

UNCLASSIFIED

AD 297 124

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

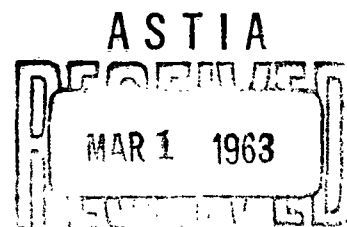
CATALOGED BY ASTIA
AS AD No. 297124

63-2-5

January 15, 1963
DMIC Memorandum 163

REACTIVITY OF METALS WITH LIQUID AND
GASEOUS OXYGEN

DEFENSE METALS INFORMATION CENTER
BATTELLE MEMORIAL INSTITUTE
COLUMBUS 1, OHIO



COPIES AVAILABLE FROM OTS \$

The Defense Metals Information Center was established at Battelle Memorial Institute at the request of the Office of the Director of Defense Research and Engineering to provide Government contractors and their suppliers technical assistance and information on titanium, beryllium, magnesium, refractory metals, high-strength alloys for high-temperature service, corrosion- and oxidation-resistant coatings, and thermal-protection systems. Its functions, under the direction of the Office of the Secretary of Defense, are as follows:

1. To collect, store, and disseminate technical information on the current status of research and development of the above materials.
2. To supplement established Service activities in providing technical advisory services to producers, melters, and fabricators of the above materials, and to designers and fabricators of military equipment containing these materials.
3. To assist the Government agencies and their contractors in developing technical data required for preparation of specifications for the above materials.
4. On assignment, to conduct surveys, or laboratory research investigations, mainly of a short-range nature, as required, to ascertain causes of troubles encountered by fabricators, or to fill minor gaps in established research programs.

Contract No. AF 33(616)-7747
Project No. 2(8-8975)

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY.	1
IMPACT SENSITIVITY OF TITANIUM UNDER LOX	2
Cleanliness and Surface Condition	2
As-Received Titanium	3
Effect of Grit	3
Dilution by LN_2	4
Protection of Titanium to Impact Reaction	4
RUPTURE SENSITIVITY OF TITANIUM IN LOX AND GOX	6
Tensile Rupture in LOX.	6
Machining or Galling Under LOX	6
Ignition in Low-Temperature GOX	7
Ignition at and Above Room Temperature in GOX	7
Fatigue Fracture or Cracking	9
REACTION SENSITIVITY UNDER CONDITIONS ASSOCIATED WITH SPACE VEHICLES	9
Ignition of Bulk Metals by High Temperature	12
Ignition by Explosive Shock	13
Ignition by Electric Discharge	15
Ignition by Puncture.	16
Puncture by Bullet Under LOX	16
Mechanical Puncture.	16
Simulated Micrometeoroids	19
Pressure.	21
Flow Through an Orifice	21
Simulated Loose Equipment in LOX Tank	21
Vibration	22
Acoustic Energy	22
Ultrasonic	22
Sonic.	22
CONCLUSIONS.	23
REFERENCES	25

REACTIVITY OF METALS WITH LIQUID AND GASEOUS OXYGEN

J. D. Jackson, W. K. Boyd, and P. D. Miller*

INTRODUCTION

Since the first observation of a violent reaction in early 1959, the compatability of titanium and its alloys with liquid oxygen (LOX) has received considerable attention. Initially, laboratory investigations were primarily limited to impact studies utilizing the ABMA impact tester or modifications thereof. Later the Air Force initiated a program to determine the mechanism of the reaction. The results of these early studies were previously summarized in DMIC Memorandum 89, dated March 6, 1961.

More recently, the factors necessary to promote reactions between titanium and liquid or gaseous oxygen (GOX) have been studied under conditions similar to those which would be encountered in missile and space service. It is the purpose of this memorandum to summarize the present state of the art in the light of both past and present developments.

