CR-128496

(NASA-CR-128496) INVESTIGATION OF THE
REACTION OF 5Al-2.5Sn TITANIUM WITH
HYDROGEN AT SUBZERO TEMPERATURE Final
Report, 24 D.N. Williams, et al (Battelle
Memorial Inst.) 15 May 1972 36 p CSCL 11F G3/17

N72-30474

Unclas
39874

RESEARCH REPORT

Battelle

Columbus Laboratories

FINAL REPORT

(June 24, 1971, through April 15, 1972)

on

INVESTIGATION OF THE REACTION OF 5Al-2.5Sn TITANIUM WITH HYDROGEN AT SUBZERO TEMPERATURE

to

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION
Contract No. NAS 9-12044

May 15, 1972

by

D. N. Williams and R. A. Wood

Burgess; K. Cowell 2746
Tech Mon; Len 660R1050 E55

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

FOREWORD

The use of 5Al-2.5Sn titanium pressure vessels to store hydrogen at 250 psig for periods of up to 2 months at subzero temperatures is contemplated in the SkyLab system. Previous studies supported by NASA Manned Spacecraft Center, Houston, Texas, under Contracts NAS 9-5298, NAS 9-6565, and NAS 9-7549, have indicated that surface hydriding reactions are possible at room temperature. However, surface hydriding rates can be expected to be much reduced at subzero temperature, and it is feasible in the SkyLab system to control the maximum storage temperature as low as -200 F. The Manned Spacecraft Center initiated a study at Battelle's Columbus Laboratories under Contract NAS 9-12044 to determine the effects of temperature on the hydriding reaction and to define an acceptable storage temperature for SkyLab hydrogen pressure vessels. The program was active from the period of June 24, 1971, through April 15, 1972.

These studies were administered under the direction of S. V. Glorioso, NASA Manned Spacecraft Center. Battelle-Columbus personnel who participated in the investigation were D. N. Williams, Technical Advisor, and R. A. Wood, Senior Metallurgist, both of the Nonferrous Metallurgy Division.

INVESTIGATION OF THE REACTION OF 5Al-2.5Sn TITANIUM WITH HYDROGEN AT SUBZERO TEMPERATURE

by

D. N. Williams and R. A. Wood

ABSTRACT

An investigation of the effect of temperature on the surface hydriding reaction of 5Al-2.5Sn titanium exposed to hydrogen at 250 psig was made. The temperature range studied extended from 160 F to -160 F. Reaction conditions were controlled so as to expose a vacuum-cleaned, oxide-free alloy surface to an ultrapure hydrogen atmosphere. Reaction times up to 1458 hours were studied.

The hydriding reaction was extremely sensitive to experimental variables and the reproducibility of reaction behavior was poor. However, it was demonstrated that the reaction proceeded quite rapidly at 160 F; as much as 1 mil surface hydriding being observed after exposure for 162 hours. The amount of hydriding appeared to decrease with decreasing temperature at 75 F, -36 F, and -76 F. No surface hydriding was detected either by vacuum fusion analysis or by metallographic examination after exposure for 1458 hours at -110 F or -160 F. Tensile properties were unaffected by surface hydriding of the severity developed in this program (up to 1 mil thick) as determined by slow strain rate testing of hydrided sheet tensile samples.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF TABLES

INVESTIGATION OF THE REACTION OF 5Al-2.5Sn TITANIUM WITH HYDROGEN AT SUBZERO TEMPERATURE

by

D. N. Williams and R. A. Wood

SUMMARY

The objective of this investigation was to examine the effects of temperature on the surface hydriding behavior of 5Al-2.5Sn titanium exposed to hydrogen gas at 250 psig and to select a temperature below which no significant hydriding would be expected under the most favorable conditions within 2 months. Previous work supported by NASA Manned Spacecraft Center has shown that surface hydriding can occur at room temperature and can, under certain conditions, lead to structural failure. The SkyLab system presently under development proposes the storage of hydrogen at 250 psig in 5Al-2.5Sn titanium pressure vessels for periods of up to 2 months. However, the maximum storage temperature can be controlled as low as -200 F, if necessary, and it seemed probable that a maximum storage temperature could be selected which would eliminate concern regarding surface hydriding.

Surface hydriding reactions are known to be highly sensitive to a number of variables. Foremost among these, based on prior work, are initial surface cleanliness and purity of the hydrogen atmosphere. In this investigation, surface oxides were removed by high-temperature vacuum annealing and the alloy samples were then exposed to ultrapure hydrogen (dew point of -90 F) at 250 psig without intermediate exposure to air. Equipment was designed and constructed to permit both vacuum annealing and exposure to high pressure hydrogen within a single closed system.

Studies of hydriding behavior were conducted for times of up to 1458 hours at temperatures ranging from 160 F to -160 F. Hydriding proceeded moderately rapidly at 160 F. In 162 hours at 160 F, surface hydride films approaching 1-mil thickness were developed and some spalling of the surface hydride was observed. At temperatures of -110 F and -160 F, on the other hand, no evidence of hydriding was detected after 1458 hours either by vacuum fusion analysis for hydrogen or metallographic examination for surface hydrides. Behavior at intermediate temperatures of 75 F, -36 F, and -76 F was quite erratic but, in general, decreased hydriding was observed as temperature was decreased. Assuming parabolic reaction behavior, an activation energy of about 13,000 calories per mole described the temperature dependence of surface hydriding. However, the scatter in experimental results was so great that the kinetic nature of the hydriding reaction could not be uniquely determined.

Tensile properties of hydrided 5Al-2.5Sn titanium at 75 F were determined using machined sheet samples exposed to surface hydriding and tested with no subsequent surface preparation. Surface hydride films within the thickness range produced in this investigation, from 0 to about 1 mil thick, appeared to have no significant effect on tensile properties.

It was concluded on the basis of these studies that a maximum hydrogen storage temperature of about -100 F would preclude the possibility of structural failure from surface hydriding in the SkyLab system. This temperature specification is probably quite conservative in view of the small amount of surface hydriding observed at -36 F and -76 F and the absence of any observable effect of surface hydrides up to 1-mil thickness on tensile properties.

INTRODUCTION

In previous investigations conducted at Battelle's Columbus Laboratories for the Manned Spacecraft Center (Contracts NAS 9-5298, NAS 9-6565, and NAS 9-7549), hydrogen gas was shown to react with several titanium alloys at room temperature.(1)* Under proper conditions, titanium alloys exposed to hydrogen gas were subject to surface hydriding, spalling of the hydride, and ultimately to material failure. It was recommended that the use of titanium pressure vessels to store hydrogen gas at room temperature be approached with caution based upon these results.

The SkyLab system presently under development proposes storage of hydrogen in 5Al-2.5Sn titanium pressure vessels. Hydrogen will be stored at 250 psig for up to 2 months at a variable temperature ranging from about -415 F to -200 F or higher. Extensive prior experience with storage of liquid hydrogen in titanium vessels suggests that surface hydriding reactions are not encountered at very low temperatures (~ -423 F). The question arises, therefore, as to the minimum temperature at which surface hydriding might be anticipated assuming all other conditions were favorable for the initiation of a reaction. If this temperature were known, a maximum storage temperature could be specified for the SkyLab system with some assurance that structural failure from surface hydriding would not be encountered.

The objective of the present investigation was to measure the reaction behavior of hydrogen gas at 250 psig with 5Al-2.5Sn titanium as a function of temperature in order to define a temperature below which no significant reaction would be anticipated over a 2-month period under the most favorable conditions for a reaction to occur. Prior work at Battelle-Columbus has indicated that, although the surface hydriding reaction is quite sensitive to a variety of factors, it is especially favored by increased purity of the hydrogen gas supply and by an oxide-free alloy surface. It can be assumed that if no significant hydriding occurs under a specified temperature:time:pressure regime when these conditions prevail none would be anticipated in service regardless of other conditions.

---

* References are listed on page 30.

MATERIALS

A 5Al-2.5Sn titanium pressure vessel, rejected for manufacturing defects, was supplied by NASA for use in this investigation. This spherical tank was approximately 28 inches in diameter and consisted of two forged and machined hemispheres joined by a circumferential weld. Nominal wall thickness was 46 mils. The surface condition was variable, some areas finished by machining and others by grinding. The microstructure of the hemisphere was also quite variable, ranging from a more or less equiaxed structure in some areas to a coarse acicular structure in others. Examples of the variation in microstructure are shown in Figure 1. In general, the degree of acicularity increased with distance from the weld region. However, it was quite variable both in extent and coarseness and undoubtedly affected reaction behavior during surface hydriding studies. The microstructure of the weld region used to join the two hemispheres is shown in Figure 2.

The tensile properties of the as-received pressure vessel material are shown in Table 1. Tensile samples were cut with the stress axis perpendicular to the circumferential weld from a region between the weld and a midlatitude line. Samples were tested without prior flattening.

