A STUDY OF THE MECHANISM OF THE TITANIUM-LIQUID OXYGEN EXPLOSIVE REACTION

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None of these factors per se was found to be the primary cause of the reaction. The mechanism proposed was that the heat generated by impact produces a pocket of gaseous oxygen in the LOX. This trapped gas is compressed at the point of impact. The fresh surface exposed by the impact tends to react with the high-pressure oxygen gas present. Propagation is dependent on the balance between the amount of heat generated and the rate of heat loss from the site of the reaction.

The present investigation was initiated to define more closely the mechanism of the titanium-LOX reaction. Particular emphasis was placed on establishing whether reactions could occur between titanium and gaseous oxygen at low temperatures approaching that of LOX under a wide range of conditions.

A second major phase of study was directed toward investigating possible methods for inhibiting the oxygen-titanium reaction.

This present report summarizes the experimental program carried out at Battelle Memorial Institute from October 1, 1960, to September 1, 1961.

SUMMARY

The reactivity of a freshly formed titanium surface has been investigated in high-pressure gaseous oxygen over a range of temperatures from that of LOX to room temperature. The oxygen atmosphere was maintained at the desired pressure in a specially fitted autoclave. A fresh surface was exposed to the oxygen by breaking a titanium tensile specimen in situ.

Unalloyed titanium (Ti-75A) and Ti-6Al-4V alloy were consumed by violent reactions when ruptured in gaseous oxygen under suitable pressure at from -190 F to room temperature. The threshold pressure for the propagating reactions was found to be extremely low. An oxygen pressure of only 100 psig was sufficient to ignite Ti-75A at -190 F, and only 75 psig was needed at room temperature. The Ti-6Al-4V alloy was slightly less reactive and required 125 psig at -190 F and 100 psig oxygen at room temperature.

The results from the experimental program continue to support the hypothesis for the mechanism of the reaction of titanium impacted in LOX. It has been shown that reactions will occur at freshly formed titanium surfaces in gaseous oxygen under pressure over a wide temperature range down to near LOX temperatures. Apparently, the fresh surface is essential for the reaction. Other investigators have shown that titanium will not ignite in high-pressure oxygen until the temperature of the metal surface is raised to near the melting point.

A literature survey showed that the impurity content of LOX is very low. Only solid impurities in LOX are believed to affect the impact sensitivity of titanium.

The experimental program included an investigation of means of eliminating or minimizing the reaction of titanium when ruptured in gaseous oxygen. Two means were tried, namely (1) gaseous additions to the oxygen atmosphere and (2) the coating of titanium surfaces. These experiments were conducted under conditions of oxygen pressure at which reactions had occurred previously. It was found that the addition of 2 per cent HF gas to oxygen at room temperature raised the threshold pressure for the reaction from 75 to about 200 psig. An inert gas also reduced the titanium sensitivity by acting as a diluent. However, the addition of about 5 per cent or more of argon was required to raise the threshold to about 200 psig. Fluorine additions apparently increased the reactivity of the fresh titanium surface.

Coated titanium tensile specimens were ruptured in gaseous oxygen at room temperature. No reduction in reactivity was noted when using coatings of a fluoride-phosphate or a vapor-deposited aluminum. In fact, the experiments indicated that somewhat greater damage occurred with an aluminum coating than with uncoated specimens.

Impact studies showed some effectiveness for the fluoride-phosphate and vapor-deposited aluminum coatings for inhibiting reactions in LOX, particularly for 75A material.

EXPERIMENTAL PROGRAM

Tensile Rupture of Titanium in High-Pressure Oxygen

The following paragraphs describe an experimental program which was designed to investigate the reactivity of a fresh titanium surface in gaseous oxygen over a wide range of temperatures. The fresh surface was obtained by breaking a titanium tensile specimen, and the atmosphere was maintained in a specially outfitted autoclave system.

Equipment and Operation

A standard 1-liter AISI Type 316 stainless steel autoclave was used as the container. It was fitted with a holder so that a tensile specimen could be fractured while being exposed to high-pressure gaseous oxygen at low temperature. Figure 1 is a schematic diagram of the autoclave system used.