SUMMARY

Of all the metals studied to date, titanium exhibits the greatest sensitivity to impact when immersed in LOX. In fact, its sensitivity approaches that of many organic materials such as greases and oils. Reactivity is observed in liquid oxygen and mixtures of liquid oxygen and liquid nitrogen at 20 ft-pounds until the LOX concentration is reduced to 30 per cent. Titanium can be partially protected from reactivity in LOX under impact by certain protective coatings, provided the coatings are not broken. Protection is given by electroless copper and nickel, possibly aluminum, and to a lesser extent by Teflon and a fluoride-phosphate coating. Protection is also obtained by nitriding which adds a protective film to the surface, and by annealing which increases the thickness of the oxide film.

Titanium exhibits no great reactivity in LOX when deformed by compression, by exposure of a fresh surface by machining or rupture, or by exposure of bulk titanium to high-pressure or high-velocity LOX.

In gaseous oxygen, titanium is highly reactive when a freshly formed surface is exposed at even moderate pressures. Under conditions of tensile rupture, a pressure of about 100 psig will initiate a violent burning reaction with titanium from about -250 F up to room temperature. Above room temperature, the pressure required to initiate the reaction is decreased somewhat. When 2 per cent HF is added as an inhibitor or 5 per cent argon as a diluent, the pressure must be increased about twofold at room temperature before reaction occurs. Titanium could not be made to react even at very high pressure when the oxygen content was 35 per cent or less.

*Corrosion Research Division, Battelle Memorial Institute.

BATTELLE MEMORIAL INSTITUTE

When a titanium vessel containing LOX or gaseous oxygen is ruptured by a bullet, by a simulated micrometeoroid, or by other mechanical puncture, violent burning begins at almost 0 psig. If the vessel is not fractured by external impact, vibration, acoustic energy, thermal effects, or with slowly propagated cracks, such as fatigue cracks, no reactivity is noted.

When bulk titanium is heated in high-pressure oxygen, ignition and burning will occur at a temperature somewhat below its melting point. Similar reactions have been noted in CO₂. Ignition of titanium is also initiated under conditions of explosive or electrical shock.

The mechanism for the Ti=O₂ reaction is described as a reaction between a freshly formed titanium surface and gaseous oxygen.

Of other metals discussed, only zirconium shows similar reactions in oxygen. Stainless steels are found to exhibit almost no reactivity in oxygen under impact, rupture, explosive shock, or heating. Aluminum is similarly unreactive, but will ignite under conditions of high-explosive shock. Magnesium shows reactivity to explosive shock lying about midway between that of aluminum and titanium.

For high-pressure oxygen systems, stainless steel and Monel were found to be satisfactory.

IMPACT SENSITIVITY OF TITANIUM UNDER LOX

When the first indications of titanium sensitivity to LOX became known, investigators began to study the reaction. Most of the early studies used the drop-weight impact test equipment developed to indicate the sensitivity of special greases to LOX. These machines vary as to the weight of plummet and height of fall. In general, the plummets weigh from 10 to 50 pounds and the height of fall varies from 1 to several feet to give an impact level of from 10 to several 100 foot-pounds per square inch of striker area. The arbitrary acceptable limit for a material is no reaction out of 20 impacts at the 70 foot-pound level, using a new specimen each time.

Cleanliness and Surface Condition

In the early work, investigators agreed that titanium was quite impact sensitive, but the level of sensitivity reported varied with each investigator. It was found that cleanliness and surface condition greatly affected the results. Careful cleaning procedures were instituted which eliminated much of this discrepancy. Results on as-received titanium and the effect of grit are discussed briefly.

As-Received Titanium

In general, unalloyed titanium is less sensitive than the alloys. In the case where an alloy can be heat treated to a hardened condition, the hardened material appears more sensitive to impact. The reactivity is in the 10 to 20 foot-pound range.

Aerojet-General(1)* reports that small (3/8-to 1/2-inch square) specimens of Ti-75A, Ti-5Al-2.5Sn, Ti-16V-2.5Al, and Ti-6Al-4V were sensitive at 10 foot-pounds (three out of ten specimens exhibit burning). (If, however, the specimens were precooled in liquid nitrogen, no reaction was observed.) Riehl(2) reported that Ti-75A, Ti-140A, Ti-6Al-4V, Ti-5Al-2.5Sn, and Rem-Cru 24S were reactive in the 20 to 70 foot-pound range. Aeronautical Systems Division, Wright-Patterson AFB(3) showed that, at the 70 foot-pound level, Ti-13V-11Cr-3Al was more reactive than Ti-6Al-4V, and Ti-75A was least reactive.

