SUMMARY REPORT

on

AN INVESTIGATION OF THE REACTION OF TITANIUM WITH HYDROGEN

to

NASA - MANNED SPACECRAFT CENTER
STRUCTURES AND MECHANICS DIVISION

July 14, 1966

Contract No. NAS 9-5298

by

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SUMMARY

The purpose of this investigation was to determine whether titanium and titanium alloys could be made to react consistently with hydrogen at low temperatures and low to medium pressures. The work was undertaken in three phases characterized as follows: (1) pressurized H_2 environment with unstressed specimens; (2) pressurized H_2 environment with stressed specimens; and (3) experiments where unstressed specimens were enclosed in a special glass system design.

Pressurized-Unstressed

A number of Ti-50A specimens were sealed in stainless steel reactors, annealed for 2 hours at 1500 F, and then pressurized to 15, 315, or 1000 psia hydrogen. Specimens at each pressure level were held at 75, 170, and 300 F, respectively, for periods of from 10 to 1000 hours.

Only 10 of 86 specimens reacted with hydrogen, and these did so in no apparent pattern. Deliberate contamination of a specimen with iron resulted in a slight reaction at 300 F and 315 psia hydrogen. Specimens contaminated with grease or nickel did not react during the same exposure.

Pressurized-Stressed

Eight tensile specimens of Ti-50A were exposed under various constant and cycling loads at 300 F and under 315 psia of hydrogen for periods of from 6 to 46 hours. No reaction occurred in any of the tests.

Seven specimens were galled with iron and nickel, or wrapped with iron and nickel wire, and exposed without concurrent stress for 22-1/2 hours at 300 F in 315 psia of hydrogen. Four of the seven specimens showed evidence of having reacted with hydrogen.

Glass-System Experiments

A glass vacuum system capable of maintaining pressures on the order of 0.05 micron or less was used to investigate, at room temperature and atmospheric pressure:

(1) The effect of galling of the specimen surface with iron and nickel. Galling appeared to promote reactions in some experiments.

(2) The necessity of producing and maintaining a clean surface on the specimen to assure a reaction with hydrogen. This factor was of extreme importance in inducing the reaction to proceed at room temperature.

(3) The need for removing contaminants, especially oxygen, from the hydrogen. A liquid nitrogen cold trap was generally required to insure that the reaction would proceed.

(4) The reaction of the titanium alloys B120VCA, Ti-6Al-4V, and Ti-5Al-2.5Sn with hydrogen. The first two alloys reacted more readily than unalloyed titanium, while the last alloy was less reactive. However, a definite reaction was observed in all three alloys.

Proposed Future Work

The following are areas worthy of investigation in future work:

(1) A study of the effect of increased pressures on the reactions previously demonstrated at atmospheric pressure.

(2) An investigation of the effect of annealing treatments designed to promote the reaction on the surface of the specimens.

(3) A study of the effect of stressing specimens while in a very low impurity-content hydrogen atmosphere. A stress treatment might cause the reaction to proceed without a high-temperature surface cleaning treatment.

(4) A search for a possible coating for titanium or the minimum quantity of contaminant to be added to the hydrogen to reliably inhibit the reaction with hydrogen.

INTRODUCTION

Titanium alloys would be desirable, because of their relatively low density, in future space vehicles for the construction of liquid-hydrogen storage vessels. As liquid hydrogen is consumed, the tank walls and plumbing come into contact with gaseous hydrogen, occasionally at moderately elevated temperature and pressure. Little is known about the reaction of hydrogen gas with titanium at moderate temperatures. It has been reported that hydriding occurs at a low rate when unalloyed titanium is exposed to hydrogen gas at 300 F[(1)*] and that precleaned titanium will react with hydrogen at room temperature[(2)].

During testing of several liquid-hydrogen storage tanks, failures have occurred that were attributed to excessive surface hydriding.[(3)] The erosion resulting from spalling of the surface hydride was restricted largely to the heat-affected zone of welds, suggesting that either microstructure or contamination may have affected the reaction. However, in at least one case, surface hydriding extended several inches away from the weld.

In view of the contemplated use of titanium-alloy liquid-hydrogen tanks in a number of critical components, it is desirable to determine the factors that affect the reaction of gaseous hydrogen with titanium and titanium alloys. This study was initiated to determine these factors.

MATERIAL

Titanium materials were obtained from Titanium Metals Corporation of America (TMCA). The chemical analysis and mechanical properties of the materials purchased are given in Table 1.

Hydrogen gas was obtained from the Matheson Company. Ultrapure-grade hydrogen with a dew point of lower than -80 F and impurities of <1 ppm O_2, <5 ppm N_2, and <1 ppm total hydrocarbons (as CH_4), was used for most of the program.

*References are listed on page 41.

TABLE 1. ANALYSIS AND MECHANICAL PROPERTIES OF THE TITANIUM AND TITANIUM ALLOYS

Chemical Analysis of Alloys As Received[a]

Alloy	Percent by Weight									
	C	Fe	N	Al	V	Cr	H	Sn	Mn	O
Ti-50A	.023	.10	.012	--	--	--	.003	--	--	.11[b]
Ti-75A	.025	.15	.019	--	--	--	.004	--	--	.33
Ti-5Al-2.5Sn ELI	.023	.12	.013	5.2	--	--	.009	2.4	.006	.08
Ti-6Al-4V ELI	.023	.12	.013	5.9	3.9	--	.007	--	--	.08[b]
B-120-VCA	.019	.16	.028	3.1	13.6	11.1	.016	--	--	.17

Mechanical Properties of Alloys As Received[a]

		Yield Strength, psi	Tensile Strength, psi	Elongation percent	Bend Test	Gage, in.
Ti-50A	L[c]	53,500	66,100	29.0	1.5	.032
Ti-75A	L	80,000	97,300	24.5	2.0	.059
	T	86,700	96,400	26.0	1.5	
Ti-5Al-2.5Sn ELI	L	104,300	110,600	18.5	3.5	.057
	T	110,300	113,900	17.0	3.5	
Ti-6Al-4V ELI	L	133,800	142,400	12.0	4.0	.036
	T	134,600	140,200	14.0	4.0	
B-120-VCA[d]	L	134,900	138,500	16.0	2.5	.025
	T	139,800	142,500	13.0	2.5	
B-120-VCA	L[e]	182,500	198,900	5.5	--	--
	T	190,600	203,800	4.0	--	--

(a) Data furnished by TMCA, except as noted.
(b) Battelle analysis.
(c) L = longitudinal to the rolling direction, T = transverse to the rolling direction.
(d) B-120-VCA was received in the solution-treated condition; the values here are for the as-received condition.
(e) Information supplied on mill tests; aged 20 hr at 900 F.

PHASE 1. PRESSURIZED-UNSTRESSED EXPERIMENTS

Experimental Methods

Nine pressure reactors for use in this phase of the work were constructed of Type 304 stainless steel tubing of 1-inch ID by 2-inches OD and 10-inch length. A 4-foot length of 1/4-inch ID pressure tubing was welded to one end of the reactor. This was used to facilitate evacuation during annealing in a large muffle furnace, in addition to serving as a means of filling the reactor with hydrogen and handling in an oil bath. A solid, threaded, stainless steel plug was welded in the opposite end of the reactor after the specimens were placed inside. All reactors were cleaned with cp acetone before each experiment.

Specimens 4 inches long by 3/4 inch wide and 0.032 inch thick were cut from the Ti-50A sheet and prepared as follows:

(A) Mill annealed – no treatment

(B) Heat treated 1/2 hr at 1750 F, slow cooled

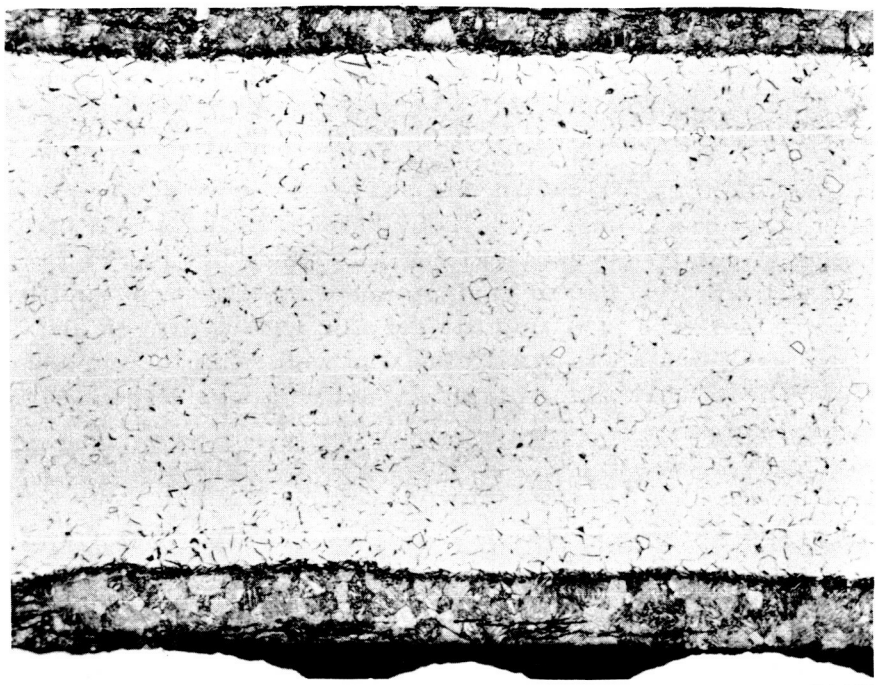
(C) Heat treated 1/2 hr at 1750 F, water quenched

(D) Mill annealed, with a weld bead laid on the length of the specimen.

Heat treatments were made in Vycor glass capsules under a partial pressure of argon. The glass capsule was broken under water to quench the (C) specimens as they were removed from the furnace. The (B) specimens in their capsules were buried in a barrel of vermiculite as soon as they were taken from the furnace. The quenched samples (C) were somewhat distorted and covered with a very adherent oxide film that had to be removed by blasting grit. Figures 1 to 3 illustrate the microstructures resulting from these treatments. These may be described as equiaxial alpha [treatment (A)], coarse acicular alpha [treatment (B)], and fine acicular alpha [treatment (C)].

All of the specimens, except where noted, were pickled for about 20 seconds in a solution of 30 parts concentrated HNO_3, 5 parts 28 percent HF, and 60 parts H_2O, rinsed in H_2O and methyl alcohol, then placed in the reactor and a plug welded in the open end. Those specimens not pickled were abraded dry with No. 240 grit SiC paper and rinsed in cp acetone. One each of the mill-annealed, slow-cooled and water-quenched specimens were used in each reactor. Periodically, a fourth specimen, the one with the weld bead, was added.

After sealing the specimens inside the reactors, the reactors were evacuated in groups of three to a pressure of 10 microns or less by a mechanical pump, then placed in a muffle furnace that had been preheated to 1500 F, and held at temperature for 2 hours. During this anneal, any surface oxide was dissolved. The best vacuum that could be obtained during the annealing period was about 5 to 10 microns. The specimens were cooled under vacuum, then the reactors were sealed and transferred to a manifold where they were filled with ultrapure hydrogen, trapped with liquid nitrogen, calculated to give the required pressure at the temperature of the experiment.