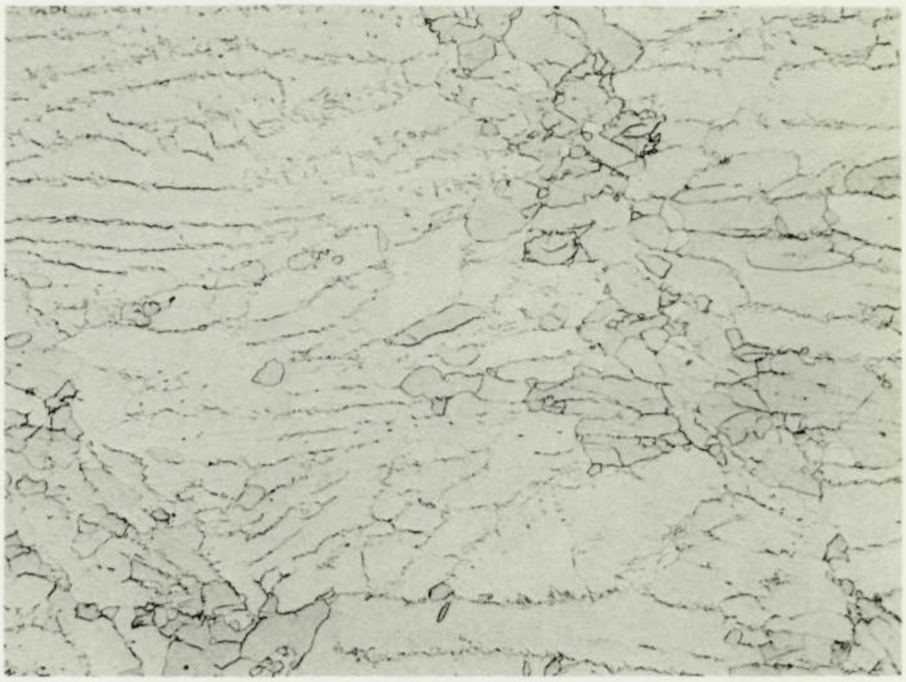
TABLE 1. TENSILE PROPERTIES OF 5Al-2.5Sn TITANIUM PRESSURE VESSEL

Surface Preparation at Battelle	Ultimate Strength, ksi	0.2 Percent Offset Yield Strength, ksi	Elongation, percent	Reduction in Area, percent
None	122.0	110.6	14	33
None	119.0	110.4	14	26
Surface ground	122.5	112.3	16	33
Surface ground	119.0	107.8	9(a)	39
AVERAGE	120.8	110.3	15	33

(a) Broke outside gage mark. This value excluded in calculating the average elongation.

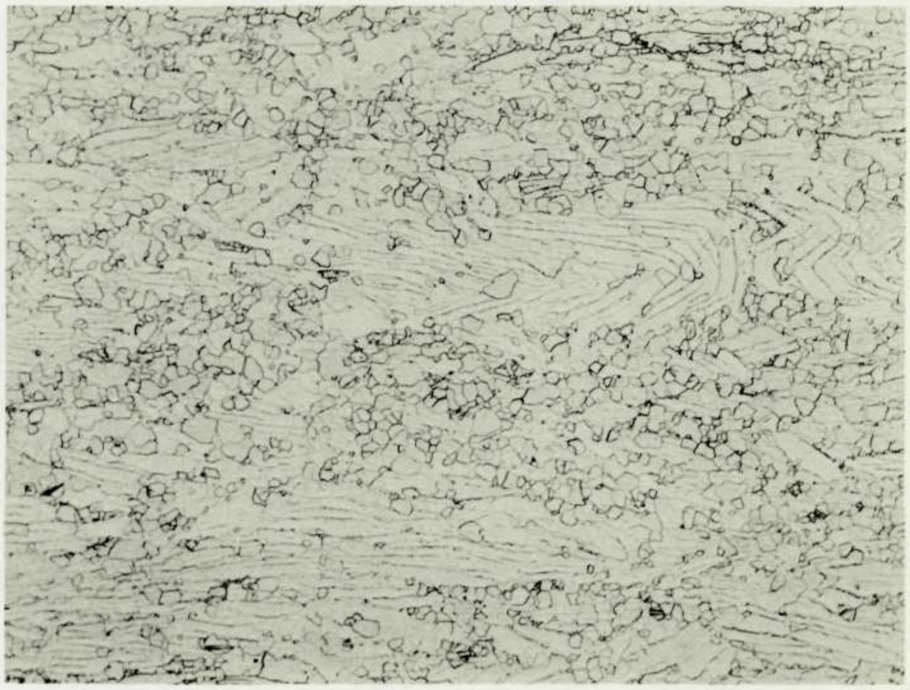
The pressure vessel was sectioned at Battelle's Columbus Laboratories to provide material for use in reaction studies. Three types of samples were prepared:

(1) Sheet tensile samples having a 1/4-inch-wide by 1-1/2-inch-long reduced section. All were cut from a region above the midlatitude line



100X 6F527

a. Area near top of hemisphere dome



100X 6F530

b. Area near weld region

FIGURE 1. VARIATION IN MICROSTRUCTURE OBSERVED IN FORGED 5Al-2.5Sn TITANIUM HEMISPHERES

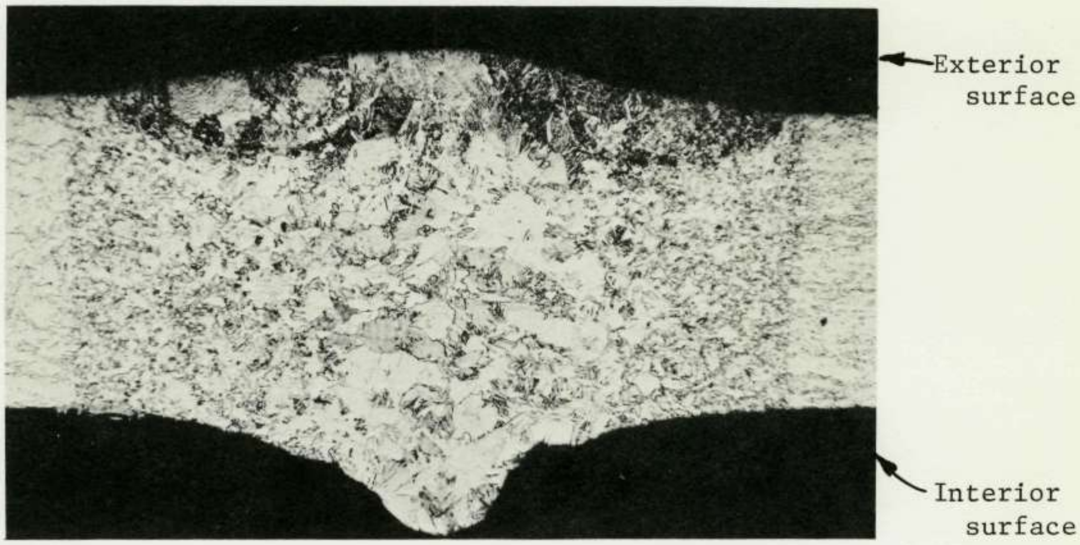


FIGURE 2. SECTION THROUGH THE CIRCUMFERENTIAL WELD USED TO JOIN THE 5Al-2.5Sn TITANIUM HEMISPHERES

with the stress axis perpendicular to the circumferential weld.

(2) Wall samples measuring approximately 1-1/2 by 1/4 inch from the same vessel region from which tensile samples were cut.

(3) Weld samples measuring approximately 1-1/2 by 1/4 inch from the circumferential weld with the weld bead parallel to the 1-1/2-inch dimension and centered in thesample.

None of the specimens were surface ground or flattened prior to exposure. A light pickling treatment in a $HF:HNO_3:H_2O$ solution was used to remove grease and other slight surface contamination.

Ultrahigh purity hydrogen gas was purchased from the Matheson Company for use in this investigation. The nominal analysis of the hydrogen gas is listed below.

O_2	$<$ 1 ppm
N_2	$<$ 5 ppm
Total hydrocarbons	$<$ 1 ppm
Dew point	-90 F .

The gas was used without any further purification treatments.

Prior work at Battelle-Columbus indicated that reaction between titanium and hydrogen gas was favored by using a titanium getter to trap any impurity gases in the system. A quantity of 3-mil-thick unalloyed titanium foil was purchased for this purpose and a portion of this foil was included in each reaction run.

EXPERIMENTAL PROCEDURES

A clean, oxide-free surface can most readily be produced on titanium alloys by annealing at elevated temperatures in a vacuum. Surface oxides are rapidly dissolved under such conditions, but are reformed immediately on exposure to air. Equipment was constructed to permit vacuum annealing of titanium alloy samples followed by exposure to hydrogen at the desired pressure without opening the system to the atmosphere. A photograph of this equipment is shown in Figure 3. The reaction unit consists of the following basic parts:

(a) A stainless steel reaction tube approximately 18 inches long by 1 inch in diameter (0.87 inch I.D.), which could be removed from the reaction unit for