Battelle Memorial Institute(4) reported that Ti-75A and Ti-6Al-4V exhibit sensitivity at the 70 foot-pound level with a loud report and a bright flash. The sensitivity seemed to be about the same whether the specimen was struck with stainless steel or with a piece of titanium of similar composition. When the Ti-75A specimen and striker were abraded, sensitivity was noted at levels of 10 and 30 foot-pounds. No change in sensitivity was found with abraded Ti-6Al-4V. One specimen of Ti-5Al-2.5Sn exhibited no sensitivity with an impact of 70 foot-pounds.

Convair Astronautics(5) reported finding sensitivity with annealed Ti-5Al-2.5Sn in the 30 to 70 foot-pound range. When Convair used a pointed striker instead of a flat face, little sensitivity was found for this alloy.(6)

Reaction Motors, Inc.(7), has reported what it calls threshold values for titanium in LOX. The threshold value is the highest impact level at which no reactions occur out of 20 tries. Data are as follows:

<u>Material</u>	<u>LOX Threshold, ft-lb/in.²</u>
Unalloyed titanium	78
Ti-6Al-4V	78
Ti-25Zr	78
Ti-13V-11Cr-3Al (solution treated)	122
Ti-13V-11Cr-3Al (aged 72 hr at 900 F)	67

These data indicate that the harder (aged) Ti-13V-11Cr-3Al is more sensitive than its softer counterpart, and more reactive than Ti-6Al-4V and Ti-75A, although all values are higher than are believed normal.

Effect of Grit

Titanium surfaces not completely cleaned or having particles of grit and dirt on the surface are more reactive. For example, grit such as sand, alundum, or silicon carbide on a titanium surface causes a much higher

*References are listed on page 25 of this memorandum.

incidence of reactions on impact.⁽⁸⁾ When slivers of titanium are left on the titanium surface, reactions occur at these local sites.⁽⁹⁾

With Ti-6Al-4V alloy panels polished almost to mirror finish, specially cleaned, and examined microscopically to insure cleanliness, no reactions in 11 tries at the 70 to 100 foot-pound range were observed in tests at Battelle.⁽⁹⁾ MSFC reports no such improvement on either hand-sanded or electropolished specimens.⁽⁸⁾ The reasons for these differences are not known.

Dilution by LN₂

Experiments have shown that titanium is impact sensitive in LOX even when it is diluted with large amounts of liquid nitrogen (LN₂)⁽⁸⁾. Only when the LN₂ dilution reaches 70% (almost liquid air) does the titanium become nonreactive at the 70 foot-pound level. See Table 1.

TABLE 1. EFFECT OF LN₂ DILUTION ON LOX IMPACT SENSITIVITY OF Ti-5Al-2.5Sn TITANIUM (0.063 in. thick)⁽⁸⁾

LN ₂ , per cent	Reactions per Number of Tests, at Indicated Impact, ft-lb							
	72	65	58	51	43	36	22	7
0	11/20					3/20	1/20	0/20
50	1/20	3/20	3/20	0/20	0/20			
60	2/20			2/20	1/20	0/20		
70	0/20	0/20						
100	0/20							

Protection of Titanium to Impact Reaction

Attempts made to reduce or eliminate the impact sensitivity of titanium to LOX have resulted in only limited or partial success.

Anodizing Titanium. Both Battelle⁽⁴⁾ and Martin⁽¹⁰⁾ have investigated the impact sensitivity of anodized titanium disks of Ti-75A, Ti-13V-11Cr-3Al and Ti-6Al-4V supplied by ASD. These samples, which had been punched from treated sheets, were slightly dished and had sharp burrs at the exposed edges. Battelle filed the edges to remove the larger burrs, which slightly damaged some of the anodized coatings at the edge. Martin applied a proprietary plastic material to the edges. Both report that burning or detonation

occurred at the 70 foot-pound level. However, anodizing reduced the sensitivity somewhat.