The load was applied to the system from a hydraulic ram connected to the specimen through the pull rod. The relative size and shape of the components are shown in Figure 2.

The top of the specimen was attached to the pull rod and the bottom of the specimen to the stainless steel support bracket by use of stainless steel pins about 0.25 inch in diameter. To protect the autoclave in the event of a violent increase in temperature, a Pyrex cylinder was placed around the specimen within the support bracket, as shown in Figure 2. In later experiments, it became expedient to use a ceramic liner between the walls of the autoclave and the support bracket.

Figure 3 shows the support used for mounting the autoclave and pull jack. The pull rod was sealed at the top of the extension tube with a Teflon O-ring. The autoclave was cooled in a large stainless steel Dewar, shown in the photograph. The temperature was measured wich a copper-Constantan thermocouple located about 1 inch from the center of the specimen. Additional thermocouples were attached to the outer autoclave surface at several other areas.

Procedure

Both Ti-75A and Ti-6Al-4V tensile specimens were prepared from sheet stock. The physical properties and the chemical analysis for each alloy is listed in Table 1. The specimens were machined 2-11/16 inch long by 9/16 inch wide with a reduced section 1 inch long by 0.19 inch wide and 0.050 inch thick. The original surface was left in the as-received condition, and the edges were surface ground.

TABLE 1 ANALYSES OF TITANIUM MATERIALS (a)

Specimens were 0.050 inch thick

Physical Analysis					Chemical Analysis, %					
Yield Strength, psi	Tensile Strength, psi	Elongation, per cent	Bend Test (b)	Surface Roughness, microinches	C	Fe	N_2	H_2	Al	V
				Ti-75A, Heat M7826						
L-80,500	100,150	22	2.0T	15-20	.025	0.08	.009	.005	--	--
T-91,600	105,800	21	2.0T	35-40						
				Ti-6Al-4V, Heat M8545						
L-138,300	147,400	14	2.8T	18-20	.020	0.17	.020	.007	6.0	4.1
T-143,700	150,500	15	3.6T	25-30						

(a) Produced by TMCA

(b) Press brake at 105 degrees.

TABLE 3. RESULTS OF TENSILE-RUPTURE EXPERIMENTS IN GASEOUS OXYGEN WITH UNALLOYED TITANIUM (TI-75A)

Experiment	Temperature, F	Initial Pressure, psig	Oxygen Concentration, g/cc	Final[a] Pressure, psig	Reaction ?	Remarks
1	-250	100	0.031	80	No	Pressure drop due to ram movement
2	-190	550	0.162	>2000[b]	Yes	Rupture disk blew; autoclave damaged
3[c]	-190	450	0.116	655	Yes	Specimen grips ignited; severe autoclave damage
4[c]	-190	250	0.055	325	Yes	Moderate damage to specimen grips
5	-190	150	0.032	150	Yes	Moderate damage to specimen grips
6[c]	-190	100	0.022	100	Yes	Portions of titanium specimen remain[d]
20	-190	75	0.016	75	No	Bright metallic surface at fracture
7[c]	-190	50	0.012	50	No	Bright metallic surface at fracture
24	-50	100	0.014	100	Yes	Severe damage to specimen grips
25	-50	75	0.011	75	Yes	Small piece of titanium specimen remains
26	-50	50	0.008	50	No	Bright metallic surface at fracture
8[c]	77	250	0.039	275	Yes	Severe damage to specimen grips
9[c]	78	150	0.015	150	Yes	Moderate damage to specimen grips; some of titanium specimen remains[d]
12	79	100	0.010	75	Yes	Small piece of titanium specimen remains; grips damaged
18	76	100	0.010	100	Yes	Large piece of titanium specimen remains
13	83	75	0.008	65	Yes	Upper half of specimen showed no reaction
14	80	75	0.008	70	Yes	Large pieces of titanium specimen remain
16	78	60	0.007	60	No	Very small burned spot on fractured face
15	77	50	0.006	50	No	Bright metallic surface at fracture

(a) Oxygen pressure released 10 to 30 seconds after rupture in all experiments except 1, 2, and 3.
(b) LOX may have been condensed during cooling. Rapid evaporation may have produced the pressure rise.
(c) Stainless steel pins brazed in titanium specimens.
(d) See Figure 6.