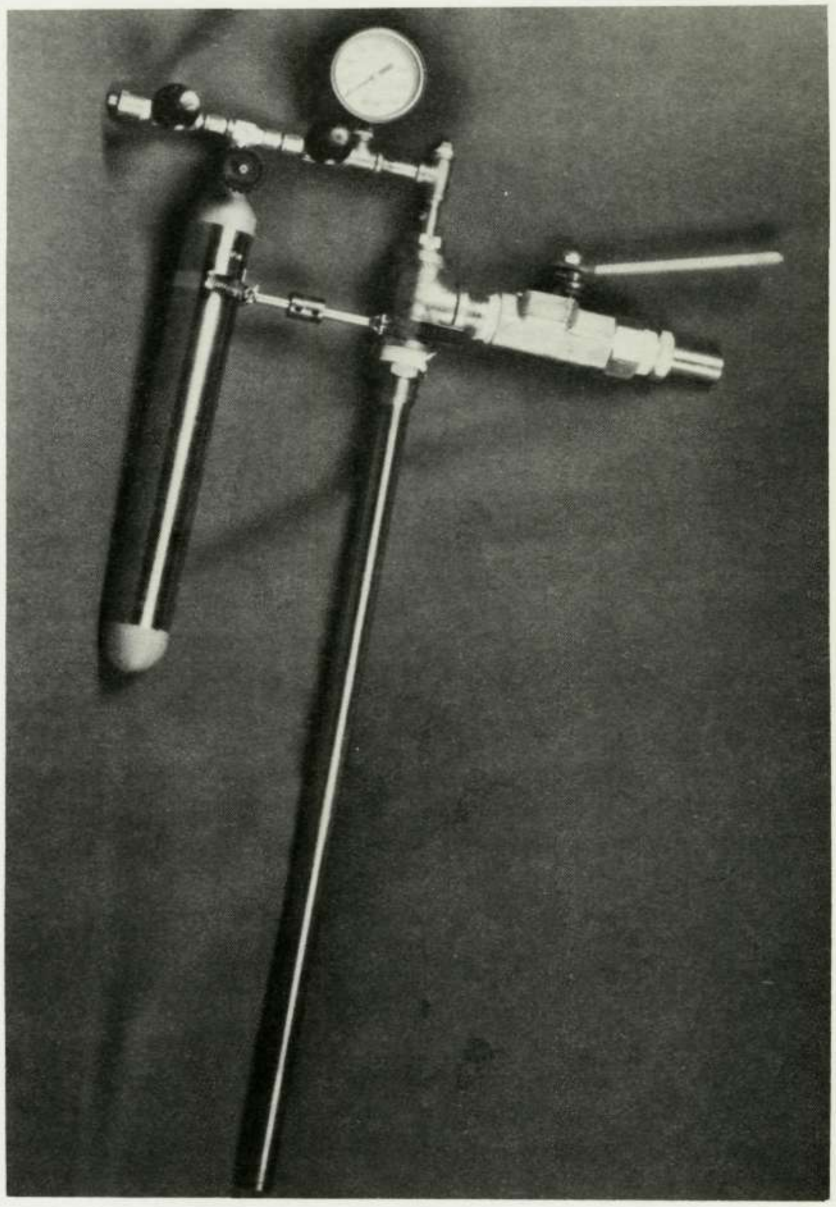


FIGURE 3. HYDROGEN REACTION UNIT CONSTRUCTED FOR LOW TEMPERATURE REACTION STUDIES

C

loading with titanium alloy samples. The samples for exposure to hydrogen were placed in the lower 6 inches of this tube.

(b) A ball valve capable of operation in vacuum and of withstanding a pressure of 250 psig hydrogen in the closed position. This valve was attached using a Goddard seal to the primary vacuum system. The reaction unit was evacuated through this valve during vacuum annealing. The internal diameter of valve and connection system was 7/8 inch.

(c) A high-pressure hydrogen reservoir and related high-pressure valves and pressure gage for introducing hydrogen from the reservoir into the reaction tube at the desired pressure after vacuum annealing.

Twelve reaction units were constructed for use in this program, but as a result of scheduling changes and problems in locating leaks during pressure checkout runs, only ten were actually used in the hydriding studies.

Some modifications in operating procedures were made during the hydriding studies to overcome certain experimental difficulties encountered as the studies progressed. However, the basic operating steps used throughout the program were as follows:

(a) Titanium alloy samples and gettering foil were loaded into the reaction tube which was then attached to the reaction unit. In general, each run contained one tensile sample, four wall samples, two weld samples, and 40 square inches of 3-mil foil. Two wall samples and one weld sample were stacked vertically in a small open-ended tube made from foil. Two of these tubes were then placed alongside the tensile sample--one on each side--in a large foil tube and the entire assembly inserted into the reaction tube.

(b) The reaction unit was pressure checked with 250 psig helium. Pressure was usually monitored for at least 24 hours before starting a reaction run.

(c) The reaction unit was evacuated and high-purity hydrogen was introduced into the hydrogen reservoir (which was closed to the reaction chamber) at 900 to 1800 psig.

(d) The reaction unit was attached to a high-vacuum system and, except for the hydrogen reservoir, was evacuated to a vacuum level of 10^{-4} torr.

(e) A furnace was placed around the reaction tube and the reaction tube and 5Al-2.5Sn titanium samples were annealed at 1500 F to 1600 F with continuous evacuation to dissolve surface oxides.

(f) The furnace was removed and the reaction tube was cooled to liquid nitrogen temperature. At this point, a hydrogen atmosphere of about 50 psig was introduced from the hydrogen reservoir to prevent ingress of air and the reaction unit was removed from the vacuum system. The reaction unit was then transported in liquid nitrogen to the cryogenic storage area.

(g) The reaction tube was placed in the appropriate cryogenic system and when the desired temperature was reached hydrogen was added from the hydrogen reservoir to increase pressure to 250 psig. Additional hydrogen was added as necessary during storage to maintain pressure at 250 ± 25 psig.

(h) At the end of the exposure period hydrogen was vented off and the unit was removed from the cryogenic system. The titanium alloy samples were then removed from the reaction tube and examined for evidence of reaction.

Early in the program, it became apparent that the equipment originally selected for pressuring the hydrogen reservoir [Step (c)], a manifold system used in conjunction with the helium pressure tightness checks, was not maintaining adequate gas purity. Analysis of the hydrogen gas in three reservoirs after reaction runs showed the following results:

Run No.	Impurity Content, ppm	
	N_2	O_2
3	120	7
5	17	< 1
7	< 1	< 1

Although a progressive improvement in purity of the gas was apparently obtained with increased use of the manifold system, it was decided to fill the reservoirs using a system which would permit vacuum bakeout of the reservoir at about 200 F and evacuation to vacuum levels of 10^{-5} torr or better. The reservoirs were attached to the reaction units after filling with high pressure hydrogen. Pressure checks [Step (b)] and evacuation [Step (d)] were then conducted on the entire unit with the reservoir containing hydrogen under high pressure.

Another change instituted after the first eight runs consisted of a slight modification in the vacuum annealing treatment to provide more complete solution of surface oxides. Originally, the units were heated to 1500 F for 1 hour and then to 1550 F for an additional 1/2 hour. Temperature measurements made during an early run showed that the samples were somewhat cooler than the furnace. Therefore, the furnace was controlled to 1600 F for 2 hours [Step (e)]. The latter treatment was probably about twice as effective in removing surface oxide as the earlier treatment.(2)

A major experimental variable was the cooling procedure following vacuum annealing [Step (f)]. In early runs, the reaction tube was water cooled for a variable period, usually from 20 to 30 minutes, and then placed in a liquid nitrogen bath. After about 2 to 5 minutes in this bath, the system was pressurized to 50 psig with hydrogen. Temperature measurements made during a midproject run indicated that the samples might be at a temperature as high as 300 F after 20 minutes of cooling. However, the cooling rate upon introduction of 50 psig hydrogen was very rapid, and the samples cooled to below room temperature in less than 1 minute. Significant hydriding was not anticipated during the short exposure to hydrogen at 75 F to 300 F. However, subsequent base runs in which samples were removed after a short storage period at liquid nitrogen temperature showed that this assumption was incorrect; major hydriding occurred during this treatment. Therefore, a long cooling period, totaling 60 minutes, was used in later runs consisting of four steps:

Air Cooling	~ 5 minutes
Water Cooling	~ 25 minutes
Air Cooling	~ 25 minutes (to permit attachment of cryogenic control thermocouples)
Liquid Nitrogen Cooling	~ 5 minutes .

Temperature measurements made during two runs using this procedure are shown in Figure 4. With this treatment, the samples were cooled to 100 F at the point at which hydrogen was introduced and they were cooled to subzero temperature within a few seconds after hydrogen was added. Three of four base runs made with this cooling treatment showed no evidence of reaction on hydrogen introduction. The fourth showed a slightly higher than normal hydrogen content (18 ppm as compared to the expected 11 ppm).

Exposures to high pressure hydrogen were conducted for periods ranging from 18 to 1458 hours (60-1/4 days) at temperatures of 160 F, 75 F, -36 F, -76 F, -110 F, and -160 F. Temperature control problems were encountered only in three runs at -36 F (Runs 27, 36, and 37). In these cases, problems with the cryogenic system necessitated moving the reaction units to an alternate storage area (in a liquid nitrogen bath) on one or more occasions. Maintaining hydrogen pressure provided no problems, although several units which were pressure tight when checked with helium required moderately frequent additions of hydrogen to maintain pressure