MSFC(8) investigated three types of anodizing but found no benefit.

Fluoride-Phosphate Coating. Battelle(11) reports only slightly reduced sensitivity with this coating at the 70 foot-pound level while the MSFC indicates no improvement.

Nitriding. Nitride coatings were found to reduce sensitivity of Ti-5Al-2.5Sn specimens(8). However, nitriding as a means of reducing impact sensitivity in LOX is not recommended because of the chance for embrittlement and other deleterious effects on titanium properties associated with nitrogen.

Teflon Coating. Three types of commercial Teflon-based coatings (0.5 to 3 mils thick) were studied under impact.(8) Although the coatings gave some protection, the sensitivity to impact was still in the 20 to 30 foot-pound range.

Flame-Sprayed Metal. Flame spraying with an 80 Ni-20 Cr alloy on Ti-6Al-4V raised the impact level from 10 to nearly 50 foot-pounds.(8) However, the coatings were difficult to apply.

Ceramic Coating. Four ceramic coatings were used with no significant improvement.(8)

Electroplated and Inversion-Plated Metal. Electroplated and inversion (electroless) coatings of Ni and Cu effectively desensitized titanium to the impact reaction.(8) An electroplated coating 1 mil thick protected Ti-6Al-4V under impact at the 72 foot-pound level. With 0.5 mil Cu, two faint flashes were observed in 20 impacts. Electroless coatings of only 0.2 to 0.3 mil were effective in preventing impact sensitivity on Ti-5Al-2.5Sn. The Cu coating was slightly more protective than the Ni coating, which tended to spall off. The electroless Cu required about 2 hours for application compared with 5 to 10 minutes for the Ni coating.

Some improvement may also be obtained by vapor-deposited aluminum (triisobutyl aluminum).(11)

A recent Russian patent(12) states that titanium and titanium alloys are clad with aluminum on both sides to prevent spontaneous ignition when exposed to pressurized LOX.

Corrosion Inhibitors. It is reported that the application of two commercial formulations* to titanium diaphragms before rupture tended to decrease the severity of reaction.(13) However, it was pointed out that an insufficient number of tests were carried out to warrant a firm conclusion. It should be mentioned that the solutions are mixtures of mineral oils, alcohols, and/or trichloroethylene, aromatics, and "rust inhibiting additives". The coating dries to a varnish-like finish.

Other Treatments. Treatments such as annealing, pickling, and passivation were investigated.(8) Annealing, followed by air cooling, indicated reduced sensitivity, as evidenced by an increased impact threshold. This improvement is probably due to increased or more adherent oxide film produced by the air cooling. Both a pickling and passivation treatment resulted in increased sensitivity for titanium. The mixture of HNO_3 -HF used for pickling probably removed the protective oxide scale. The passivation treatment included pickling followed by exposure to concentrated H_2O_2 .

RUPTURE SENSITIVITY OF TITANIUM IN LOX AND GOX

Several investigations were carried out to determine the factors involved in the reaction between titanium and oxygen. The following sections summarize the results.

Tensile Rupture in LOX

The reactivity of a freshly formed titanium surface was investigated at Battelle(9) by rupturing titanium tensile specimens exposed to LOX. No propagating reactions were obtained in over 30 experiments at strain rates from 100 to 10,000 inches/inch/minute. Only on one specimen was one small discolored spot found. However, a bright flash of light was observed when the specimen ruptured. Martin(10) has also observed this. Aluminum foil also flashes when ruptured. It is believed the flash is the result of the oxidation of a thin surface film.

Machining or Galling Under LOX

Titanium panels were machined under LOX with no reaction.(9) The chips thus produced were shiny and bright. However, when heat was generated with galling under a rotating stainless steel cylinder, an observable reaction occurred. At contact pressures of 2600 psi and speeds of 220 ft/min., propagation did not occur.

*WD-40 is manufactured and sold by Rocket Chemical Company, San Diego, California.

CRC3-36 is manufactured by Corrosion Reaction Consultants, Philadelphia, Pennsylvania.