Reactivity at -50 F and at Room Temperature. Reactions were obtained at both -50 F and at room temperature for oxygen pressures of 75 psig and above. In Experiment 13 conducted at room temperature, however, only one-half of the specimen burned.

In Experiment 16 conducted at room temperature at 60 psig, no propagating reaction was obtained. However, one very small burned spot was found on the fractured face upon examination (see Figure 7). This shows that the reaction initiated but did not propagate, and apparently represents a borderline case for propagation.

With a pressure of 50 psig, at both -50 F and room temperature, no indication of any reaction was observed. Thus the threshold pressure is between 50 and 75 psig at both these temperatures.

Rupture of Alloyed Titanium

Tensile specimens of Ti-6Al-4V were ruptured in gaseous oxygen at -190 F and at room temperature using the same techniques as for the unalloyed titanium experiments. The results are given in Table 3.

TABLE 3. RESULTS OF TENSILE RUPTURE EXPERIMENTS IN GASEOUS OXYGEN WITH ALLOYED TITANIUM (Ti-6Al-4V)

Experiment	Temperature, F	Initial Pressure, psig	Oxygen Concentration, g/cc	Final[a] Pressure, psig	Reaction?	Remarks
30	-190	125	0.026	115	yes	Specimen largely consumed; grips damaged
29	-190	100	0.022	--	No	Bright metallic surface at fracture
10[b]	75	150	0.015	150	yes	Some of titanium specimen remains; grips damaged[c]
28	79	100	0.010	100	yes	Specimen largely consumed; grips damaged
27	77	75	0.008	75	no	Bright metallic surface at fracture
11[b]	80	75	0.008	75	no	Bright metallic surface at fracture

(a) Oxygen pressure released 10 to 30 seconds after rupture.
(b) Stainless steel pins brazed in titanium specimens.
(c) See Figure 8.