100X OA039

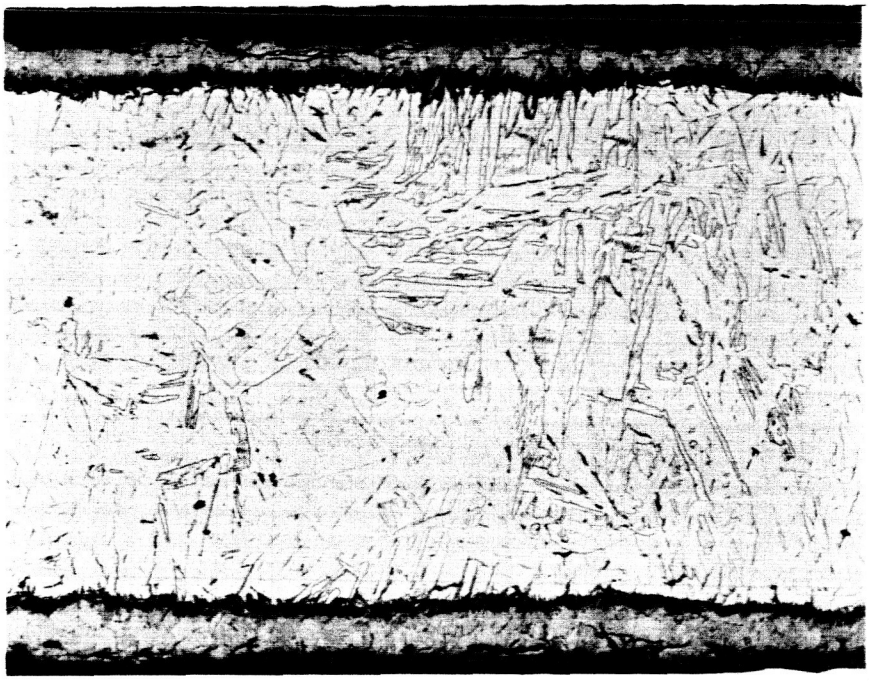
FIGURE 1. MILL-ANNEALED Ti-50A AFTER 10-HOUR EXPOSURE TO HYDROGEN AT 300 F AND 315 PSIA

As-received material, previously vacuum annealed 2 hr at 1500 F. Note uniformity of hydride coating.

100X OA040

FIGURE 2. Ti-50A SLOW COOLED FROM ABOVE BETA TRANSUS, AFTER 10-HOUR EXPOSURE TO HYDROGEN AT 300 F AND 315 PSIA

Note uneven penetration and tendency of hydride to spall. This structure is similar to that found in the heat-affected zone of a weld.



100X OA041

FIGURE 3. Ti-50A QUENCHED FROM ABOVE BETA TRANSUS, AFTER 10-HOUR EXPOSURE TO HYDROGEN AT 300 F AND 315 PSIA

The manifold used for filling the reactors with hydrogen was constructed of high-pressure, 1/4-inch ID stainless steel tubing, high-pressure valves, a gage, and "Ermeto" high-pressure fittings. A U-shaped bend in the tubing was utilized as a cold trap. Later, a stainless steel reactor filled with zirconium turnings was connected in the line and when heated to ~1560 F acted as a getter for the hydrogen (Figure 4).

Removal of the reactor from the manifold was accomplished by closing the high-pressure valve at the end of the long tube welded to the reactor. This served to isolate the hydrogen in the reactor. No leaks were ever detected in the reactors or the valves.

After filling with hydrogen to the correct pressure and removal from the manifold, the reactors were placed in one of two oil baths maintained at 300 F and 170 F, respectively, and allowed to remain at temperature for the specified time of the experiment. For the experiment at 75 F, the pressurized reactors were placed in a constant-temperature room maintained at 75 F.

At the completion of each experiment the specimens were removed from the reactors and sectioned. A portion was sent to the Vacuum Fusion Laboratory for hydrogen analyses and a portion to the Metallographic Laboratory to be mounted and polished for microscopic examination.

Results and Discussion

The supporting data and results of all the work on this phase are shown in Table 2. Table 3 is a summary of the data shown in Table 2. From Table 3, one can see at a glance those conditions that resulted in a titanium-hydrogen reaction. It is interesting to note that seven of the ten specimens that reacted with hydrogen did so at 315 psia. The six containing the heaviest hydride concentration (over 4000 ppm) were exposed for only 10 or 100 hours. The thickness of the hydride layer on these specimens is given in Table 4 and typical photomicrographs in Figures 1 to 3. The hydride layer was quite uniform and slightly heavier on those specimens reacted for 100 hours than on those reacted for 10 hours. In both cases, the layer on the slow-cooled (B condition) specimens was the heaviest and most irregular. Hydride spalling from the B samples had occurred. The remaining 4 samples that showed hydride formation reacted to much less an extent and in a spotty manner. There was no evidence that hydride reaction at one point on the specimen results in general hydriding. Cases of very localized attack were noted. No reactions occurred at temperatures of 170 F or 75 F.

Another point that is worth noting but unexplained is that nine of the ten specimens that reacted did so in reactors that were used for the first time. Possibly some contaminant remained in the new reactors, and during the anneal sensitized the specimen surfaces so that some would react with the hydrogen.

In the light of findings in subsequent work, Phase 3 of this project, it is believed that surface oxide contamination remaining after the rather poor vacuum obtained during the 2-hour, 1500 F anneal inhibited a hydride reaction. No definite explanation is available for why 10 specimens of a total of 86 did react; however, again in the light of our subsequent work, a possible explanation is forthcoming. As will be discussed in a later section of this report, it was found to be possible to cause a titanium-hydrogen reaction to occur by galling or scratching the specimen with iron or nickel. All the specimens in this first phase of the work were cut on a steel shear and handled with

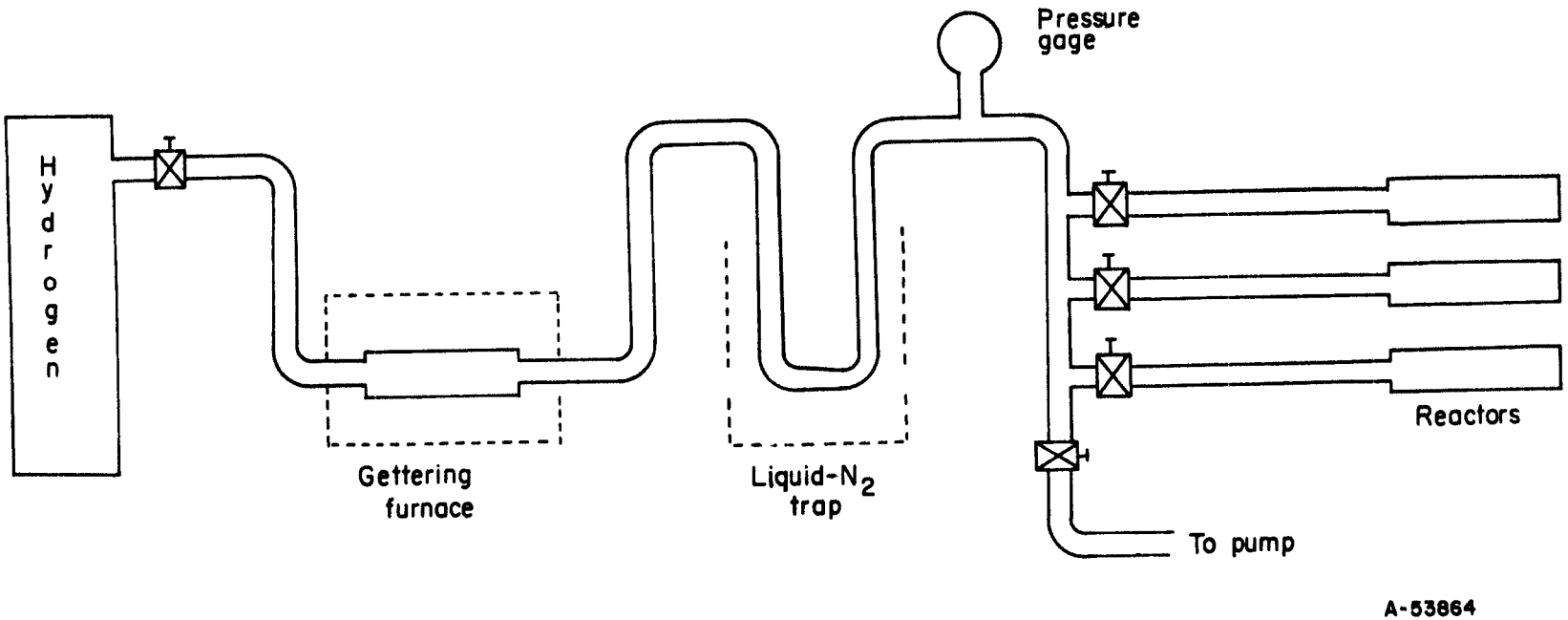


FIGURE 4. DIAGRAM OF MANIFOLD FOR FILLING REACTORS WITH HYDROGEN

Sketch does not show tees, unions, pressure-relief valve, or pressure-regulating valve.

TABLE 2. RESULTS OF PRESSURIZED-UNSTRESSED EXPERIMENTS

Reactor	Specimen	Condition[a]	Exposure: Temperature, F	Exposure: Time, hr	Exposure: H_2 Pressure, psia	Gas Analysis: H_2, ppm	Gas Analysis: O_2, ppm	Gas Analysis: H_2 (ends), ppm[b]	Remarks
--	--	As received	--	--	--	19	948	--	--
1	1	A	--	--	--	60	1110	--	After vacuum anneal
	2	B	--	--	--	54	1015	--	Ditto
	3	C	--	--	--	54	1257	--	"
1	4	A	300	10	15	26	--	--	No reaction
	5	B	300	10	15	27.5	--	--	Ditto
	6	C	300	10	15	33	--	--	"
7	7	A	300	10	315	4355	--	--	All heavily hydrided; Specimen B was pitted and hydride had spalled
	8	B	300	10	315	4315	--	--	
	9	C	300	10	315	4320	--	--	
4	10	A	300	10	1000	88	--	--	No reaction
	11	B	300	10	1000	83	--	--	Ditto
	12	C	300	10	1000	81	--	--	"
9	13	A	300	100	15	91	--	--	Ditto
	14	B	300	100	15	68	--	--	"
	15	C	300	100	15	73	--	--	"
6	16	A	300	100	315	5090	--	--	All heavily hydrided; Specimen B was pitted and hydride had spalled
	17	B	300	100	315	5235	--	--	
	18	C	300	100	315	5050	--	--	
3	19	A	300	100	1000	71	--	--	No reaction
	20	B	300	100	1000	67.5	--	--	Ditto
	21	C	300	100	1000	70.5	--	--	"
	22	Weld	300	100	1000	77	--	--	"
7	23	A	170	100	15	44.5	--	--	Ditto
	24	B	170	100	15	46	--	--	"
	25	C	170	100	15	48	--	--	"
	26	Weld	170	100	15	46	--	--	"
4	27	A	170	100	315	43	--	--	"
	28	B	170	100	315	41	--	--	"
	29	C	170	100	315	48	--	--	"
	30	Weld	170	100	315	46	--	--	"
1	31	A	170	100	1000	32.5	--	--	"
	32	B	170	100	1000	38	--	--	"
	33	C	170	100	1000	39	--	--	"