Martin(10) has reported experiments on the effect of galling under LOX. These tests were conducted by rotating the end of a stainless steel rod on a titanium specimen in an aluminum cup filled with LOX. The rod was mounted in a drill press and operated at peripheral speeds of up to 40 inches per second (200 feet per minute) and different pressures up to 1600 psi. The reaction, as indicated by the intensity of light flash, increased with increase in speed and/or pressure. The temperature generated was estimated to be about 1000 F, as observed from the color of the stainless steel rod.

Coating of the mating faces with a film of Kel-F and MoS_2 resulted in a reduction in the severity of the reaction. By itself, MoS_2 was not considered very effective. These observations are of interest, since aluminum, when abraded in contact with fluorocarbons such as Kel-F, may explode. No reactions have been observed for titanium with forces up to four or five times that required to fire aluminum in contact with Kel-F.

Ignition in Low-Temperature GOX

In other investigations at Battelle(11), the reactivity of titanium was studied in gaseous oxygen. This was done by rupturing titanium tensile specimens at a rate of about 2 inches/inch/minute using a hydraulic ram in an enclosed high-pressure autoclave filled with oxygen. Low temperatures were obtained by cooling with LN_2 .

The results of this study showed that unalloyed titanium, Ti-75A, would ignite and burn violently when ruptured in gaseous oxygen at 100 psig at -190 F or at 75 psig at room temperature. An alloy, Ti-6Al-4V, was slightly less reactive, i.e., it required 125 psig at -190 F and 100 psig at room temperature to ignite. The oxygen threshold pressures of reaction for these metals are shown in Figure 1. On one specimen ruptured slightly below the threshold pressure, a small burned spot was found. This indicated that the reaction initiated but did not propagate.

Battelle also showed that the reaction could be inhibited somewhat at room temperature by the addition of 2 per cent HF to the oxygen. This raised the threshold pressure for Ti-75A from 75 to about 200 psig. Dilution with 5 per cent argon also produced similar results. On the other hand, additions of gaseous fluorine appeared to increase the reactivity of titanium.

As one would expect, coating of the specimen with fluoride-phosphate or aluminum did not prevent reaction at the freshly exposed surface.

Ignition at and Above Room Temperature in GOX

The effect of oxygen concentration on the reactivity of titanium was studied at SRI.(14) In static tests, unalloyed titanium was ruptured in a reaction bomb pressurized with oxygen. At room temperature, 350 psig of oxygen was required to ignite and burn the fresh surface. This pressure is somewhat higher than that reported in later work by Battelle. When the oxygen was diluted with steam or helium, higher pressures were required. With