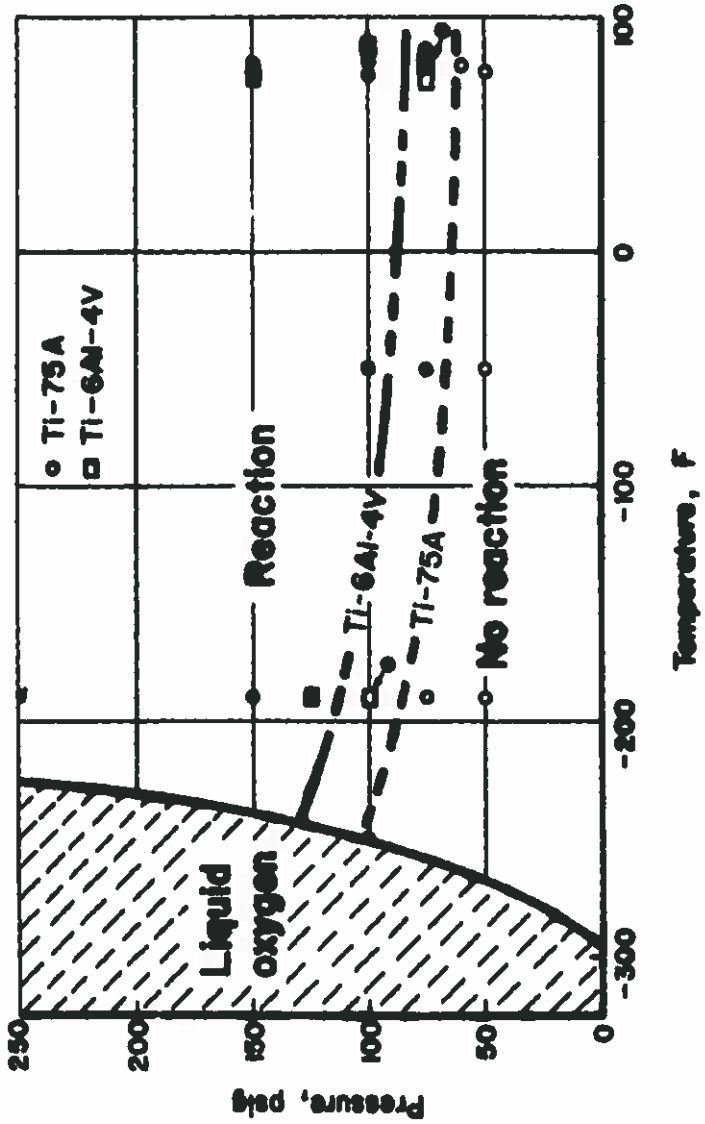

FIGURE 8. REACTIVITY OF TITANIUM RUPTURED IN GASEOUS OXYGEN

Argon (Dilution). It was postulated that the effectiveness of hydrogen fluoride might be related to a dilution effect, rather than to corrosion inhibition by the formation of a film. In order to determine what role dilution of the oxygen by the hydrogen fluoride played in the decreased sensitivity of titanium, argon was substituted for hydrogen fluoride in two experiments. Table 5 shows that a reaction occurred with additions of both 5 and 2 per cent argon. However, in the case of the addition of 5 per cent argon, only a few burned spots could be seen on the titanium pieces where normally the metal is almost completely consumed. Therefore, it appears that the role of hydrogen fluoride may be mostly related to inhibition and partly to dilution of the oxygen.

Protection of Titanium by a Coating

Several experiments were made to study the inhibitive properties of chemical-conversion coatings and metallic coatings on titanium. It was recognized that the coating would not cover the freshly exposed area at a fracture. However, it was thought possible that the coating near the ruptured area might afford some protection from the spread of ignition (1) by providing an inert barrier or (2) by promoting higher rates of heat transfer (as with an aluminum coating) and thereby tending to quench the reaction.

Fluoride-Phosphate Coating. The first type of coating used was a fluoride-phosphate treatment. Originally, this coating was developed to facilitate forming operations with titanium. In wire drawing, for example, titanium tends to gall badly when bare. The specimens were prepared for coating by first degreasing in a boiling alkaline cleaner, pickling in HNO_3-HF solution, and coating in a sodium phosphate-potassium fluoride-hydrogen fluoride bath[5] for 1 to 2 minutes (see tabulation below). The specimens then had a dark gray-brown color.

Pickle Bath	Coating Bath
600 ml H_2O	1000 ml H_2O
352 ml 70% HNO_2	50 g $Na_3PO_4 \cdot 12H_2O$
70 ml 48% HF	8 g $KF \cdot 2H_2O$
	26 ml 48% HF for 75A
	150 ml 48% HF for 6Al-4V

Table 6 shows that very little benefit, if any, was gained from the presence of this coating on Ti-75A tensile specimens. At least, it appears that it is not so effective as hydrogen fluoride gas.

TABLE 5. RESULTS OF STRESS-RUPTURE STUDIES WITH INHIBITORS IN GASEOUS OXYGEN AT ROOM TEMPERATURE WITH UNALLOYED TITANIUM

Experiment	Addition, per cent	Time of Contact, hr	Total Pressure, psig	Reaction ?	Observations After Rupture
32	5 HF	19	110	No	Thin brown scale on specimen
33	5 HF	19	208	No	Heavy brown scale which appeared moist on specimen
37	2 HF	19	212	No	Thin brown scale on specimen[a]
39	2 HF	20	199	No	Some scale on specimen
38	2 HF	2	208	Yes	Portions of titanium specimen remained; grips damaged
41	5 Fluorine	22	215	Yes	Very severe damage to specimen grips
40	2 Fluorine	6	210	Yes	Upper half of specimen unburned except for one small burned spot
35	5 Argon	--	210	No	Three very small burned spots
36	2 Argon	--	211	Yes	Severe damage to specimen grips

(a) Scale rinsed off easily in water.