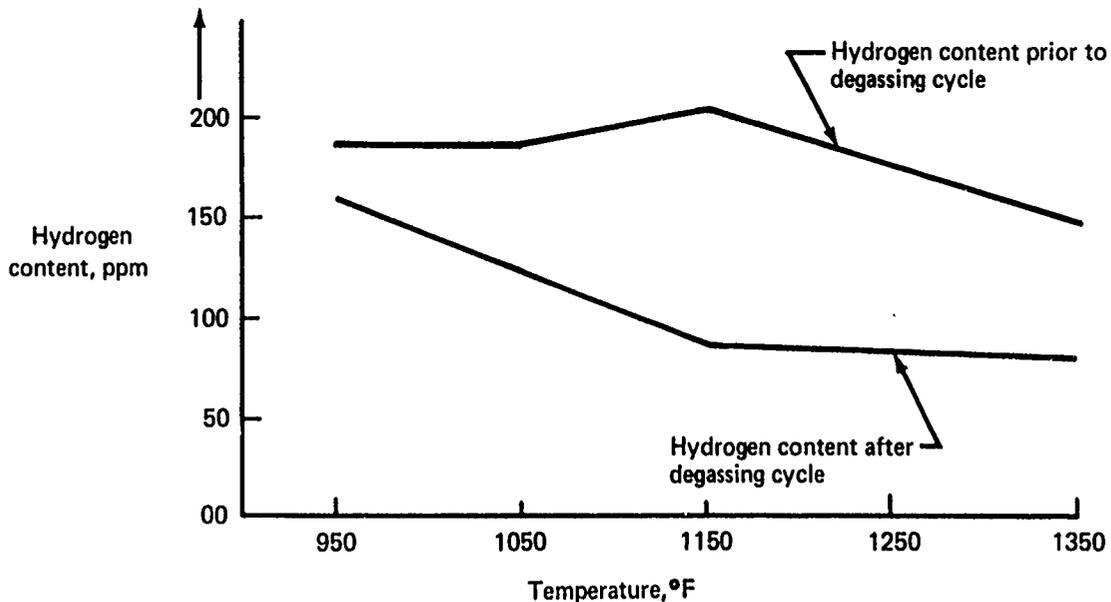
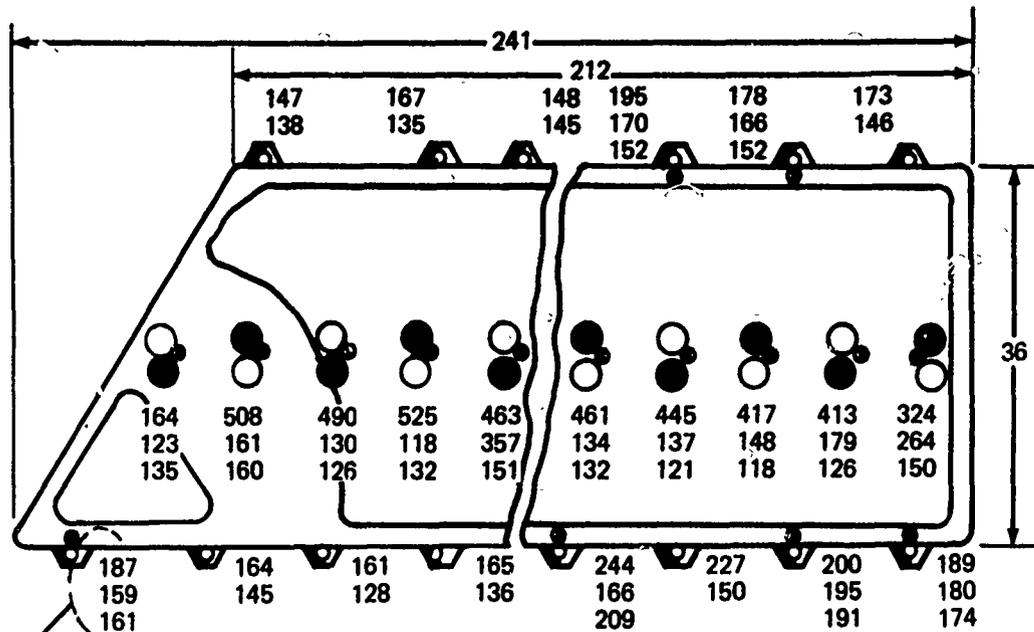


FIGURE 25.—HYDROGEN DEGASSING TESTS IN 12-BY 12-IN. RETORT



- Shaded areas are locations of samples analyzed for hydrogen content prior to degassing cycle.
- Blank areas are locations of samples analyzed for hydrogen content after first degassing cycle.
- ⊗ Crossed areas are locations of samples analyzed for hydrogen content after second degassing cycle.