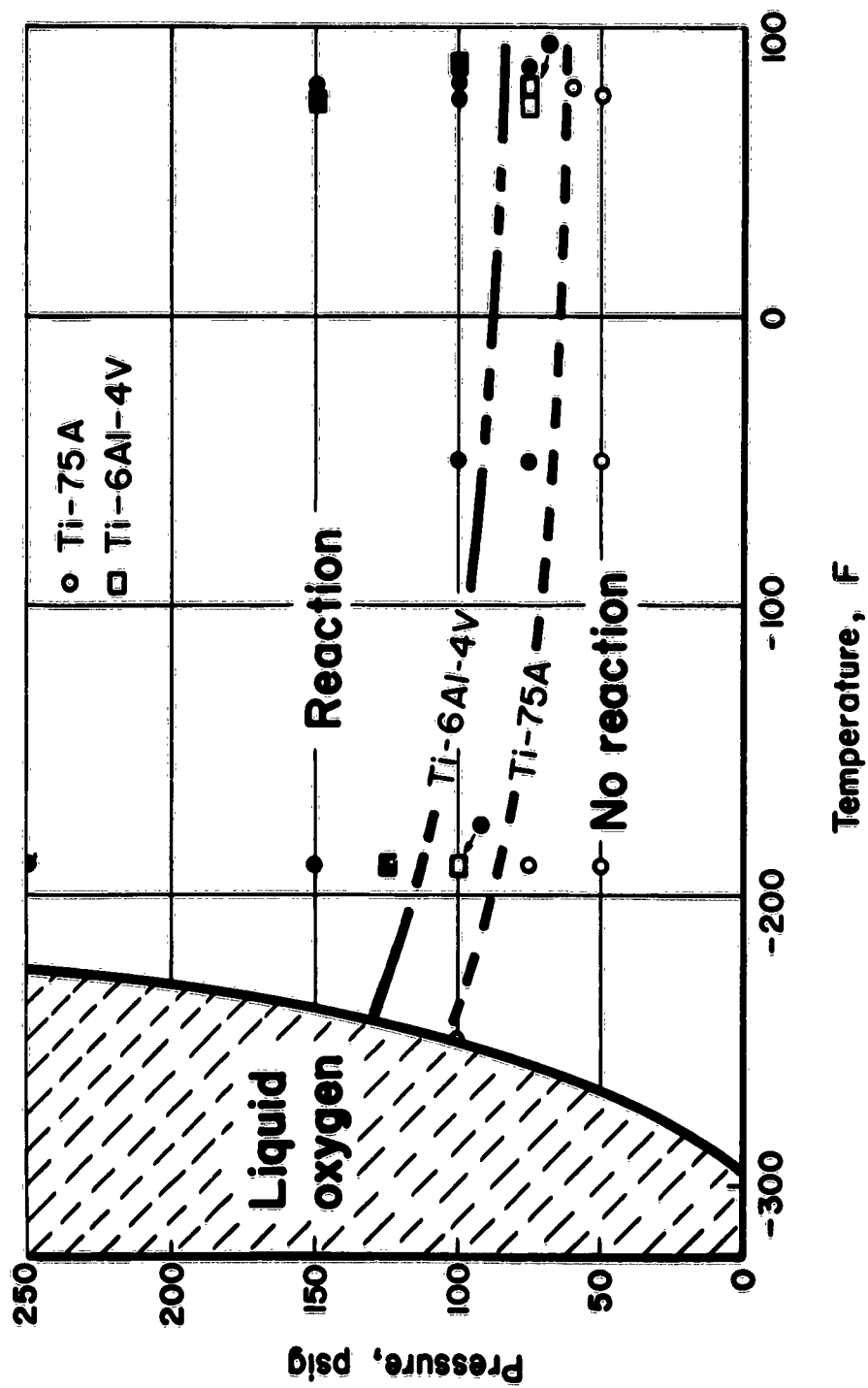


FIGURE 1. REACTIVITY OF TITANIUM RUPTURED IN GASEOUS OXYGEN

NI678

oxygen concentrations of less than 35 per cent, titanium would not be expected to burn under any pressure. Figure 2 illustrates data from these tests.

Under dynamic flow conditions, lower oxygen pressures were found to be sufficient for reaction. Dynamic conditions were obtained by puncturing a 12-mil titanium rupture disk in a pressure vessel. A 50-psig oxygen pressure was sufficient to ignite and propagate the reaction. These data are also shown in Figure 2.

The limits of propagation of the titanium reaction were also investigated. SRI found that once a reaction was initiated, less than 1 per cent oxygen in steam would sustain the reaction. See Figure 2.

Temperature also affects the Ti-O₂ reaction.⁽¹⁵⁾ As the temperature is increased from room temperature, the required oxygen pressure needed to ignite a ruptured specimen decreases to only about 50 psig at 2200 F. See Figure 3.

Of several other metals investigated, only zirconium evinced similar behavior. Iron, stainless steel, aluminum, magnesium, tantalum, columbium, and molybdenum did not react when ruptured in 2000 psi oxygen at 572 F.

Fatigue Fracture or Cracking

The reactivity of a slowly propagated crack was investigated using a fatigue-testing apparatus.⁽⁸⁾ Samples of Ti-5Al-2.5Sn were fatigued and cracked during approximately 10 hours' exposure to gaseous oxygen at pressures up to 60 psig. No propagating reactions were obtained. However, minute burned spots were found on 6 of 8 specimens exposed to oxygen at 50 to 60 psig. These burned areas probably indicate a reaction threshold as suggested by Battelle. (See Figure 1.) This could mean that reactions would occur at slightly higher pressure.