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TABLE 2. (Continued)

Reactor	Specimen	Condition[a]	Exposure: Temperature, F	Exposure: Time, hr	Exposure: H_2 Pressure, psia	Gas Analysis: H_2, ppm	Gas Analysis: O_2, ppm	Gas Analysis: H_2 (ends), ppm[b]	Remarks
8	34[c]	A	300	1000	15	189, 61, 66	--	80, 77	
	35	B	300	1000	15	67, 129, 213	--	310, 38	Very heavy hydride on one end
	36	C	300	1000	15	69, 67	--	71, 72	
	37	Weld	300	1000	15	69, 43, 90	--	193, 74	Spotty reaction found metallographically
5	38	A	300	1000	315	79, 53, 110	--	62, 107	No reaction
	39	B	300	1000	315	73, 70	--	64, 72	Ditto
	40	C	300	1000	315	141, 222	--	139, 198	Start of extensive reaction
	41	Weld	300	1000	315	110, 81	--	86, 69	No reaction
2	42	A	300	1000	1000	58	--	--	Ditto
	43	B	300	1000	1000	67.5	--	--	"
	44	C	300	1000	1000	77	--	--	"
9	45	A	170	1000	15	34	--	33	"
	46	B	170	1000	15	35.5	--	31	"
	47	C	170	1000	15	35.5	--	34	"
	48	Weld	170	1000	15	40	--	36	"
6	49	A	170	1000	315	43	--	43	"
	50	B	170	1000	315	42	--	41.5	"
	51	C	170	1000	315	41	--	43	"
	52	Weld	170	1000	315	39	--	46.5	"
3	53	A	170	1000	1000	43	--	47	"
	54	B	170	1000	1000	41	--	40	"
	55	C	170	1000	1000	44	--	60, 42	"
7	56	A	75	1000	15	33	--	--	"
	57	B	75	1000	15	33.5	--	--	"
	58	C	75	1000	15	36.5	--	--	"
	59	Weld	75	1000	15	32	--	--	"
4	60	A	75	1000	315	31	--	--	"
	61	B	75	1000	315	31	--	--	"
	62	C	75	1000	315	32.5	--	--	"
	63	Weld	75	1000	315	32.5	--	--	"
1	64	A	75	1000	1000	34	--	--	"
	65	B	75	1000	1000	31	--	--	"
	66	C	75	1000	1000	32.5	--	--	"
2	67[d]	A	300	20	15	(f)	--	--	"
	68	B	300	20	15	(f)	--	--	"
	69	C	300	20	15	(f)	--	--	"
	70	Weld	300	20	15	(f)	--	--	"

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TABLE 2. (Continued)

Reactor	Specimen	Condition[a]	Exposure: Temperature, F	Exposure: Time, hr	Exposure: H_2 Pressure, psia	Gas Analysis: H_2, ppm	Gas Analysis: O_2, ppm	Gas Analysis: H_2 (ends), ppm[b]	Remarks
5	71	A	300	20	315	(f)	--	--	No reaction
	72	B	300	20	315	(f)	--	--	Ditto
	73	C	300	20	315	(f)	--	--	"
	74	Weld	300	20	315	(f)	--	--	"
8	75	A	300	20	1000	(f)	--	--	"
	76	B	300	20	1000	(f)	--	--	"
	77	C	300	20	1000	(f)	--	--	"
9	78[e]	A	300	20	15	(f)	--	--	"
	79	B	300	20	15	(f)	--	--	"
	80	C	300	20	15	(f)	--	--	"
7	81	A	300	20	315	(f)	--	--	"
	82	B	300	20	315	(f)	--	--	"
	83	C	300	20	315	(f)	--	--	"
3	84	A	300	20	1000	(f)	--	--	Possible very small areas of surface
	85	B	300	20	1000	(f)	--	--	reaction, Specimens 84 and 85
	86	C	300	20	1000	(f)	--	--	Extensive surface-hydride formation

(a) A = mill annealed; B = slow cooled from 1750 F; C = quenched from 1750 F. All specimens were vacuum annealed 2 hrs at 1500 F just before exposure.
(b) Additional specimens were taken from near the outer ends of some specimens because of the very erratic results obtained from analysis of Specimens 34 through 41. Metallographic examination of Specimens 35 and 37 also disclosed very great differences in nearby areas.
(c) All analyses are the average of two determinations, except on Specimens 34 through 41, where duplicate analyses tended to vary too greatly to justify reporting only the average value.
(d) For Specimens 67 through 77, the zirconium-filled gettering furnace was used for the first time.
(e) For Specimens 78 through 86, abraded samples only; used zirconium-filled gettering furnace.
(f) No analysis was made on Specimens 67 through 86, inclusive, since it appeared certain that no hydrogenization had occurred except as noted.

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TABLE 3. SUMMARY OF THE RESULTS OF PRESSURIZED-UNSTRESSED EXPERIMENTS

Temperature, F	Time, hr	Number of Samples that Reacted[a] at Indicated Pressure		
		1000 psi	315 psi	15 psi
300	1000	0	1	2
	100	0	3	0
	20	1	0	0
	10	0	3	0
170	1000	0	0	0
	100	0	0	0
75	1000	0	0	0

(a) In each case, three samples of differing microstructure were exposed. In some cases, a weld sample was also exposed.

TABLE 4. THICKNESS OF HYDRIDE LAYER ON SPECIMENS HYDRIDED AT 300 F AND 315 PSIA

Specimen[a]	Condition[b]	Thickness of Hydride Layer, Average, in.	Time of Exposure, hr
7	A	0.0025	10
8	B	0.0035[c]	10
9	C	0.00275	10
16	A	0.0030	100
17	B	0.0045[c]	100
18	C	0.0028	100

(a) Specimen numbers correspond to those in Table 2.

(b) Condition: A - mill annealed
B - 1/2 hr at 1750 F and slow cooled
C - 1/2 hr at 1750 F and quenched

All specimens were subsequently heat treated 2 hr at 1500 F and slow cooled to room temperature under vacuum prior to exposure to hydrogen.

(c) Some hydride spalling had occurred on these samples.

nickel-plated forceps. It is possible that these contacts were sufficient to start the reaction in a few cases.

In order to attempt to explain the erratic hydriding behavior of the specimens just discussed, eight specimens were given the standard pickling treatment, and were then deliberately contaminated as shown in the following tabulation:

Reactor	Specimen	Condition	Method of Contamination
1	87	B	Two large fingerprints
	88	B	Rubbed with pure-iron rod chucked in lathe; part of the specimen was roughened with a file
	89	B	Welded specimen that had been smeared with grease before welding
2	90	B	A piece of mild steel wire was covered with oil and placed in one end of the bomb, not in contact with the titanium
3	91	A	Impure hydrogen
	92	B	Impure hydrogen
	93	C	Impure hydrogen
	94	B	Scratched with iron and nickel and impure hydrogen

Specimens 91 through 94 were dry abraded with No. 240 grit SiC paper and the reactor filled with ordinary tank hydrogen with a dew point of -40 F or above.

All eight specimens were given the 2-hour 1500 F vacuum anneal, then the reactors were filled with hydrogen calculated to give 315 psia at temperature, and placed in an oil bath at 300 F. Reactors 1 and 2 were reacted for 112 hours and Reactor 3 for 120 hours.

Only Specimen 88 in Reactor 1 showed any evidence of hydriding. The hydride was quite spotty, on one side of the specimen only (Figures 5 and 6). The reaction observed in this run suggests that iron contamination may favor the initiation of the hydriding reaction. Further investigation of the role played by iron and nickel galling is reported in a subsequent section of this report.

Tank hydrogen contains a high percentage of oxygen (0.06%). This was not trapped with liquid nitrogen prior to exposure of the samples in Reactor 3. Later work has shown that very small amounts of oxygen mixed with the hydrogen strongly inhibit the hydriding reaction. This no doubt prevented any reaction between the specimens and hydrogen in Reactor 3.

Since the specimens exposed to oil or grease did not react, it may tentatively be concluded that these agents were not the cause of the reaction being found in certain cases. It had been suggested that oil or grease could be present in new reactors, leading to the preferences for reaction during the first exposure in the reactor.

250X 2A731

FIGURE 5. Ti-50A SPECIMEN CONTAMINATED WITH IRON AFTER 112-HOUR EXPOSURE TO HYDROGEN AT 300 F AND 315 PSIA

Hydride has formed in contaminated areas.

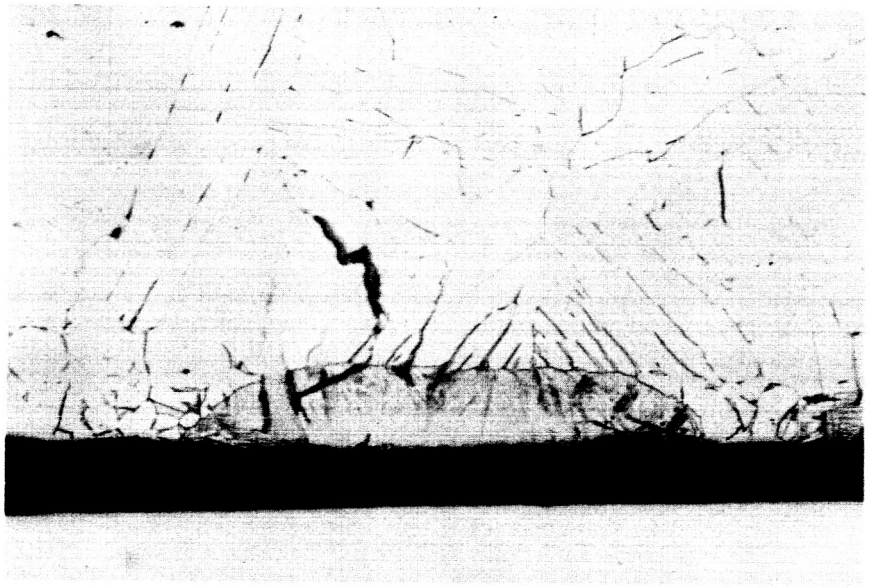

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FIGURE 6. ANOTHER AREA OF SPECIMEN SHOWN IN FIGURE 5

PHASE 2. PRESSURIZED-STRESSED EXPERIMENTS

Equipment

The second phase of the work was performed to determine whether stress applied to the titanium specimens while pressurized to 315 psia hydrogen at 300 F would initiate a reaction with hydrogen.

Tensile specimens were cut from 32-mil Ti-50A material with the following dimensions: length, 2-11/16 inches; gage length, 1 inch; and gage width, 0.19 inch. The specimens were etched in the same manner as those in Phase 1, and, where noted, some were dry abraded with No. 240 grit SiC paper.