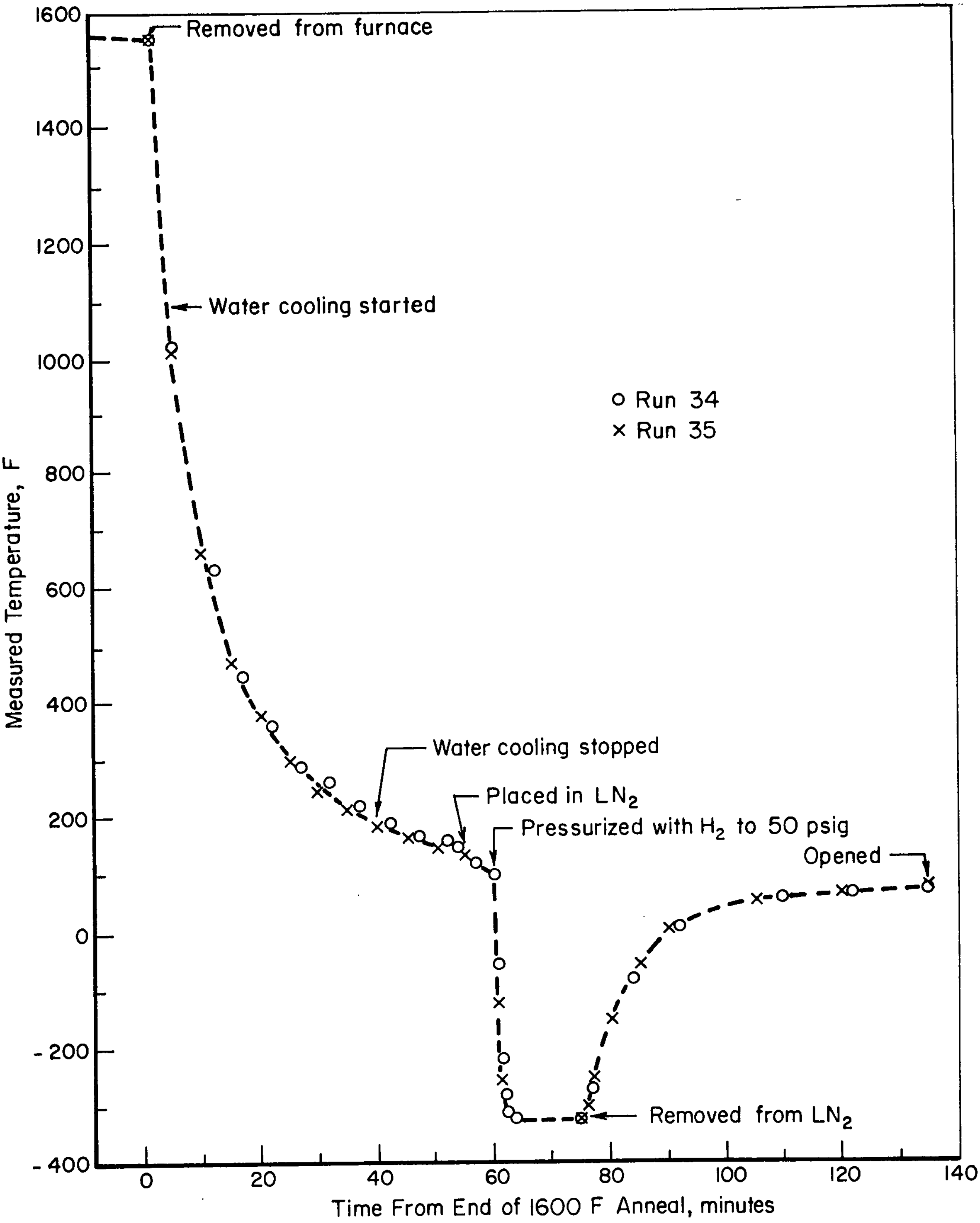


FIGURE 4. TEMPERATURES MEASURED DURING BASE RUNS 34 AND 35

within the desired range of 250 ± 25 psig. In only one instance was it necessary to terminate a run due to inability to maintain pressure (Run 5, scheduled for 1458 hours at -36 F, had to be terminated after 890 hours).

A summary of experimental variables included in the 38 hydrogen exposures conducted during this investigation is given in Table 2. In addition to those variables already mentioned, this tabulation indicates the final vacuum level just prior to pressurizing with hydrogen to 50 psig, notation of multiple use of hydrogen reservoirs (some were used two or three times before refilling), and an indication of the vacuum level attained during reservoir outgassing before filling with hydrogen.

Evaluation of samples for evidence of hydriding after exposure was conducted by vacuum fusion analysis of sample sections weighing approximately 0.7 gram with no prior sample preparation except shearing to remove sample ends, and by metallographic study of sectioned samples. One weld sample and two wall samples were examined by analysis, while the remaining weld sample and wall samples were sectioned for metallographic study. A reasonably consistent trend was observed throughout the program for the amount of hydriding on the reaction samples to vary with location in the reaction tube as shown by selected analytical results given below.

Run No.	Measured Hydrogen Content, ppm Top	Middle	Bottom
7	38	130	258
21	12	75	66
31	54	276	319
38	334	574	760

This behavior was apparently related either to differences in temperature during vacuum annealing or to atmospheric leaking during the cooling cycle since it was seen both in base runs and in samples exposed to hydrogen at 250 psig. Microstructural differences may have increased the magnitude of the effect since weld samples were usually placed in the bottom of the reaction tube and previously work has suggested that acicularity promotes hydriding.(1) The differences in hydriding behavior as a function of sample location indicated by analysis was also apparent in metallographic examination. For convenience in comparing the effects of exposure conditions, an average hydrogen content was calculated from the results obtained for the three samples.

Sheet tensile samples were tested at a machine speed of 0.005-inch per minute to yield and then at 0.02-inch per minute to failure. The samples were placed in hydrogen exposure in a finished machined condition and were tested after removal from exposure with no subsequent surface preparation.

TABLE 2. SUMMARY OF EXPERIMENTAL VARIABLES

Run No.	H_2 Exposure		Unit No.[(a)]	Final Vacuum[(b)] 10^{-4} torr	Annealing Treatment[(c)]	Cooling Time, min	Reservoir Vacuum,[(d)] torr	Reservoir Previously Used[(e)]	Repressurization[(f)]	
	Temp., F	Time, hr							Times H_2 Added	psi H_2 Added
1	Base	Base	5	1.8	1500/1550	---	$\sim10^{-3}$	---	---	---
2	75	162	1	2.7	1500/1550	27	$\sim10^{-3}$	---	1	8
3	75	1458	10	2.2	1500/1550	21	$\sim10^{-3}$	---	0	0
4	-36	162	6	1.7	1500/1550	26	$\sim10^{-3}$	---	0	0
5	-36	890	5	2.6	1500/1550	38	$\sim10^{-3}$	---	12	184
6	-110	162	7	1.7	1500/1550	29	$\sim10^{-3}$	---	0	0
7	75	162	7	1.8	1500/1550	25	$\sim10^{-3}$	6	0	0
8	-160	162	6	2.9	1500/1550	37	$\sim10^{-3}$	4	0	0
9	-110	1458	1	1.2	1600	60	8x10^{-6}	---	0	0
10	-160	486	7	2.0	1600	60	$\sim10^{-3}$	6, 7	0	0
11	75	54	6	1.9	1600	60	$\sim10^{-3}$	4, 8	0	0
12	75	18	4	2.1	1600	60	2x10^{-5}	---	0	0
13	-36	18	6(4)	3.0	1600	60	2x10^{-5}	12	1	10
14	-36	54	6(4)	3.0	1600	60	2x10^{-5}	12, 13	0	0
15	75	162	11	4.2	1600	60	5x10^{-4}	---	0	0
16	75	18	4(8)	2.1	1600	25	5x10^{-4}	---	0	0
17	-160	1458	6	3.3	1600	60	2x10^{-5}	---	3	46
18	-36	~1030	4	2.7	1600	25	8x10^{-6}	---	12	104
19	75	~890	5	3.4	1600	25	1x10^{-5}	---	11	180
20	75	162	7	2.5	1600	25	8x10^{-6}	---	2	14
21	Base	Base	8	3.0	1600	25	5x10^{-4}	16	---	---
22	75	486	7	2.7	1600	25	8x10-6	20	14	437
23	-36	486	3	3.4	1600	25	8x10^{-6}	---	1	10
24	-76	486	11	2.4	1600	25	2x10^{-6}	---	0	0
25	Base	Base	1	3.8	1600	25	5x10^{-5}	---	---	---
26	Base	Base	8	2.9	1600	25	1x10^{-5}	---	---	---
27	-36	1458	10	3.0	1600	60	1x10^{-5}	---	5	56
28	-76	1458	7	4.1	1600	60	9x10^{-6}	---	6	110
29	75	1458	8	2.8	1600	60	1x10^{-5}	26	5	125
30	Base	Base	2	2.6	1600	60	6x10^{-6}	---	---	---
31	75	486	3	3.0	1600	60	6x10^{-6}	---	2	30
32	Base	Base	4	2.8	1600	60	8x10^{-6}	18	---	---
33	Base	Base	6(12)	3.0	1600	30	6x10^{-6}	---	---	---
34	Base	Base	4	3.4	1600	60	8x10^{-6}	18, 32	---	---
35	Base	Base	4	2.3	1600	60	8x10^{-6}	18, 32, 34	---	---
36[(g)]	-36	486	6(12)	2.0	1600	60	6x10^{-6}	33	6	164
37	-36	162	2	3.0	1600	60	6x10^{-6}	30	0	0
38[(h)]	160	162	3	2.2	1600	60	6x10^{-6}	31	3	35

(a) A hydrogen reservoir from one unit was occasionally used on a second unit. When this was done, the reservoir number is included in parenthesis.

(b) Vacuum level indicated upon conclusion of cooling cycle just prior to pressurization to 50 psig with hydrogen.

(c) Either 1 hour at 1500 F plus 1/2-hour at 1550 F (1500/1550) or 2 hours at 1600 F (1600). The latter treatment is believed about twice as effective as the former in dissolving surface oxides from 5Al-2.5Sn titanium alloy.

(d) Vacuum level attained in reservoir prior to introduction of hydrogen. Those reservoirs evacuated to $\sim10^{-3}$ torr were not baked out during outgassing.

(e) Hydrogen reservoirs occasionally used more than once.

(f) Hydrogen pressure was maintained at 250 ±25 psig during reaction runs. If leaks occurred, hydrogen was added to maintain the pressure within the desired range. The number of times hydrogen was added (usually 10 to 20 psig per addition) and the total hydrogen added (expressed as the sum of incremental pressure increases) is reported.

(g) Samples in this run were previously exposed in Run 18 which was terminated early and discarded when problems with the short cooling period were discovered.

(h) Samples from this run were previously exposed in Run 19 which was terminated early and discarded when problems with the short cooling period were discovered.

TABLE 3. HYDROGEN CONTENT OF BASE LINE SAMPLES

Run	Cooling Period Time Segments, minutes(a)					50 psig H_2 Exposure, minutes(b)			250 psig H_2 Exposure, minutes(c)	Temperature at Termination of Run, F	Hydrogen Content by Analysis, ppm			
No.	Air	H_2O	Air	LN_2	Total	LN_2	~RT	Total			Top(d)	Middle(d)	Bottom(e)	Average
			Short Cooling Period											
21	3	7	---	15	25	15	---	---	---	-320	12	74	66	50.7
25	3	7	---	15	25	15	---	---	---	-320	40	---	107(d)	73.5
26	3	7	---	15	25	15	---	---	---	-320	256	---	263(d)	260
33	5	15	---	10	30	20	60	80	60	75	124	---	126(d)	125
			Long Cooling Period											
30	5	37	13	5	60	15	---	15	---	-320	14	22	18	18.0
32	5	30	20	5	60	7	60	67	60	75	12	---	11(d)	11.5
34	5	37	12	5	60	15	60	75	---	75	12	---	10(d)	11.0
35	5	30	20	5	60	15	60	75	---	75	10	---	8(d)	9.0
			No Exposure to Hydrogen											
1	8	7	65	---	80	---	---	---	---	75	11	11	12	11.3

(a) The reaction tube was removed from the furnace, cooled a short period in air, a somewhat longer period in water, in some cases a further period in air, and finally in liquid nitrogen.