187 Hydrogen content prior to degassing, ppm  
 159 Hydrogen content after first degassing cycle, ppm  
 161 Hydrogen content after second degassing cycle, ppm

□ — typical all places

**FIGURE 26.—SAMPLE LOCATIONS AND RESULTS OF HYDROGEN DEGASSING OF A LARGE FACE SKIN CYCLED AT 1150°F FOR 1 HR AT 50 TORR OR GREATER VACUUM**

The vacuum retort assembly shown in figure 7 is adequate to reduce hydrogen levels to below 150 ppm in Ti-6Al-4V. However, additional testing will be required to verify that all areas of a large panel can be degassed to this level. The procedure schedule developed to date is:

- Purge and heat retort per XBAC 5767 (ref. 7) and 6M 64-053 (ref. 8).
- Maintain a minimum vacuum of 50 torr for temperatures above 800° F.
- Hold at 1150° F for 1 hr.
- Maintain vacuum to 300° F during cooling.

#### 4.0 CONCLUSIONS

- Hydrogen contents up to 750 ppm have no appreciable effect on the fracture toughness of beta-mill-annealed and beta-STA 1250° F Ti-6Al-4V.
- Hydrogen contents up to 750 ppm have no appreciable effect on the stress-corrosion resistance,  $K_{ISCC}$ , of beta-mill-annealed and beta-STA 1250° F Ti-6Al-4V.
- No delayed failure is obtained in Ti-6Al-4V sheet specimens (0.050 in. thick) with up to 270-ppm hydrogen content after 2500 hr when loaded to 50%-75% of baseline fracture toughness.
- Delayed failure occurs in Ti-6Al-4V precracked Charpy specimens (0.400 in. thick) with hydrogen contents of 154-275 ppm when loaded to 50%-75% of baseline fracture toughness. Failure times are shorter in the STA 1000° F heat-treated condition than in the beta-annealed or beta-STA 1250° F condition.
- Average hydrogen pickup for Ti-6Al-4V during chemical milling is generally low and depends upon heat-treatment condition, as follows:

Condition I (mill annealed)	10 ppm
Condition V (duplex annealed)	30 ppm
Condition IC (continuously annealed)	50 ppm

- The amount of hydrogen pickup in Ti-6Al-4V during chemical milling appears to be related to the amount and distribution of the retained beta phase in the microstructure.
- Outgassing of hydrogen in complicated finished parts can be accomplished by holding at 1150° F for 1 hr in a 50-torr vacuum. This procedure is successful in reducing the hydrogen content below 150 ppm.

## 5.0 RECOMMENDATIONS FOR FUTURE WORK

### 5.1 DELAYED FAILURE

A more detailed program is required to investigate the following parameters and their effect on delayed failure in Ti-6Al-4V:

- Hydrogen Content—Evaluate more hydrogen contents in the range of 130-270 ppm.
- Microstructure—Evaluate in more detail the distribution and amount of beta phase, and the morphology of the alpha phase, as well as the effect of Ti<sub>3</sub>Al ordered-phase formation.
- Heat Treatment—Evaluate all heat treatments.
- Thickness Effects—Determine the effect of thickness and the plane strain/plane stress effects.
- Texture—Determine the effect of basal plane (0002) preferred orientation on delayed failure.
- Chemical Composition—Determine the effect of chemical composition (Al, V, O<sub>2</sub>) variations on delayed failure.
- Other Alloys—Investigate all the above variables for other titanium alloys including alpha, alpha-plus-beta, and beta alloys.

### 5.2 HYDROGEN PICKUP

The following parameters need to be evaluated with respect to hydrogen pickup in Ti-6Al-4V:

- Microstructure—Evaluate distribution and amount of retained beta phase and other microstructural effects.
- Heat Treatment—Evaluate common heat treatments, solution treatment and age, and various annealing procedures, and expand the data as reported herein.
- Hydrogen Distribution—Determine the hydrogen distribution within phases, gradients, etc. Neutron radiography, ion, and laser microprobes could prove useful here.
- Texture Effects—Determine the effect of preferred orientation on hydrogen pickup in titanium.
- Chemical Composition—Investigate variation in Al, O<sub>2</sub>, V, and Fe contents.
- Other Alloys—Evaluate other alloys with respect to hydrogen pickup. The study should include the investigation of microstructure, heat treatment texture, and compositional effects.

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**APPENDIX A**

Specimen number	Sample	H <sub>2</sub> ppm	Specimen number	Sample	H <sub>2</sub> ppm
DH 7	1	301	DH6	1	154
	2	286		2	150
	3	276		3	157
	4	277		4	156
	5	284 avg 285		5	154 avg 154
DH 1	1	118	CH-1	1	213
	2	105		2	213
	3	111		3	217
	4	114		4	216
	5	119 avg 113		5	211 avg 214