The experiments were carried out in a standard high-pressure autoclave that had been modified so that a known load could be placed on the specimen by a small, hand-operated, hydraulic pump. The force was applied to a piston that in turn applied a load to the specimen through a stainless steel rod connected to the specimen. This rod passed through a Teflon-gasketed hole in the autoclave cover. A drawing of the autoclave is shown in Figure 7.

Preliminary tests were made both in air and in hydrogen, on a tensile machine, to determine the yield strength at 300 F of the Ti-50A material. Yield strength was determined to be 32,400 psi in both atmospheres. This value was used in calculating the loads to be applied in subsequent tests.

The manifold used in Phase 1, with a few minor changes to accommodate the autoclave, was used to evacuate and fill the autoclave.

Results and Discussion

Eight tests were made in this phase of the work. Table 5 summarizes the results. In two tests, the load was cycled every 15 minutes for 6 hours; in five tests, the load was held constant; in one test, the load was increased progressively with time. One specimen (T-6) was preoxidized to produce an oxide layer that, it was hoped, would crack under load and expose a clean surface to the hydrogen. Specimen T-10 was purposely hydrided to 500 ppm, then degassed. This procedure was intended to open rifts in the metal that would provide paths for the hydrogen to enter. After 46 hours under load, including 6 hours of cycling the load every 15 minutes, Specimen T-10 was removed. As there was no evidence of a reaction having taken place, the specimen was rehydrided and degassed nine additional times, reabraded and returned to the autoclave for test under load. The 130-lb load was applied for 4 hours and then increased until the specimen broke.

There was no indication of reaction with hydrogen in any of the tests. Even Specimen T-10, which was broken in hydrogen at 300 F, showed no hydride layer along the broken edge; it showed only widened grain boundaries, presumably caused by interstitial hydrogen that had been added to attempt to open rifts in the metal and then removed.

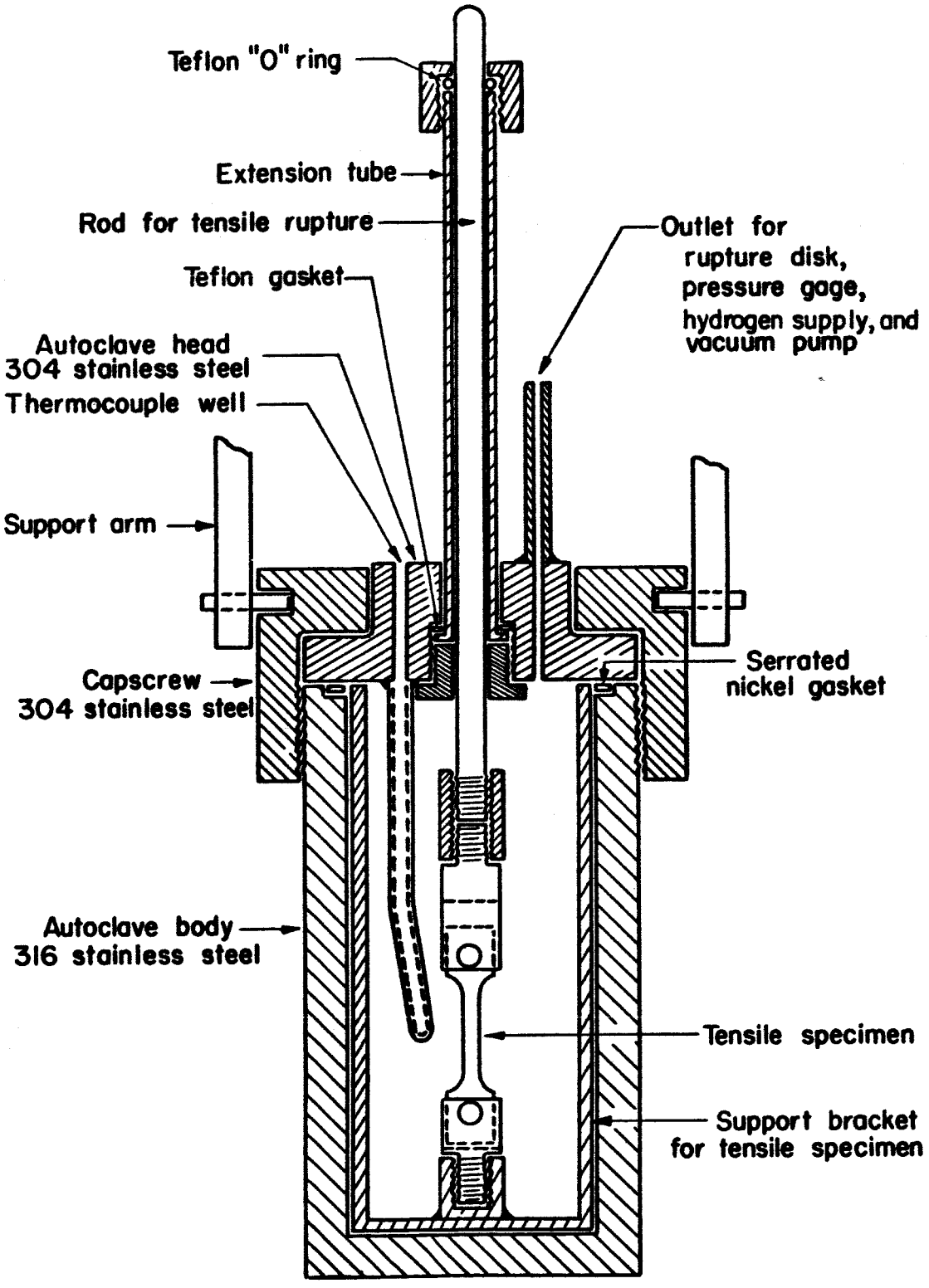


FIGURE 7. DIAGRAM OF STRESS ASSEMBLY

TABLE 5. SUMMARY OF DATA ON STRESSED Ti-50A SPECIMENS AT 300 F IN 315 PSIA HYDROGEN

Specimen[a]	Time, hr	Stress, psi[a]	Load, lb	Permanent Elongation 1", percent	Remarks
T-3	6	21,600	129	0.0	Held under constant load
T-4	6	32,400	200	2	Held under constant load
T-5	6	980	59		Cycled each 15 min between the low and high stress
		32,400	196	2.3	"
T-6	6	32,400	197	0.0	Oxidized 45 min at 1300 F in air before test
T-7	6	32,400	197	<3	Same sample as T-6; load progressively increased[b].
		38,300	233		Degreased only; analysis after run 56 ppm hydrogen
T-8	6	39,000	354	4	Larger sample; abraded, pumped on overnight
T-9	29	39,000	358	6.5	Larger sample; abraded, evacuated 1 hr, added H_2, began run
T-10	46	980	59		Check of the Rift Theory[4] (see text for details); cycled
		32,400	194	11.0	each 15 min between low and high stress

(a) Specimens T-3 through T-7 and T-10, with a mill annealed structure, had a cross-section area in the gage length of 0.0060+ in^2. Specimens T-8 and T-9, with a coarse, acicular structure (Condition B), had a cross-section area of ~0.0091 in^2.
(b) Stress on Specimen T-7 was successively 32,400 psi for 2.5 hr; 35,200 psi for 3.2 hr; and 38,300 psi for 0.3 hr.

In this phase, as in Phase 1, a high vacuum was not attained prior to hydrogen addition. Although a diffusion pump was added to the pumping system and evacuation continued overnight, the best vacuum obtainable was about 2 to 4 microns. Another factor that tended to favor contamination of the specimens was the time interval between pickling or abrading and evacuation. This, of a necessity, was often 1/2 to 3/4 hour. In addition, the specimen surfaces could not be cleaned and activated by annealing at 1500 F because of the construction of the autoclave.

From the information acquired later in Phase 3 of this work relative to the need for surface cleanliness of the titanium before a reaction can take place with hydrogen, it is not surprising that no reactions occurred here.

The autoclave was also used to test more thoroughly than in Phase 1 the effect of iron and nickel contaminants on the reaction of hydrogen with titanium. Seven pieces of as-received Ti-50A, 2 inches x 3/4 inch, were prepared as follows (pickling, where noted, was done before contaminating; all specimens were contaminated on both sides in the same manner):

Specimen	Pickled	Method of Contamination
B-1	No	Rubbed[a] in separate areas with Fe and Ni rods
B-2	No	Rubbed with iron bolt on one end, wire brushed on other end
B-3	No	Wound on opposite ends with Ni ribbon and Fe wire
B-4	Yes	Rubbed with Fe rod on one end, bound with Fe wire on other
B-5	Yes	Rubbed with Ni rod on one end, bound with Ni ribbon on other
B-6	Yes	Rubbed with iron bolt on one end, scratched with nickel-plated steel tweezers on other
B-7	Yes	Wire brushed all over

(a) "Rubbing" with iron and nickel rods and with an iron bolt was accomplished by putting the rods or bolt in a drill press and bearing down heavily with the rotating piece onto the specimen.

To avoid other contaminants, the specimens were handled with clean gloves and suspended in the autoclave by tungsten wires passed through small holes that previously had been drilled near one end of each specimen. All seven specimens were exposed at one time.

The autoclave was evacuated and filled with hydrogen on the manifold in the usual manner. The specimens were held at 300 F in 315 psia hydrogen for 22-1/2 hours. Examination of the specimens after exposure showed reaction occurring on four of the seven specimens in the following manner:

B-1 Galled with iron rod; showed small hydrided areas on one side where heavily galled and on one unscratched area. The opposite side, also galled, showed none.

B-1 Galled with nickel rod; showed small hydrided areas where galled heavily on both sides.

B-2 Galled with an iron (low-carbon steel) bolt; showed no hydrided areas.

B-2 Wire brushed; showed no hydride.

B-3 Wound with iron wire; probably showed no reacted areas, although a strange marking was noted in one spot.

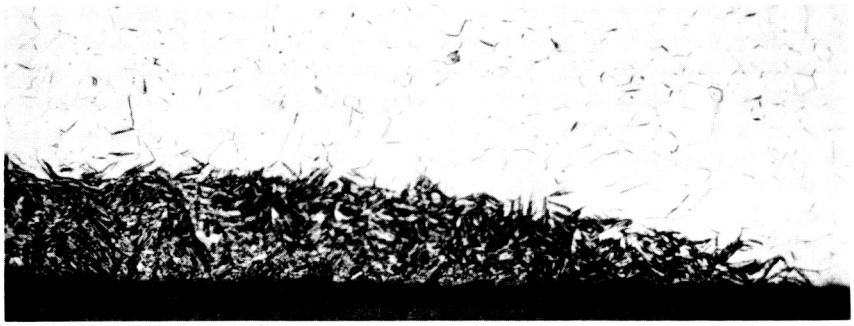
B-3 Wound with nickel ribbon; was definitely hydrided in spots on both edges. Hydride spots also were noted on three of the four corners.