(b) Low pressure hydrogen was introduced while the reaction tube was in a liquid nitrogen bath. In some cases, the tube was removed from the bath after a short time period and allowed to return to room temperature.

(c) In two cases, the samples were exposed to hydrogen at 250 psig for 60 minutes at room temperature before examination.

(d) Wall samples

(e) Weld samples unless otherwise noted.

RESULTS

Base-Line Studies

The length of the cooling period following vacuum annealing was found to be an important factor in the observation of hydriding. If too short a cooling period was used, it was possible for hydriding to occur in the interval immediately following hydrogen introduction. Results of base-line runs showing this effect are given in Table 3. Four of these runs, with cooling periods of 25 or 30 minutes, showed average hydrogen contents by analysis ranging from 50.7 to 260 ppm. In view of the apparent similarity in procedure, the large difference in hydrogen content is surprising. Although the correlation is not exact, the data given in Table 2 suggest that differences in vacuum level attained in the reservoir prior to filling may be a factor. If so, the reaction rate during the short exposure to hydrogen at 50 psig between 75 F and 300 F must be extremely sensitive to contaminants. Three of the four base samples receiving a long exposure period showed no reaction on hydrogen introduction based on comparison with the samples processed through vacuum annealing but not exposed to hydrogen (Run 1). From these runs, it is concluded that vacuum annealing as performed in this program developed a base hydrogen content of about 11 ppm. The fourth long cooling period base run (Run 30) contained 18 ppm hydrogen after processing. No reason for this difference in behavior is apparent from an examination of the experimental procedures as outlined in Tables 2 and 3. The only difference between this run and other similar runs was that it was opened at -320 F after only 15 minutes contact with low pressure hydrogen instead of being opened at room temperature.

TABLE 4. TENSILE PROPERTIES OF VACUUM ANNEALED 5Al-2.5Sn TITANIUM

Run No.	Ultimate Strength, ksi	0.2 Percent Offset Yield Strength, ksi	Elongation, percent	Reduction in Area, percent
21	110.3	104.6	5(a)	30
30	108.8	100.2	10	26
1	115.8	105.0	8(a)	23
AVERAGE	111.6	103.3	10	26

(a) Broke outside gage mark. These values excluded in calculating the average elongation.

Tensile samples were included in three of these base runs. The results of tests of these samples are shown in Table 4. The differences shown are believed the result of microstructural differences in the pressure vessel material rather than differences in base run processing treatments. Comparison with tensile data shown in Table 1 for as-received material indicates that the vacuum annealing treatment reduced both strength and ductility.

Hydriding Studies

Vacuum Fusion Measurements of Hydrogen Content

The effects on hydrogen content, as indicated by analysis, of exposing samples to hydrogen at 250 psig at various temperatures for times up to 1458 hours are shown in Table 5. Examination of analytical data indicates appreciable variability in hydriding behavior under presumably similar experimental conditions and makes an exact analysis of the significance of these results quite difficult. However, several trends are apparent, and can be used to assess the effect of temperature on reaction behavior.

Of most significance is the observation that no reaction was found in any of the tests at -160 F. At -110 F, the small reaction indicated in the 162-hour exposure (Run 6) is most probably the result of hydriding in low pressure hydrogen following a short cooling period. Interestingly, it was observed that samples exposed for long periods of time at low temperature showed hydrogen contents less than the base hydrogen content (11 ppm).

A limited amount of reaction was indicated by analysis after each of two runs made at -76 F. However, Run 24 was processed using a short cooling period and it is probable that this contributed the major part of the hydriding observed in this run. Run 28, on the other hand, appears to be a reliable run and indicates that reaction can occur at -76 F.

Reaction behavior at -36 F was extremely erratic. Several of these runs (Runs 4, 5, and 23) were processed using a short cooling period, but none showed significant amounts of reaction. The amount of reaction observed in Run 27 was less than would be expected based on behavior observed in Run 28 at -76 F. A plot of the average hydrogen pickup (average hydrogen content minus the base hydrogen content of 11 ppm) as a function of exposure time is shown in Figure 5a. Although the data scatter precludes much confidence in this relationship, a tentative relationship between amount of hydriding and time is shown assuming parabolic reaction kinetics. The larger than anticipated reaction observed in Run 37 may have resulted from temperature control problems. This run reached -20 F at one point during exposure (as did Run 27, also).

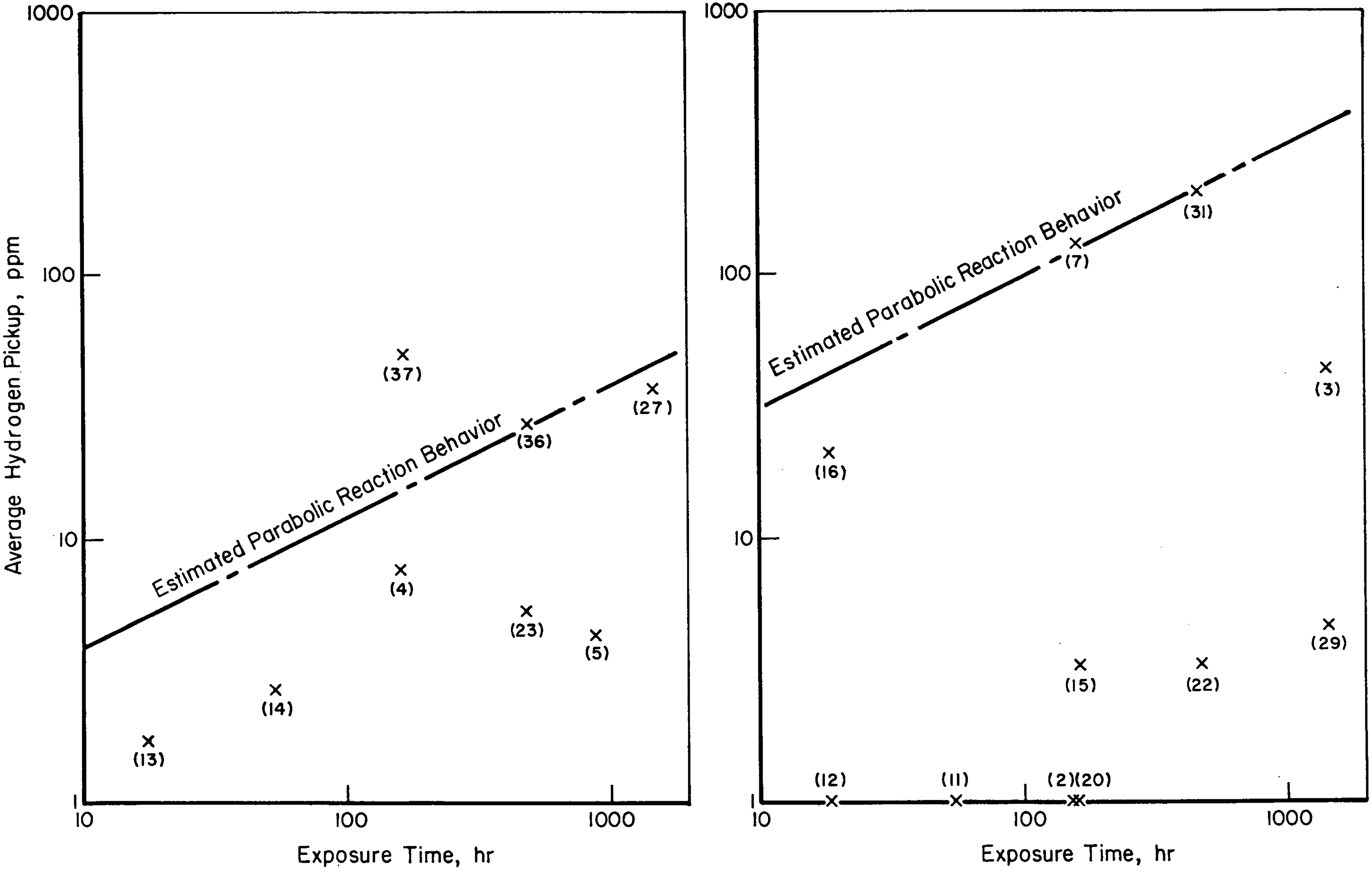
The hydrogen contents of the samples after exposure to hydrogen at 250 psig for various times at 75 F also show appreciable scatter. One

TABLE 5. HYDROGEN CONTENT OF SAMPLES EXPOSED TO HIGH PRESSURE HYDROGEN

Run	Exposure Conditions		Hydrogen Content by Analysis, ppm			
No.	Temp., F	Time, hr	Top(a)	Middle(a)	Bottom(b)	Average
38	160	162	334	574	760	556
12	75	18	9	10	9	9.3
16	75	18	28	43	30	33.7
11	75	54	10	10	12	10.7
2	75	162	11	10	11	10.7
7	75	162	38	130	258	142
15	75	162	15	14	14	14.3
20	75	162	11	11	12	11.3
22	75	486	12	13	18	14.3
31	75	486	54	276	319	216
3	75	1458	15	53	93	53.7
29	75	1458	10	10	30	16.6
13	-36	18	13	13	12	12.7
14	-36	54	13	12	16	13.7
4	-36	162	12	15	29	18.7
37	-36	162	38	66	80	61.3
23	-36	486	19	14	16	16.3
36	-36	486	12	46	55	37.7
5	-36	890	14	14	16	15.3
27	-36	1458	31	48	60	46.3
24	-76	486	42	62	46	50.0
28	-76	1458	33	57	63	51.0
6	-110	162	16	17	15	16.0
9	-110	1458	9	8	7	8.0
8	-160	162	11	11	11	11.0
10	-160	486	10	10	10	10.0
17	-160	1458	9	8	8	8.3

(a) Wall sample.