B-4 Pickled, then galled with iron rod; was definitely hydrided under the galled areas on both sides of the specimen.

a. Specimen B-1.
Hydride on area galled with iron rod

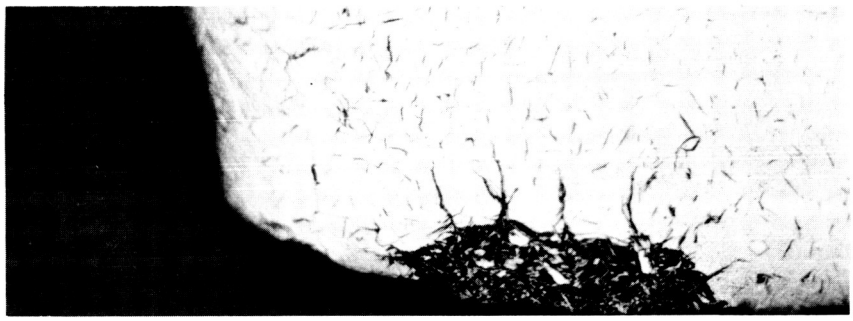
250X 2A956

b. Specimen B-3.
Hydride under nickel ribbon



250X 2A962

c. Specimen B-3.
Hydride near corner of specimen, away from ribbon or galling



250X 2A963

d. Specimen B-4.
Hydride under area galled with iron rod

250X 2A958

FIGURE 8. MILL-ANNEALED, CONTAMINATED, Ti-50A, AFTER 22-1/2-HOUR EXPOSURE TO HYDROGEN AT 300 F AND 315 PSIA

No pretreatment by vacuum annealing.

B-4 Pickled, bound with iron wire; showed no signs of having reacted with hydrogen.

B-5 Pickled, bound with nickel ribbon; did not react.

B-5 Pickled, galled with nickel rod; did not react.

B-6 Pickled, galled with iron (steel) bolt; did not react.

B-6 Pickled, scratched with tweezers; did not react.

B-7 Pickled, wire brushed all over; did not react.

Figure 8 shows various areas of some of these specimens.

From these data the conclusion can be drawn that galling with nickel and iron, and contact with nickel ribbon, will cause hydriding to take place in some cases. Evidently pickling tends to passivate the surface and to minimize the chance for reaction as only half of one specimen which had been pickled, reacted with hydrogen. None of the samples were precleaned by vacuum annealing. It should also be noted that no evidence of rapid lateral growth of the hydride from the areas of initial reaction were observed.

It is not known at this time how iron and nickel function in initiating the hydriding reaction. Additional work examining the effect of iron and nickel is discussed in Phase 3 of this report.

PHASE 3. GLASS-SYSTEM EXPERIMENTS

Experimental Methods

The somewhat erratic and unreliable results obtained in the work completed on Phases 1 and 2 of this project emphasized the need for equipment where conditions could be reproduced and more closely controlled. A system was needed where an accurate measurement of the quantity of hydrogen absorbed by the titanium could be made and above all a system where a good vacuum could be maintained. Such a system, shown schematically in Figure 9, was available at Battelle. With a general overall cleaning and a few minor alterations it was suitable for use on this project.

The glass system consists of a mechanical pump, glass mercury diffusion pump, and a cold trap, which together made up the pumping system. Three large gas-storage reservoirs are attached to the main pump-out line. These were not used in this work and were closed-off by means of large stopcocks. A full-length, open-end mercury manometer was connected in the line and used to measure pressure change during the experiment. Knowing the calibrated volume of the system (493 ml STP) and the pressure change, the quantity of hydrogen absorbed during a run was easily calculated. An ionization gage was used to monitor the system pressure during evacuation and annealing. The reaction tube was constructed of 25-mm Vycor and was about 12 inches in length. It was heated by a resistance-wound furnace that was monitored by a

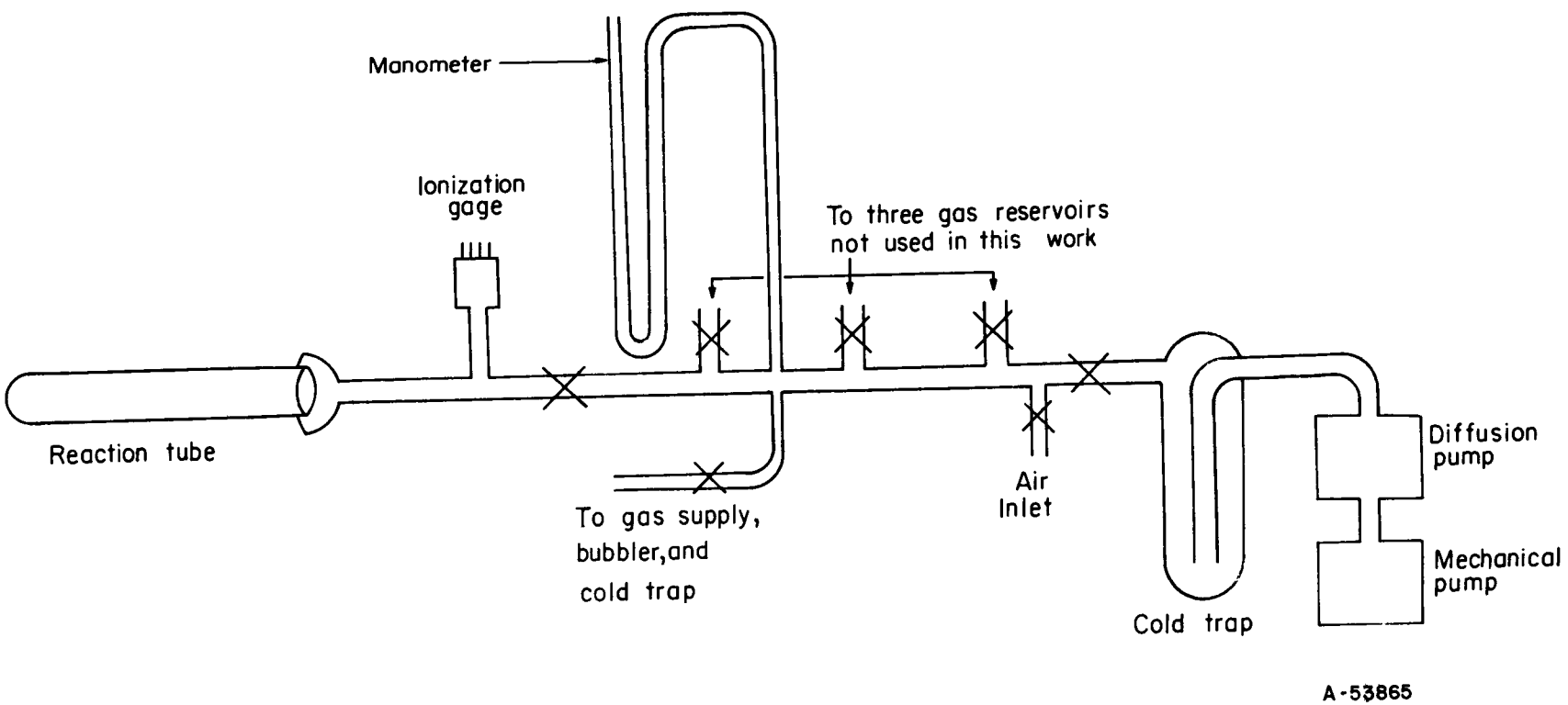


FIGURE 9. DIAGRAM OF GLASS SYSTEM

Foxboro Controller. The main pump-out line was constructed of 12-mm Pyrex tubing, except for the portion just preceding the reaction tube, which was 25 mm ID. Hydrogen was admitted to the system after first passing through a mercury safety bubbler and a liquid-nitrogen cold trap. Any departures from this procedure are noted in the tabulated data.

Specimens of all the material purchased for this project were used at some time during the phase of the work. All specimens were 3/4 inch in width, with the lengths varying from 1 to 3 inches. Ti-50A and Ti-75A specimens that had been annealed at 1750 F for 1/2 hour in argon and slow cooled with the intent of producing a coarse acicular alpha structure were used in runs in this phase unless otherwise noted in the tabulated data. The Ti-50A did develop the desired structure (B), however Ti-75A retained the equiaxed alpha structure (A). Specimens were dry abraded with 240-grit silicon carbide paper, rinsed in cp acetone, placed in the reaction tube and immediately sealed to the vacuum system and evacuated. Evacuation was continued with numerous periods of flaming the glass until the system pressure was 0.05 micron or lower. This took about 1/2 to 2-1/2 hours, depending on conditions. The leak rate, or increase in pressure when the reaction system was isolated from pumps, was highly important in this work to prevent the specimens from becoming recontaminated. A period of about 4 minutes of isolation occurred during each run while the hydrogen was being flushed through the remainder of the system to be certain that no air was present in the lines.

An observation of particular importance was that as the work progressed the leak rate tended to improve. It was found that by increasing the evacuation time by about an additional hour, the leak rate could be lowered from about 0.10-0.20 μ/min to 0.01-0.03 μ/min.

When system pressure was reduced to about 0.05 micron and the leak rate became correspondingly low, the specimens were heated to 1500 F and held for 2 hours, then cooled to room temperature in a dynamic vacuum. Specimens were sometimes arranged in the reaction tube so that only a portion of the charge was annealed. The reaction system was then isolated for approximately 4 minutes while the gas inlet lines were flushed; then hydrogen was added to bring the reaction system to atmospheric pressure. This addition normally took from 4 to 7 minutes at the rate of about 70 to 100 ml/min. The reaction with hydrogen was followed on the mercury manometer. All runs were made at room temperature, about 86-90 F, unless otherwise noted.

After removal from the reaction tube, the specimens were sectioned across the width of the sample a short distance in from both ends, and these sections sent to the Metallographic Laboratory to be mounted and polished for microscopic examination. Sections of some of the specimens were sent to the Vacuum Fusion Laboratory for hydrogen analyses.

Results and Discussion

Table 6 is a complete summary of all the runs made during this phase of the work. All the runs were made to attempt to explain certain hypotheses, and often were duplicated to test reproducibility. Because of the large number of runs made, they will be grouped in this discussion.