(b) Weld sample.



a. Tests at -36 F

b. Tests at 75 F

FIGURE 5. AVERAGE HYDROGEN PICKUP AS A FUNCTION OF TIME OF EXPOSURE TO HYDROGEN

Base Hydrogen, 11 ppm. (Run Numbers Shown in Parentheses).

run (Run 31) showed considerable reaction indicating that, under proper conditions, reaction proceeds reasonably rapidly at 75 F. Two other runs also showed appreciable reaction (Runs 7 and 16), but are suspect because of the use of a short cooling period following vacuum annealing. Samples from Run 7 showed fairly nonuniform surface hydriding on metallographic examination, which is believed a characteristic of hydrides formed during cooling from 300 F, but a significant portion of the hydride formed on this run is believed to have formed during exposure to hydrogen at 250 psig since none of the equivalently processed runs (Runs 2 through 8) showed evidence of surface hydriding during the cooling treatment. Other runs showed little or no reaction even though appreciable reaction was anticipated. Contamination is suspected to have contributed to this behavior in some cases. Runs 2 and 3, for example, are believed to have been affected by a less thorough vacuum annealing treatment and by contamination of the gas supply. Runs 11, 15, 20, 22, and 29 also showed severely retarded hydriding behavior. Examination of the experimental conditions for these runs, as shown in Table 2, suggests that Runs 11 and 15 may have been affected by an impure hydrogen supply while the system used in Run 22 showed appreciable leakage. No reason for failure to observe extensive hydriding in Runs 20 or 29 is apparent, however. Both Run 20 and Run 22 were prepared using a short cooling period which should have favored excessively large amounts of hydride formation. The average hydrogen pickup at 75 F is plotted versus time in Figure 5b. Although a meaningful correlation of these data is difficult, the parabolic relationship shown in Figure 5b is probably a reasonable estimate.

Only one reaction run was made at 160 F. At this temperature considerable reaction was observed. Hydriding was so severe that appreciable spalling of the hydride occurred and a quantity of powder was removed from the bottom of the reaction tube when the samples were removed. This hydride came largely from the lower portion of the unalloyed foil, but evidence was also seen of surface spalling on some 5Al-2.5Sn titanium alloy samples.

The effect of reaction temperature on the amount of hydriding in 1458-hour exposure is shown in Figure 6. This graph was obtained by extrapolation of the single data point at 160 F to 1458 hours assuming parabolic hydriding, by using the trend lines shown in Figure 5 for data at 75 F and -36 F, and by using measured values for hydrogen pickup in 1458 hours at -76 F, -110 F, and -160 F from Table 5. Although based on data showing appreciable scatter, this graph suggests hydriding proceeds very slowly at temperatures below -100 F. The activation energy for surface hydriding calculated from the graph is about 13,000 calories per mole, about the same value as the activation energy for hydrogen diffusion in alpha titanium.(3) The estimated hydride thickness included along the right-hand ordinate was obtained from Figure 7, discussed in the next section of this report.

Metallographic Examination of Hydride Films

Metallographic examination of sectioned samples was used in addition to vacuum fusion analysis to determine the extent of hydriding.

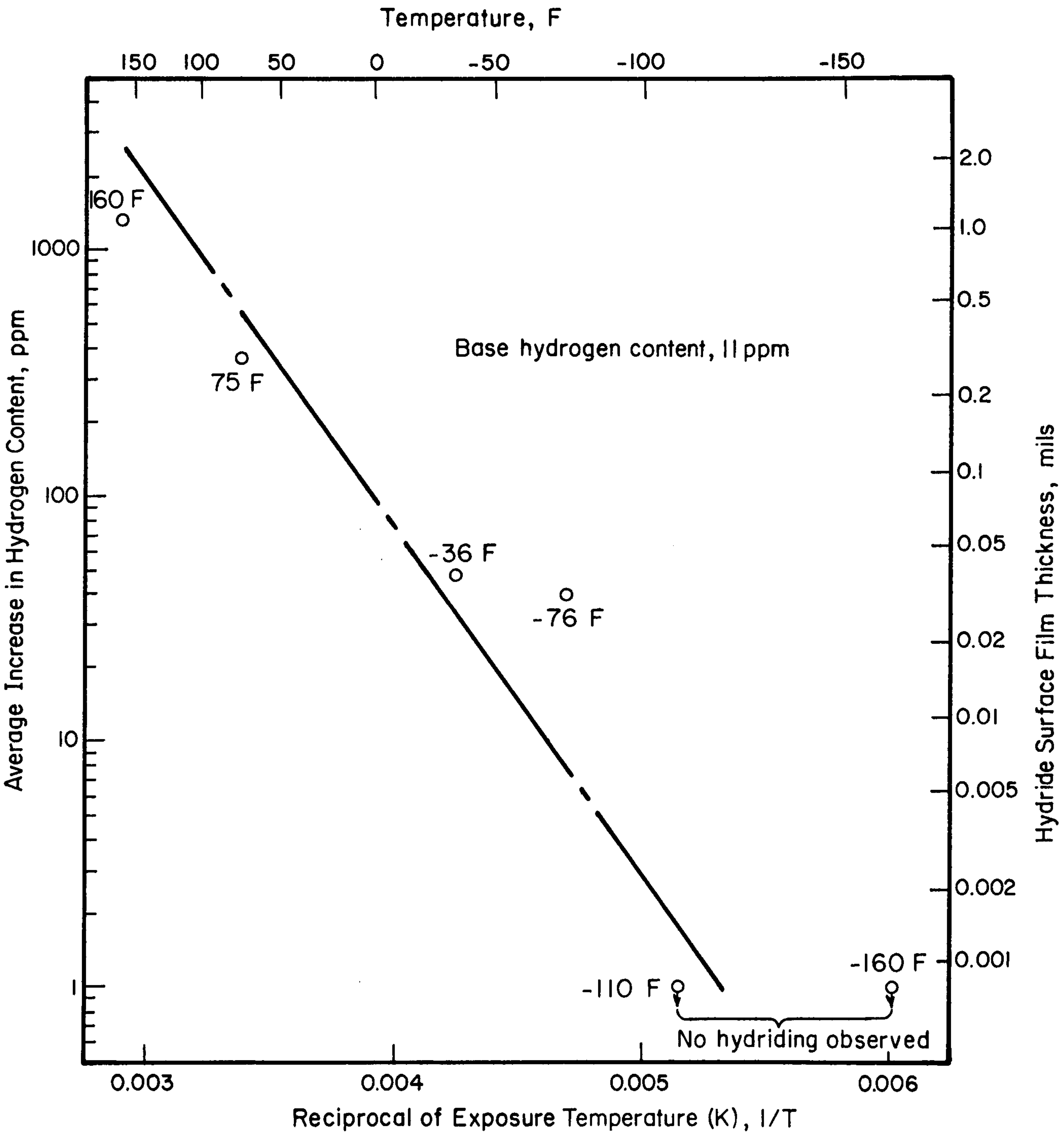


FIGURE 6. VARIATION IN HYDRIDING WITH TEMPERATURE OBSERVED IN AN EXPOSURE OF 2 MONTHS (1458 HOURS)

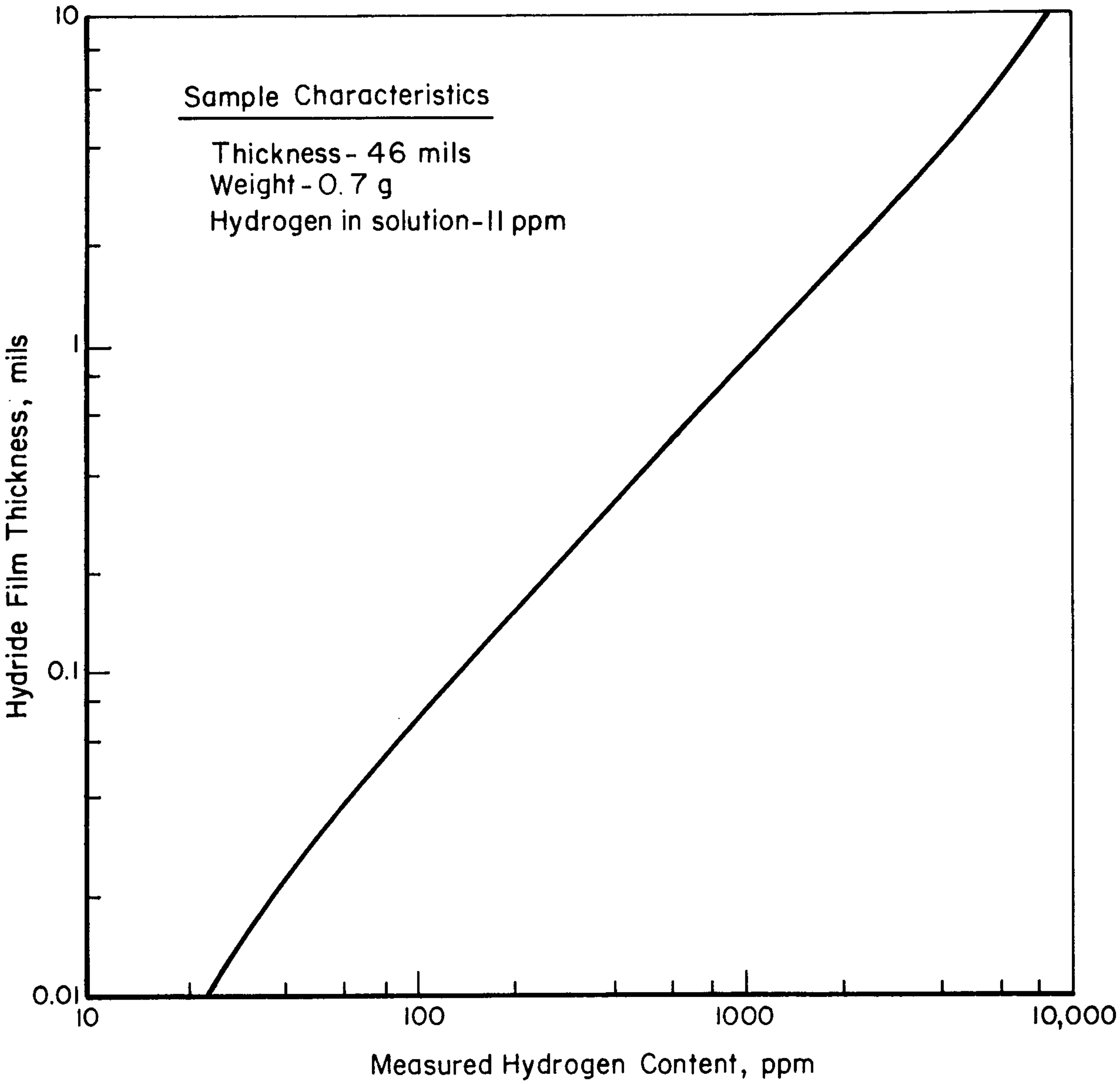


FIGURE 7. CALCULATED HYDRIDE FILM THICKNESS AS A FUNCTION OF MEASURED HYDROGEN CONTENT

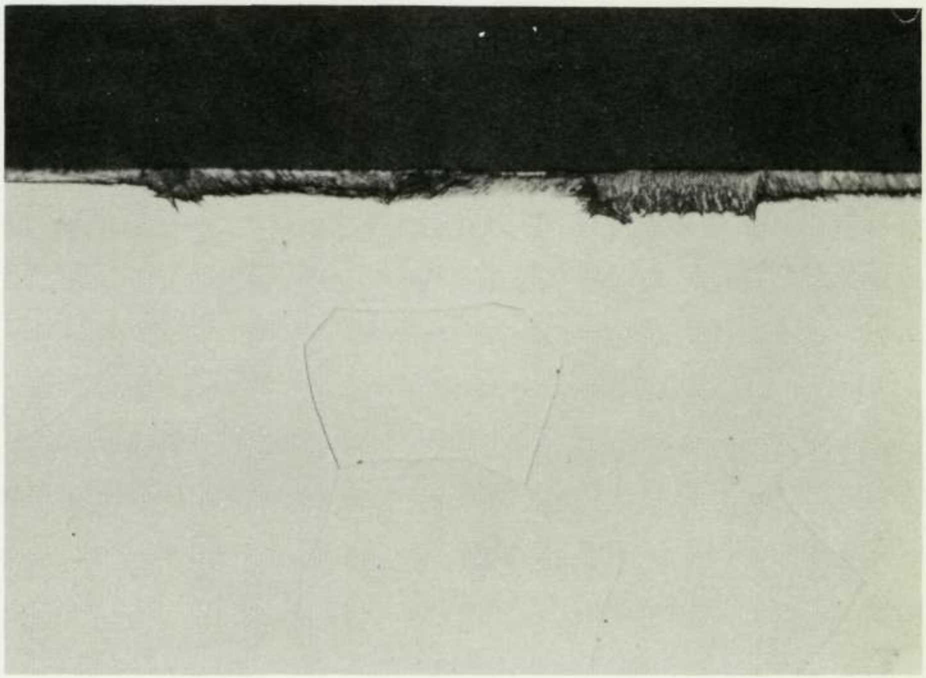
Assuming that a uniform surface film is formed, a direct correlation between measured hydrogen content and hydride film thickness should exist as shown in Figure 7. This relationship was calculated using the method described by McKinsey, et al.(4) When appreciable hydriding was present, this relationship was followed reasonably well. For example, the measured hydride thickness on weld samples compared with the value predicted from the analyzed hydrogen content as follows:

	Hydride Thickness, mil	
Run No.	Measured	Expected from Analysis
31	0.3	0.16
38	1.0	0.70

Since surface hydride films are usually of variable thickness as shown in Figure 8, agreement seems reasonably good. In general, hydride films were not detected metallographically in samples which showed less than about 70 ppm hydrogen by analysis (calculated film thickness of about 0.05 mil).

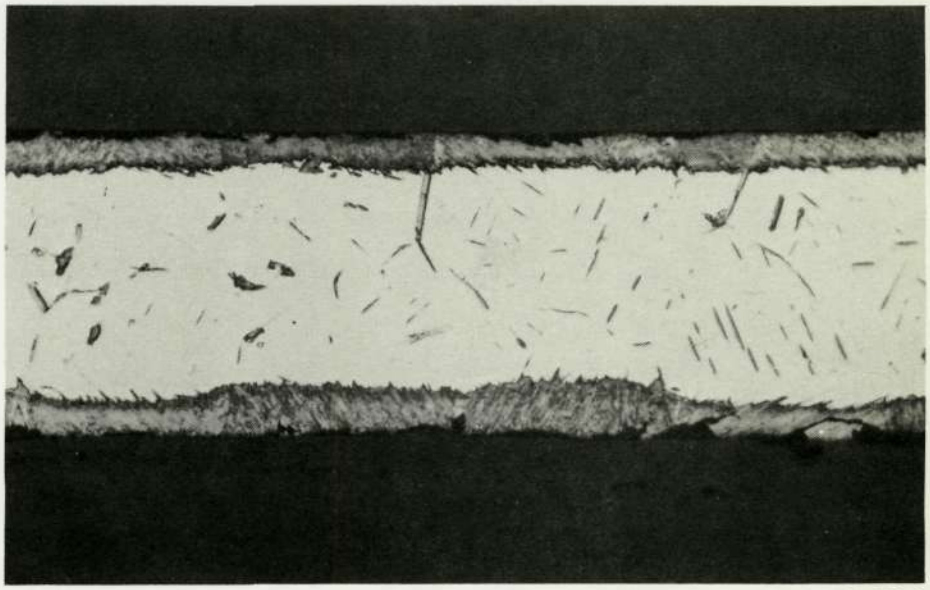
Surface hydriding was quite nonuniform in several cases as shown by selected examples in Figure 9. Extreme variability in hydride uniformity, usually observed on samples receiving a short cooling treatment, may be typical of hydride formed during short exposures above room temperature. Hydriding in these cases also appeared somewhat more lacy (compare Figure 8a with Figure 9a, for example). Preferential hydriding along former beta areas, as in Figure 9b, or in certain grain orientations, as in Figure 8a, was frequently seen. Another interesting feature is shown in Figure 10 in which subsurface hydrides are shown appearing about 1.3 mils beneath the surface hydride. Internal hydrides were also seen frequently in the foil material, as shown in Figure 8b. Diffusivity calculations based upon extrapolation of hydrogen diffusion measurements made at elevated temperatures for unalloyed titanium(3) suggest that the maximum depth of hydrogen penetration, assuming diffusion through alpha, in 486 hours at 75 F would be about 3 mils. Thus, hydride precipitation at a depth of 1.3 mils seems to require either some localized heating, which is possible in view of the exothermic nature of the hydride reaction, or diffusion along a residual beta path. Also, it is possible that the subsurface hydride is a metallographic artifact. Such artifacts are occasionally observed in titanium metallography.

Because of the marked effect of location within the reaction tube on the extent of surface hydriding, comparison of the relative hydriding behavior of 5Al-2.5Sn titanium and unalloyed titanium, as represented by the foil material, is probably not reliable. However, foil samples generally seemed to hydride somewhat more heavily than 5Al-2.5Sn alloy as shown, for example, in Figure 8.