A reaction of hydrogen with titanium that had been galled with iron and nickel occurred during studies conducted in Phases 1 and 2. Galling was investigated in a

TABLE 6. SUMMARY OF HYDRIDING EXPERIMENTS

Run	Specimen[c]	Time to Evacuate, min	Pressure Under Vacuum, μ At Heat On	At 1500 F	After 2 Hours, 1500 F	Time After Heat Off Before H_2 Added, min
1	C-1	40	0.076	0.18	0.016	20
2	C-2 C-3 C-4	27	0.15	Not annealed		
3	C-5	40	0.063	0.15	0.031	21
4	C-6	44	0.060	0.26	0.042	40[d]
5	C-7 C-8 C-9	32	0.062	0.44	0.060	25
6	C-10	38	0.054	0.34	0.048	18
7	C-11 C-12 C-11 C-12 C-11 C-12	56	0.064	0.36	0.068	25
8	C-13 C-14	65	0.060	0.22	0.052	38
9	C-15 C-16	60	0.062	0.39	0.066	21
10	C-17	70	0.10	0.83	0.069	17

IN GLASS APPARATUS

Ti Grain Structure[a]	Special Sample Preparation	Hydrogen Exposure Time, hr	Hydrogen Exposure Temp, F[b]	Remarks and Description of Specimens
B	--	67.5	RT	No reaction
A	See text	22	RT	Ditto
B	--			"
C				"
A	--	1.25	RT	"
		18	200	
			300 to 600	
A	--	90.5	600	"
			600	
		0.1	700	Extensive reaction
		0.05	600	
		~17	<600	No reaction
B	None	41	RT	Thin layer TiH all over
B	Galled with iron rod			Heavily hydrided in galled areas
A	Galled with iron rod			Hydrided in galled areas
B	None[e]	19	300	No reaction
B	1/2 galled with Ni rod, 1/2 scratched with tweezers	66	RT	Ditto
B	Bound with Ni ribbon			
B	1/2 galled with Ni rod, 1/2 scratched with tweezers	4	200	"
B	Bound with Ni ribbon			
B	1/2 galled with Ni rod, 1/2 scratched with tweezers	22	300	Extensive hydriding under galled and scratched areas and under Ni ribbon
B	Bound with Ni ribbon			
B	1/2 galled with Ni rod, 1/2 scratched with tweezers	21	RT	No further reaction
B	Bound with Ni ribbon			
A	--	18.5	300	No reaction with wet hydrogen[f]
B				
B	1/2 galled with steel bolt, 1/2 wire brushed	65	212	No reaction
B	1/2 galled with iron rod, 1/2 bound with iron wire	22	300	Note: These specimens were reused in Run 11
B	Galled with iron rod on half of one side; Ti foil in reaction chamber	16	RT	Extensive reaction in galled areas; TiH layer all over

TABLE 6.

Run	Specimen[c]	Time to Evacuate, min	Pressure Under Vacuum, μ At Heat On	At 1500 F	After 2 Hours, 1500 F	Time After Heat Off Before H_2 Added, min
11	C-18-15	45	0.062	0.083	0.038	26
	C-18-16					
12	C-19	95	0.069	0.28	0.065	20
13	C-20	70	0.060	Not annealed		
	C-20	35	0.062	3.0	0.067	15
14	C-21	56	0.076	0.34	0.055	16
15	C-22	70	0.068	0.90	0.085	17
16	C-23 C-24	91	0.064	6.5	0.12	21
17	C-25 C-26	78	0.10	0.96	0.079	17
18	C-27 C-28	60	0.067	1.0	0.076	19
19	C-29 C-30	91	0.10	1.0	0.081	20
20	C-31 C-32	81	0.099	1.0	0.083	16
21	C-33 C-34	65	0.066	1.1	0.083	17

(Continued)

Ti Grain Structure[a]	Special Sample Preparation	Hydrogen Exposure Time, hr	Hydrogen Exposure Temp, F[b]	Remarks and Description of Specimens
B	1/2 galled with steel bolt, 1/2 wire brushed	18	RT	Hydride all over surface of galled region
B	1/2 galled with iron rod, 1/2 bound with iron wire			Hydride on one side of brushed area No reaction of galled area Spotty reaction in area bound with iron wire
B	Galled with Ti	65	RT	No reaction[g]
B	Galled with iron rod (See text)	21	RT	Ditto
	Ti foil in chamber; sample of foil annealed after 21 hours' exposure reaction and reexposed	20	RT	Extensive reaction on sample
B	Galled with iron rod, Ti foil not preheated	19	RT	No reaction
B	Ti foil in chamber (foil from Run 14 reused)	19	RT	Extensive reaction on sample
A A	Ti foil in chamber (foil from Runs 14 and 15 reused)	65	RT	Spotty reaction on Sample C-23 Extensive reaction on Sample C-24
B A	42 in.^{2} foil in chamber	66	RT	No reaction with untrapped commercial tank hydrogen
B A	42 in.^{2} foil in chamber	18.5	RT	No reaction with commercial tank hydrogen trapped with liquid nitrogen
B A	42 in.^{2} foil in chamber	17	RT	No reaction with commercial tank hydrogen trapped with Dry Ice-acetone
B A	42 in.^{2} foil in chamber	17	RT	No reaction with untrapped ultra-pure hydrogen
B A	42 in.^{2} foil in chamber	17	RT	Extensive reaction on both samples

TABLE 6.

Run	Specimen[c]	Time to Evacuate, min	Pressure Under Vacuum, μ At Heat On	At 1500 F	After 2 Hours, 1500 F	Time After Heat Off Before H_2 Added, min
22	C-35 C-36	65	0.062	0.88	0.069	22
23	C-37 C-38	92	0.18	0.90	0.087	18
24	C-39 C-40	70	0.070	1.0	0.096	16
24 Rerun	C-39 C-40	75	0.048	0.099	0.055	16
25	C-41 C-42	100	0.047	0.81	0.067	19
26	C-43 C-44	135	0.054	0.40	0.066	17
27	C-45 C-46	116	0.052	0.48	0.063	16
28	C-47	83	0.051	1.5	0.049	14
29	C-48	162	0.048	0.54	0.052	15
30	C-49 C-50		Not annealed			
31	C-51	88	0.040	1.5	0.051	16

(Continued)

Ti Grain Structure[a]	Special Sample Preparation	Hydrogen Exposure Time, hr	Hydrogen Exposure Temp, F[b]	Remarks and Description of Specimens
B A	21 in.^{2} foil in chamber	66	RT	No reaction, possible that some air leaked into chamber; run suspect
B A	31.5 in.^{2} foil in chamber	18.5	RT	No reaction; leak in system probable
B A	42 in.^{2} foil in chamber			No reaction; leak found; run suspended
B A	Reprepared samples, same foil	18.5	RT	79.5 ml H_2 absorbed; extensive reaction both samples; no reaction of foil
B A	21 in.^{2} foil in chamber	65.5	RT	42 ml H_2 absorbed; fairly uniform hydride on Specimen C-41, spotty reactions but with some deep penetration on C-42; no reaction on foil
B A	10.5 in.^{2} foil in chamber	18	RT	15 ml H_2 absorbed fairly uniform hydride coating on C-43, coating fairly uniform on one side only of C-44, many spots of deep penetration on C-44; no reaction of foil
B A	No foil in chamber	18	RT	About 6 ml H_2 absorbed; analyses show H_2 absorbed by C-45 (<90 ppm H_2), none by C-46 (26 ppm H_2)
A	B-120-VCA, no foil in chamber	18	RT	No reaction
A	Ti-6Al-4V, no foil in chamber	16	RT	11 ml H_2 absorbed in first hour, none after that (683 ppm H_2); no hydride layer found
B A	See text; no foil	93	RT	No reaction
A	Ti-5Al-2.5Sn, no foil in chamber	18	RT	Ditto

TABLE 6.

Run	Specimen[c]	Time to Evacuate, min	Pressure Under Vacuum, μ At Heat On	At 1500 F	After 2 Hours, 1500 F	Time After Heat Off Before H_2 Added, min
32	C-52 C-53	111	0.040	3.0	0.067	15
33	C-54 C-55	100 67	0.056 0.045	1.2 0.084	0.086 0.056	-- 17
34	C-56	135	0.062	0.13	0.066	15
35	C-57 C-58	138	0.052	0.90	0.086	15
36	C-59	127	0.050	1.4 (1700 F)	0.061	17
37	C-60	160	0.049	1.8	0.055	17
38	C-61 C-62	153	0.049	0.58	0.071	15
39	C-63 C-64	146	0.043	0.83	0.098	17

(Continued)

Ti Grain Structure[a]	Special Sample Preparation	Hydrogen Exposure Time, hr	Hydrogen Exposure Temp, F[b]	Remarks and Description of Specimens
A	B-120-VCA Ti-5Al-2.5Sn, 42 in.^{2} foil in chamber	18	RT	490 ml H_2 absorbed (B-120-VCA reacted catastrophically sometime after 2-1/2 hr); B-120-VCA showed no hydride on remaining part of specimen; possible very light hydride one side of Ti-5Al-2.5Sn; foil hydrided on both sides
B A	42 in.^{2} foil in chamber	68	RT	No reaction on samples in 16 hr when momentarily exposed to air after anneal (check of a Russian experiment); samples were then reannealed and reexposed; 192 ml H_2 absorbed; thin hydride layer on one side of Specimen C-54; highly twinned; heavy layer of hydride over all surface of C-55; foil heavily hydrided
A	Ti-6Al-4V, 42 in.^{2} foil in chamber	17.5	RT	50 ml H_2 absorbed; analysis shows: sample 28 ppm H_2, foil 1320 ppm H_2
B A	42 in.^{2} foil in chamber	17	RT	No reaction in ultrapure H_2 untrapped
A	Ti-5Al-2.5Sn, 42 in.^{2} foil in chamber; 2 hr, 1700 F anneal	17.5	RT	151 ml H_2 absorbed; even heavy hydride layer over entire surface of one sample and on one side of other sample, irregular layer on other side; very slight reaction of foil
A	B-120-VCA, 42 in.^{2} foil in chamber	65	RT	448 ml H_2 absorbed; sample was embrittled 9970 ±93 ppm H_2
B A	10.5 in.^{2} Ni ribbon in chamber	17	RT	7 ml H_2 absorbed; discontinuous hydride layer found on C-61; very light, continuous layer on C-62
B A	42 in.^{2} foil in chamber	17	RT	Tank H_2 trapped with liquid N_2 added 1/3 as fast as in Run 18; 56 ml H_2 absorbed; spotty reaction on both samples and foil

TABLE 6.

Run	Specimen[c]	Time to Evacuate, min	Pressure Under Vacuum, μ At Heat On	At 1500 F	After 2 Hours, 1500 F	Time After Heat Off Before H_2 Added, min
40	C-65	156	0.040	0.75	0.057	15
41	C-66 C-67 C-68 C-69	Not vacuum annealed				
42	C-70 C-71 C-72 C-73 Foil	164	0.048	0.28	0.047	15

(a) Grain structure: A – Equiaxed alpha
B – Coarse acicular alpha obtained by slow cooling from above beta transus
C – Fine acicular alpha obtained by quenching from above the beta transus.

(b) RT = room temperature.

(c) Beginning with Run 16, where no alloy is shown in the column headed "Special Sample Preparation", the odd-numbered specimens are unalloyed titanium A50, and the even-numbered specimens are unalloyed titanium A75. See samples before Run 16 are Ti-50A.

(d) Pressure after annealing = 0.039 μ.
Temperature raised to 300 F, 17 min after heat off.
H_2 added 23 min after 300 F reached.

(e) H_2 added and pumped out twice to test Rift Theory (Reference 4).

(f) H_2 bubbled through water and trapped with ice water at +4F.

(g) No reaction during first 18 hr at room temperature with hydrogen at 1 atm pressure. The H_2 was then pumped out to leave a pressure of about 14 mm and ionized by passing a sparker (leak tester) over the reaction chamber. No reaction occurred in 1 hr. Specimen then removed and exposed to air for 2 hr, after which it was reannealed for 2 hr at 1500 F. Finally, it was exposed to 1 atm pressure of hydrogen for 65 hr. Again, no reaction occurred.

(Continued)

Ti Grain Structure[a]	Special Sample Preparation	Hydrogen Exposure Time, hr	Hydrogen Exposure Temp, F[b]	Remarks and Description of Specimens
A	Ti-6Al-4V, 42 in.^{2} foil in chamber (repeat of C-56)	17	RT	384 ml H_2 absorbed; sample was embrittled (8800 ppm); foil also reacted (6400 ppm)
B	(See text) Ti-50A		RT	Three separate exposures of about 2 hr to ultrapure H_2 trapped in liquid N_2 plus 1 exposure of 15-1/2 hr; no H_2 absorbed
A	Ti-75A			
A	Ti-6Al-4V			
A	Foil, Ti-A65			
B	Ti-A50, galled with iron		RT	Only the foil was vacuum annealed; 90 ml H_2 absorbed in 17 hr; no reaction with Ti-A50; under a few of the galled areas on specimen C-72, three or four needles were visible at 500X magnification that may have been Ti hydride, but were not definitely identified; C-73 showed no hydride; the foil carried a continuous hydride coating all over
B	Ti-A50, not galled			
A	Ti-A75, galled with iron			
A	Ti-A75, not galled			

number of runs during this phase (Runs No. 5, 7, 9, 10, 11, 13, and 14). The titanium galled with iron frequently showed reaction with hydrogen at room temperature, provided the hydrogen addition was preceded by the 1500 F anneal. The hydride layer in most cases formed under the galled area but occasionally formed over the entire surface of the sample. Specimens wrapped with iron wire did not show a significant reaction at room temperature. Nickel galling did not result in a titanium-hydrogen reaction at room temperature but did so at 300 F. Nickel ribbon 20 mil thick and 1/8 inch in width also failed to initiate a reaction at room temperature but caused an extensive reaction at 300 F, as shown in Figure 10. The nickel ribbon was hammered into close contact with the specimen surface and some galling could easily have occurred at this contact.

It has been shown that iron and nickel contaminants on titanium favor a reaction with hydrogen. However, the method by which this contamination catalyzes the reaction remains unknown. One hypothesis is that the iron and nickel contaminants reduce some of the hydrogen to atomic form, which then reacts with the titanium. A run (Run 12) was tried in which the hydrogen was ionized by holding a Tesla coil against the reaction tube; no reaction resulted. Another hypothesis is that an inhibiting agent in the hydrogen is removed by exposure to an active metal such as iron, nickel, or titanium itself. In one run (Run 12), titanium was used to gall the surface of a titanium specimen; no reaction occurred with hydrogen. This seems to indicate that the increase in surface area due to the galling would not cause a reaction to begin. Of course, a hypothesis cannot be definitely eliminated on the basis of one experimental run. In later work, it was definitely proved that use of large surface areas of vacuum-cleaned titanium foil as a getter promoted the hydriding reaction. Perhaps a number of factors are working simultaneously. For the present, this problem will have to remain unsolved.

The part played by a large and varying surface area of titanium in the reaction tube, acting as a getter, was investigated in Runs 24, 25, and 26. Titanium foil was also present in Runs 15, 16, 17, 18, 20, 21, 22, 23, 32, 33, 34, 35, 36, 37, 39, 40, and 41. However, only in Runs 24, 25, and 26 was an attempt made to correlate the magnitude of the reaction with the surface area of foil present.

Two-mil-thick Ti-A65 foil, 1-1/4 inches wide and of lengths that varied to give known surface areas, was placed in the reaction tube with, but not contacting, the specimen. The foil was not abraded, only rinsed in cp acetone. The specimens were prepared in the usual manner. It was found that where the foil was annealed with the specimen, a reaction of the specimen with adequately trapped hydrogen took place at room temperature. When the foil was placed outside the hot zone of the furnace and only the specimens annealed (Run 14), no reaction took place. The magnitude of the reaction as well as the thickness of the surface layer varied directly as the surface area of the foil, as shown in Table 7. The foil showed no microscopic evidence of any hydride layer having formed during Runs 24-26. One run (Run 38) was made using nickel ribbon (20 mil x 1/8") in place of the titanium foil as a getter. Results of this run are also included in Table 7. Here, too, a reaction took place between the titanium and hydrogen. Generally speaking, no major difference was apparent in the reaction of Ti-50A specimens and those cut from Ti-75A. When one reacted, the other did also. However, specimens of Ti-75A appeared to have more spots of deeper and more irregular penetration than did those of Ti-50A.

5X

Unetched

3H414

FIGURE 10. MACROVIEW OF SPECIMEN C-12

Titanium hydride formed under turns of nickel ribbon during 22-hr exposure to 1 atm of H_2 at 300 F.

Cracks indicating embrittlement of the titanium appeared when the specimen was flattened slightly for photographing.

TABLE 7. EFFECT OF SURFACE AREA OF TITANIUM FOIL ON MAGNITUDE OF REACTION AND HYDRIDE THICKNESS

Run	Specimen	Area of Specimen Plus Foil, in.^{2}	H_2 Absorbed in 1 Hour, ml	Average Thickness of Titanium Hydride, in.
24	C-39	48	22	0.00064
	C-40	48		0.00034 to 0.00039
25	C-41	27	16	0.00054
	C-42	27		0.00033 to 0.00050
26	C-43	17.5	9	0.00026 to 0.00034
	C-44	17.5		0.00021 to 0.00028 (only one side hydrided)
27	C-45	6	0	None
	C-46	6		None
38	C-61	6Ti + 10.5Ni	5[a]	None to 0.00014
	C-62	6Ti + 10.5Ni		0.00010 to 0.00025

(a) Abraded in 1-1/3 hours.

In several of the runs noted in Table 6 that involved galled specimens and/or titanium-foil getter (which should have promoted the hydriding reaction) occasionally no reaction took place. It is strongly suspected that in such cases a small leak had occurred while the reaction system was isolated from the pumps during the 4-minute flushing of the hydrogen lines prior to addition of hydrogen. In particular, in Runs 22, 23, and 24 (first run), a minute quantity of air entrapped in the grease of the stopcock isolating the system was released on closing and allowed the pressure to increase momentarily to no more than 0.5 micron. This apparently carried enough contaminant to prevent a reaction with hydrogen. The failure of many of the earlier runs, e.g., Runs 1, 3, 4, 6, 7, and 9, to react can be attributed to the higher leak rate present in the system at that time. As mentioned previously, the leak rate fell by a factor of 10 as the work progressed.

Apparently, the surface of the titanium is made very reactive after the annealing and will react instantly with any contaminant present. To check this extreme dependence on a clean surface for reaction, a number of runs (Runs 2, 13, 30, and 41) were made with unannealed specimens. Some were abraded, rinsed, and evacuated in the normal way, except that they were not annealed; some were abraded and not rinsed; some were evacuated for only 2 to 5 minutes, after which the reaction system was flushed and reevacuated with hydrogen before the addition. In all cases, none were exposed to air for more than 1 minute before evacuation started. In all of these cases, no reaction with hydrogen took place. One run, Run 42, was made in which the foil was annealed but the specimens, galled and ungalled, were not. The foil, as would be expected, reacted but the specimens did not, although there remains a slight possibility that an almost submicroscopic amount of titanium hydride may have formed.

A recent Russian paper[5] states that exposure to moist air after annealing activates the titanium surface, helping to initiate a hydrogen reaction. This concept was investigated in Run 33. As described in Table 6, exposure to ambient air did not induce

the reaction. Upon subsequent vacuum-anneal-cleaning, specimens were activated and hydriding occurred.

The conclusion that can be drawn from the discussion to this point is that a reaction is almost certain to take place between titanium and hydrogen at room temperature if the sample and titanium foil (at least 10 in.^{2}) are both annealed for 2 hours at 1500 F and no small leak develops to contaminate the specimens after annealing. Perhaps a shorter-period and lower-temperature anneal would serve to activate the surface just as well. This possibility was not explored.

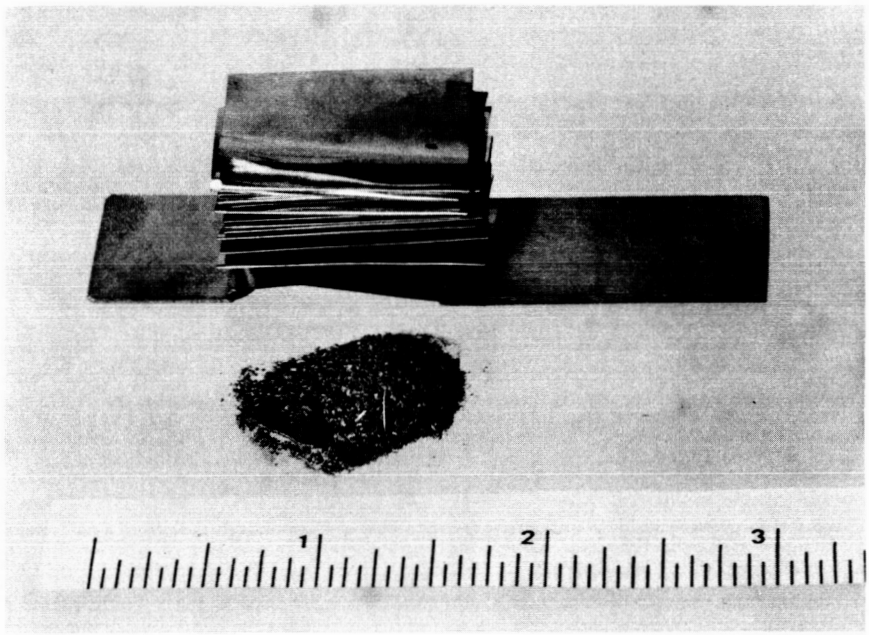
Ultrahigh-purity hydrogen trapped with liquid nitrogen was used in most runs in glass apparatus. To determine whether the very low impurity content of the ultrapure hydrogen would contaminate the highly reactive surface of the specimens after annealing, Runs 20 and 35 were made with untrapped ultrapure hydrogen. No reaction took place. A Dry Ice-acetone cold trap failed to remove the impurity contaminating the specimens (Run 19). Regular commercial tank hydrogen untrapped and trapped with liquid nitrogen (Runs 17 and 18) would not cause a reaction when added at the usual rate of about 70 ml/min. However, when the rate was slowed to about 25 ml/min, a reaction took place when tank hydrogen was trapped with liquid nitrogen (Run 39). Commercial tank hydrogen can contain as high as 600 ppm oxygen and 2300 ppm nitrogen and has a -40 F dew point, while ultrapure hydrogen contains <1 ppm oxygen and <5 ppm nitrogen and has a dew point of lower than -80 F. A liquid-nitrogen trap will remove both oxygen and moisture, but not nitrogen, from the hydrogen and a Dry Ice-acetone trap will not remove either oxygen or nitrogen, but will lower the dew point to -80 F. Therefore, it appears that oxygen is the impurity in both grades of hydrogen that must be completely removed before a reaction can be made to take place.