500X 9F727

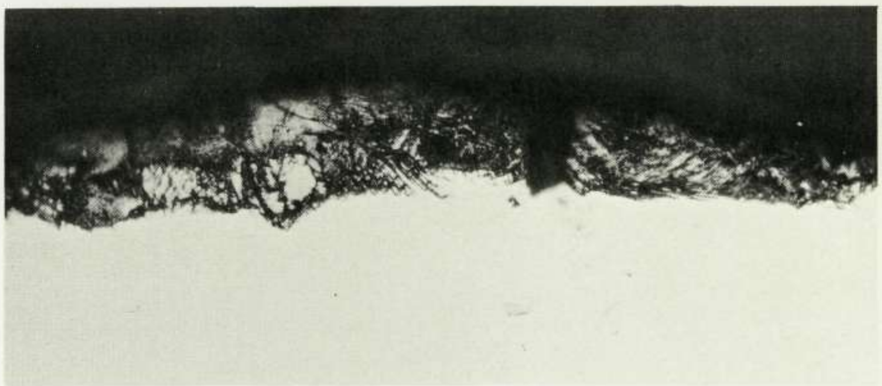
a. 5Al-2.5Sn Sample



500X 9F726

b. Foil Sample

FIGURE 8. SURFACE HYDRIDES FORMED IN RUN 31, 486 HOURS AT 75 F

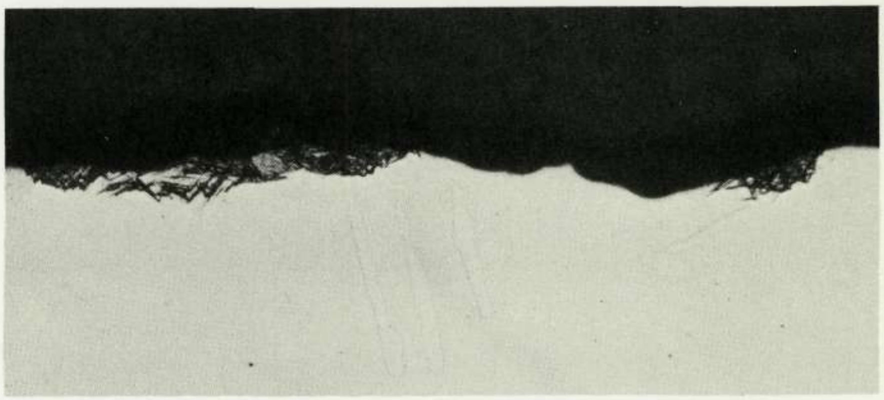


500X 8F743

a. Weld Sample — Run 7, 162 Hours at 75 F

500X 8F744

b. Wall Sample — Run 7, 162 Hours at 75 F



500X 8F700

c. Weld Sample — Run 4, 162 Hours at -36 F

FIGURE 9. SURFACE HYDRIDES ON SAMPLES SHOWING NONUNIFORM HYDRIDING

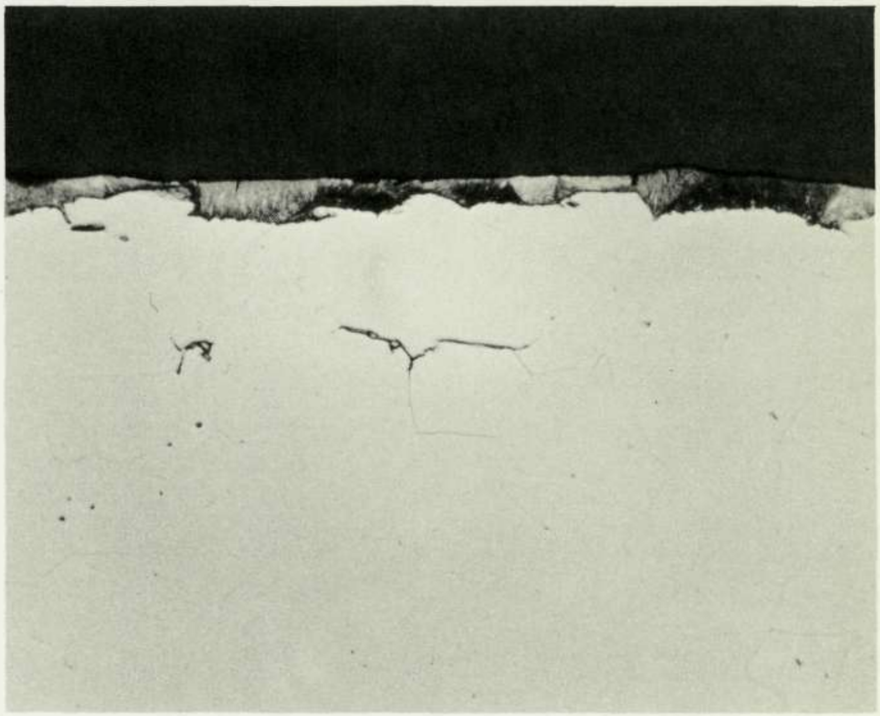


FIGURE 10. SUBSURFACE HYDRIDE IN RUN 31, 486 HOURS AT 75 F

Tensile Properties After Hydrogen Exposure

The tensile properties of 5Al-2.5Sn titanium samples exposed under various conditions to hydrogen at 250 psig are shown in Table 6. There was little evidence that surface hydriding was damaging to tensile properties as determined using conventional test procedures. The properties of samples from runs where the most extensive hydriding occurred are compared with average properties of base-line samples (from Table 4) below:

Run No.	Average Hydrogen Content, ppm	Ultimate Strength, ksi	Yield Strength, ksi	Elongation, percent	Reduction In Area, percent
Base Line	11	111.6	103.2	10	26
38	556	112.6	105.2	8(a)	30
31	216	114.0	105.4	10	23
7	142	118.7	108.0	15	32

(a) Failed outside gage marks.

Surface hydriding quite probably has a more pronounced effect on surface sensitive properties, such as fatigue behavior. Surface hydriding might also introduce surface notches leading to loss of load carrying ability under impact conditions.

Although the number of test results are too few for much reliance to be placed upon the observation, it was observed that both strength and ductility were lower after exposure at -160 F than at higher temperatures.

CONCLUSIONS

The present investigation permits the following conclusions to be made.

(1) Surface hydriding can occur when 5Al-2.5Sn titanium is exposed to hydrogen gas at 250 psig at temperatures appreciably below room temperature. The reaction is highly sensitive to experimental variables. During the present investigation, these variables were not under complete control. Incompletely resolved problems are believed to have arisen from three sources: inadequate removal of surface oxides during vacuum annealing, recontamination of cleaned surfaces as a result of air leaking into the reaction system during the cooling period, and inadequate hydrogen cleaniness.

TABLE 6. TENSILE PROPERTIES OF SAMPLES EXPOSED TO HIGH PRESSURE HYDROGEN

	Exposure Conditions					
Run No.	Temp., F	Time, hr	Ultimate Strength, ksi	0.2 Percent Offset Yield Strength, ksi	Elongation, percent	Reduction in Area, percent
38	160	162	112.6	105.2	8(a)	30
12	75	18	115.4	104.2	14	28
16	75	18	112.6	104.2	13	34
11	75	54	115.6	106.5	12	27
2	75	162	114.1	105.8	12	29
7	75	162	118.7	108.7	15	32
15	75	162	111.1	103.1	12	33
20	75	162	113.3	104.2	13	27
22	75	486	112.1	103.5	12	31
31	75	486	114.0	105.4	10	23
3	75	1458	115.5	108.9	7(a)	31
29	75	1458	110.2	101.2	12	29
13	-36	18	113.3	102.9	12	33
14	-36	54	115.0	106.6	15	32
4	-36	162	111.5	104.3	8	19
37	-36	162	115.0	106.6	11(a)	36
23	-36	486	110.8	103.3	12	30
36	-36	486	110.7	102.4	13	29
5	-36	890	116.9	108.3	15	37
27	-36	1458	112.6	101.7	16	30
24	-76	486	112.6	104.8	11	25
28	-76	1458	114.3	104.4	12	28
6	-110	162	115.8	107.1	6(a)	24
9	-110	1458	112.0	103.8	10	29
8	-160	162	111.3	113.1	7(a)	23
10	-160	486	104.8	96.5	6	25
17	-160	1458	107.0	100.0	9	30

(a) Failed on or outside gage mark.

(2) Hydriding is quite temperature sensitive. Reaction proceeds rapidly at 160 F and appreciable reaction occurs during exposures of only fractions of a minute slightly below 300 F. Reaction proceeds much more slowly at room temperature and below. Maximum hydride thickness, after two months exposure to hydrogen at 250 psig, can be expected to vary approximately as follows with temperature:

75 F	0.5 mil
0 F	0.08 mil
-50 F	0.015 mil

(3) Tensile properties as measured at 75 F with unnotched sheet samples at a slow strain rate are unaffected by hydride surface films up to about 1-mil thickness. Variations in microstructure produced during forging had more effect on tensile properties than surface hydrides.

(4) Internal hydriding at a slight depth below the surface hydride film can apparently occur in conjunction with surface hydriding. Subsurface hydride formation was observed at a depth of 1.3 mils in one sample.

(5) Hydride spalling can occur. However, it was observed only in one instance, during exposure at 160 F for 162 hours, where hydride films approximately 1-mil thickness were developed.

(6) No significant surface hydriding would be expected in 5Al-2.5Sn titanium pressure vessels used to store hydogen gas at 250 psig in 2 months if the termperature was maintained at -100 F or lower.

(7) Since surface hydride films up to 1 mil thick appear to have no detrimental effect on tensile properties (Conclusion No. 3),5Al-2.5Sn titanium pressure vessels would probably be unaffected by exposure to hydrogen at 250 psig for 2 months at temperatures appreciably above -100 F. As indicated above (Conclusion No. 2), hydride surface films less than one-tenth this thickness would be developed in 2 months at 0 F and only one-half this thickness in 2 months at 75 F.

RECOMMENDATIONS FOR FUTURE WORK

Additional work is desirable to locate the cause of the highly variable hydriding behavior observed in the present program and to eliminate it. Efforts should be made to refine the experimental techniques so as to obtain reproducible hydriding behavior in multiple tests at a selected exposure condition. This refined technique should then be used to

(a) Confirm that hydriding proceeds by parabolic kinetics.

(b) Confirm the temperature dependence of the hydriding reaction indicated by the present work.

It is also recommended that the effects of surface hydride films in the thickness range of interest (0.5 mil or less) on the fagigue and unnotched tensile impact properties of 5Al-2.5Sn titanium be determined. Relatively thin surface hydride films may prove more damaging to fatigue or impact properties than they are to tensile properties. Measurement of the effects of thin surface hydride films on tensile properties at subzero temperatures would also be of interest.

Further study of conditions under which internal hydrides form would also be desirable to determine whether subsurface hydrides are related to microstructural factors or to localized exothermic heating.

• • •

Data upon which this report is based are included in Battelle's Columbus Laboratory Record Books Number 29054 and 29424.

REFERENCES

(1) B. G. Koehl, D. N. Williams, and E. S. Bartlett, "Investigation of the Reaction of Titanium with Hydrogen", NASA CR-92389, Final Report on Contract NAS 9-7549, May 18, 1969.

(2) J. E. Reynolds, H. R. Ogden, and R. I. Jaffee, "A Study of the Air Contamination of Three Titanium Alloys", TML Report No. 10, July 7, 1955, Titanium Metallurgical Laboratory, Battelle Memorial Institute.

(3) R. J. Wasilewski and G. L. Kehl, "Diffusion of Hydrogen in Titanium", Metallurgica, Vol. 50, 1954, p 225.

(4) C. R. McKinsey, M. Stern, and R. A. Perkins, "Factors Affecting the Absorption and Distribution of Hydrogen in Titanium During Acid Pickling", Trans ASM, Vol. 50, 1958, p 438.

DNW/RAW:aas
May 15, 1972