At one time it was thought that the presence of moisture in the hydrogen might help to initiate a reaction. In Run 8, commercial tank hydrogen was given a dew point of +4 F by bubbling it through water and then passing it through a trap filled with an ice-NaCl mixture. No reaction occurred. However, this may be due to the oxygen present in the hydrogen that was not removed by the ice-NaCl trap, and does not necessarily negate the concept.

A series of runs were made to determine the effect that alloying would have on titanium in its reaction with hydrogen at room temperature. Three alloys were investigated: B120VCA, Ti-6Al-4V, and Ti-5Al-2.5Sn. Specimens of all three alloys were reacted with ultrapure hydrogen after a 2-hour vacuum anneal at 1500 F.

No titanium foil was used for a getter in the first series of runs. The Ti-6Al-4V alloy reacted for 1 hour (Run 29), at which time the reaction ceased abruptly. Analysis showed a hydrogen content of 683 ppm (average of two determinations). No other alloy reacted in the absence of the foil getter (Runs 28 and 31). When Ti foil was placed in the reaction tube with the specimens and annealed with them as in previous work, all three alloys reacted quite rapidly (Runs 32, 34, 36, 37, and 40). The Ti-6Al-4V alloy exposed with the activated getter (Run 34) analyzed 8800 ppm hydrogen (average of two determinations) as compared to 683 ppm without the use of the gettering foil. When exposed with an activated getter, the Ti-5Al-2.5Sn alloy (Run 36) absorbed less than one-half the amount of hydrogen than did the Ti-6Al-4V alloy. Extensive hydriding occurred in the reaction of the B120VCA alloy in Run 32. Some time after 3 hours and before 18 hours of reaction time had elapsed, a catastrophic reaction occurred at room temperature, causing complete disintegration of one-half of the specimen and ejecting

a portion of the powder from the reaction tube into another section of the pumping system. The specimen after reaction is shown in Figure 11. The titanium foil getter was found to be hydrided, but very little hydride was found on a Ti-5Al-2.5Sn alloy specimen also present in the reaction tube. In fact, one sample cut from the Ti-5Al-2.5Sn alloy exhibited no hydride layer whatsoever. In this run, the foil had been placed in direct contact with both alloys, which in some manner may have been a factor in producing such a violent reaction. In a repeat run with the B120VCA alloy only (Run 37), and the foil not in direct contact with the specimen, a rapid reaction did take place. Although 9970 ppm hydrogen (average of two determinations) was absorbed, there was no evidence of the specimen's disintegrating as it did in the previous run.



1.2X 32400

FIGURE 11. MATERIAL REMAINING IN REACTION TUBE AT CONCLUSION OF RUN 32

Specimen C-52 (B120VCA) on left, Specimen C-53 (Ti-5Al-2.5Sn) on right. All but 5/8 inch of original 1-1/2 inches of C-52 disintegrated into pile at front center. Specimen C-53 showed little or no reaction. Foil was heavily hydrided.

A possible explanation of this is found in the difference in specimen size. The specimen in Run 32 (the former run) was 1-1/2 x 3/4 inches and weighed 2.5 grams, while the specimen in Run 37 (the latter run) was about 2 x 3/4 inches and weighed 3.4 grams. Apparently, a fairly large quantity of hydrogen must be absorbed in solid solution before hydriding and disintegration can take place. Because of the larger size of the specimen in Run 37, this critical point had not been reached. That is, an inadequate supply of hydrogen may have been present.

It is apparent from the runs made on these alloys in the presence of titanium foil getter that the B120VCA alloy is the most reactive of the 3 alloys, followed by Ti-6Al-4V. The Ti-5Al-2.5Sn alloy is the least reactive. Compared with the Ti-50A and Ti-75A unalloyed specimens, B120VCA, and Ti-6Al-4V alloys are more reactive, while the Ti-5Al-2.5Sn alloy is about as reactive as, or less reactive than, unalloyed titanium.

In general, galling of specimens or titanium getter foil in the system was required to initiate the hydriding reaction (Run 27). Occasionally, specimens were observed to react to a limited extent under apparently less ideal conditions (see Runs 5, 27, 29). Presently, specific explanations for these isolated cases are lacking.

Another interesting observation in these runs is that no induction period was observed during any run. If the reaction did not begin immediately after adding the hydrogen, the reaction never occurred.

GENERAL DISCUSSION

The work performed at 15 psi pressure in the glass system showed that a reaction can consistently be made to occur at room temperature (86 to 90 F) between hydrogen and unalloyed titanium, or any of the three alloys examined, if the specimen surfaces are clean and the hydrogen has been trapped by liquid nitrogen. Abrading the specimen surface will not produce a surface clean enough for the initiation of the hydriding reaction, as oxidation begins almost instantly after the abrading. The specimens must be annealed in a vacuum at a temperature high enough to dissolve the oxide film on its surface. It was determined that a treatment of 2 hours at 1500 F in vacuum of 0.1 micron or better was sufficient to dissolve the oxide. Also, the hydrogen must be trapped by liquid nitrogen to eliminate any oxygen present that will contaminate the highly active surface of the specimen after annealing. Anything that will add oxygen to the surface of the specimen, whether it comes from the system itself or from the hydrogen, will inhibit the reaction. Titanium foil, which can be used to getter the last minute quantities of oxygen present in the system either from the hydrogen or the reaction-tube walls, promotes the reaction.

One might conclude that vacuum annealing of the titanium surface to remove oxide is not essential and that the clean surface is actually useful only in gettering some harmful impurity from the gas. However, in a check of this possibility in which a large amount of foil was used to getter the gas but in which the specimen itself was not cleaned, no reaction occurred. Galling with iron also was not capable of initiating the reaction at room temperature on a nonvacuum-annealed sample. At room temperature and 1 atmosphere pressure, both a clean surface and clean hydrogen appear to be essential.

An examination of the experimental conditions in the stainless steel reactors used in Phase 1 suggests that the hydrogen atmosphere was less pure and the specimen surfaces perhaps more heavily oxidized than in tests run in the glass apparatus. These differences would be the result of the much poorer vacuum which was obtained in the high-pressure reactors. Reaction might be favored in the Phase 1 work by several factors, including higher temperature, higher pressure, longer exposure times, unintentional contamination with iron or nickel during sample preparation, and relatively large surface area exposed for reaction (18 to 24 square inches). The reactions observed indicated that temperature was a major factor. Pressure and time had no consistent effects. The rather erratic nature of the reaction within the temperature:pressure:time studies in Phase 1 is most likely attributable to differences in the initial vacuum attained in the reactors. Contamination of some of the Phase 1 specimens during preparation may also have had some effect in promoting reaction among these

samples. A specimen that was intentionally contaminated with iron, for example, did react with hydrogen, while companion samples did not.

In the Phase 2 studies, it was not possible to vacuum anneal the specimen prior to introduction of hydrogen because of the reaction-vessel design. As a result, the specimen surface was undoubtedly more heavily oxidized than that of the specimens exposed in Phase 1. Also, since vacuum annealing would also assist in cleaning the atmosphere prior to introducing hydrogen, the atmosphere in the Phase 2 studies should have been less pure. A further factor tending to retard reaction in this series of tests was the small surface area of titanium. The failure to observe reaction in the eight stressed samples examined in Phase 2 is not too surprising in view of the experimental conditions. Therefore, the effect of stress on the initiation of the hydriding reaction must be considered still unresolved.

More surprising than the failure to observe reaction in the stressed samples of Phase 2 is the observation of hydrided spots in a number of the specimens intentionally contaminated with iron or nickel in these studies. Since these specimens were not vacuum annealed and the cleanliness of the atmosphere was poor, it appears that iron and nickel may be effective in promoting the reaction at 300 F and 315 psi. The specimen surface area in this case was about 21 square inches, but this factor would not be expected to have a major effect.

A reasonably consistent microstructural trend was observed in this program. Unalloyed titanium specimens having an acicular microstructure developed by heating into the beta region showed a greater tendency for reaction to occur, and thicker hydride scales were formed. This probably is related to the distribution of beta in the alloy. Hydrogen diffusion is considerably more rapid in beta than in alpha titanium. The differences among the various alloys studied also appear related to beta content, these alloys having more beta tending to react more easily. Thus Ti-6Al-4V and B120VCA reacted with hydrogen more readily than unalloyed titanium, while Ti-5Al-2.5Sn (ELI) reacted less readily.

Applying these conclusions to the results obtained at Beech Aircraft, a similar pattern is observed. At Beech, the use of liquid hydrogen as a source of hydrogen would assure the highest purity gas available. The relatively large surface area present in the tubing and fittings would serve to function as a getter, and the possibility of scratching or galling of the tubing and fittings is always present during its manufacture. Reaction tended to occur most readily in weld areas having an acicular microstructure. The thermal cycling and vibration present during purging and filling of the tank could cause the oxide layer present on the titanium surface to crack, thus exposing a clean surface to the extremely pure hydrogen. Finally, the temperature of 140 F that was occasionally reached, although not as high as that observed to be effective in overcoming inhibiting factors in the present work, may have been adequate under the conditions existing in the Beech tank.

PROPOSED FUTURE WORK

A quartz-spring, high-pressure, microbalance has been constructed at Battelle recently. This could be used to investigate the effect of pressure on the reactions that have been demonstrated at atmospheric pressure. The effects of pressure on the reaction have not been adequately studied in the present program.

A further study of the effect of annealing on the surface of the titanium should be undertaken to determine whether a shorter time and lower temperature would result in activation of the surface.

Stressing the specimen while in a hydrogen atmosphere to simulate more closely the actual conditions encountered at Beech Aircraft should be investigated. Based upon the results of the present study, it must be concluded that either stress or pressure overcomes the inhibiting effect of surface films, presumably oxides, on the reaction of titanium and hydrogen at room temperature.

The possibility of coating the titanium with nitride or some other material to inhibit a reaction should be investigated as a means of preventing the reaction. Also, determination of the minimum quantity of contaminant that could be added to the hydrogen to inhibit the titanium hydrogen would be a worthwhile experiment.

The experimental data used in the preparation of this report are recorded in Laboratory Record Books No. 22963, pages 1 to 100, and No. 23491, pages 1 to 64.

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July 29, 1966

NASA - Manned Spacecraft Center
Structures and Mechanics Division
2101 Webster-Seabrook Road
Houston, Texas 77058

Attention Mr. Sam V. Glorioso/ES
Contract No. NAS 9-5298

Dear Mr. Glorioso:

Thirty copies of a Summary Report on Contract No. NAS 9-5298, "An Investiga- of the Reaction of Titanium With Hydrogen", are enclosed. This is the number you requested during your recent visit to Battelle. Additional copies, as specified in the contract, are being sent to the General Research Procurement Branch and the Technical Information Dissemination Branch, both at Houston.

The work to date on this interesting project serves to establish guidelines for a future investigation that, it is hoped, will show how to avoid the problems encountered from the use of titanium tubing and fittings on hydrogen tankage for Apollo spacecraft. We hope to be able to continue the work until this result is obtained. Obviously, such results would also be applicable to later generations of spacecraft.

Yours very truly,

E. S. Bartlett

E. S. Bartlett

ESB:ims
Enc. (30)

cc: Mr. D. K. Ipson
Miss Retha Shirley (4)