Rupture of a precracked titanium diaphragm failed to initiate a reaction even though the pressure reached 125 psig. The air surrounding the vessel may have prevented propagation.

REACTION SENSITIVITY UNDER CONDITIONS ASSOCIATED WITH SPACE VEHICLES

Although laboratory impact and tensile rupture studies provide an indication of the reactivity of titanium in LOX, they do not necessarily indicate the behavior under conditions encountered by space vehicles. The usefulness or limits of use for titanium can best be judged from experiments which simulate conditions which might be encountered during flight.

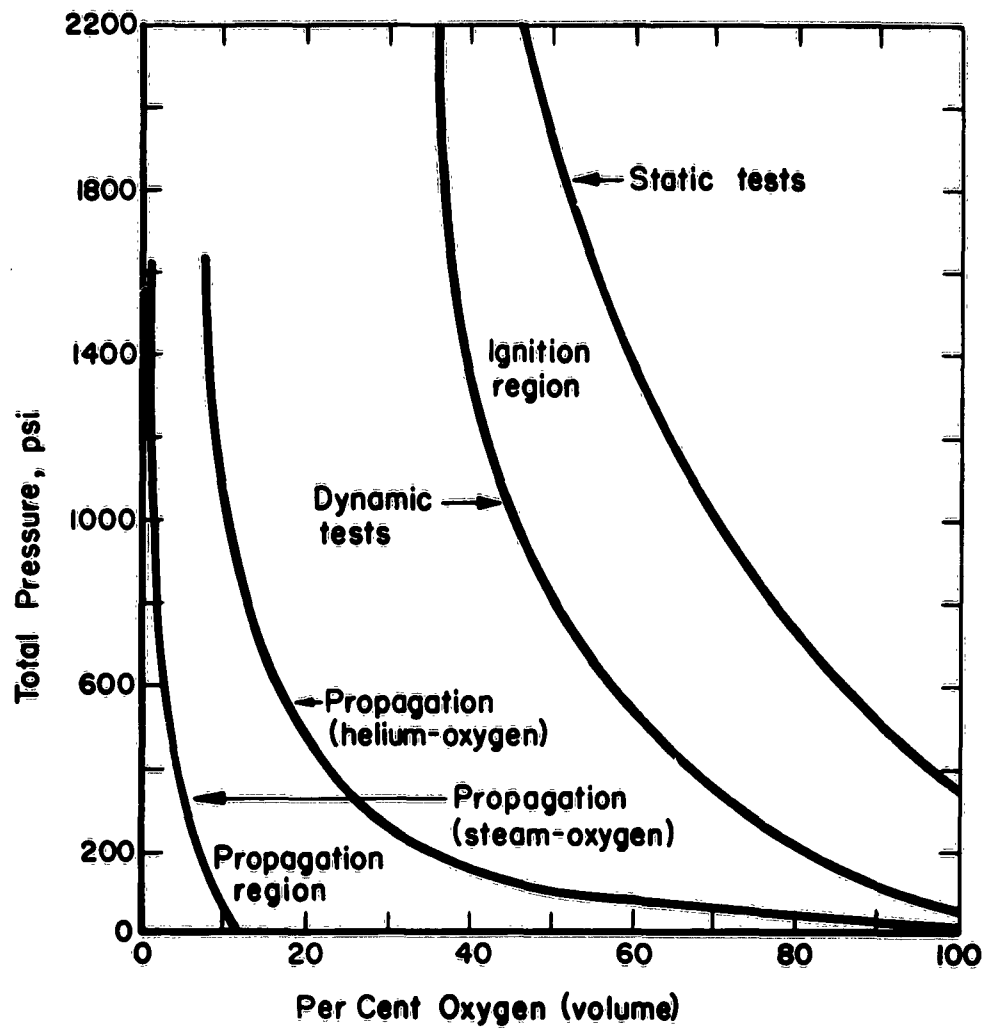


FIGURE 2. IGNITION AND PROPAGATION LIMITS OF TITANIUM IN HELIUM-OXYGEN AND STEAM-OXYGEN MIXTURES(15)

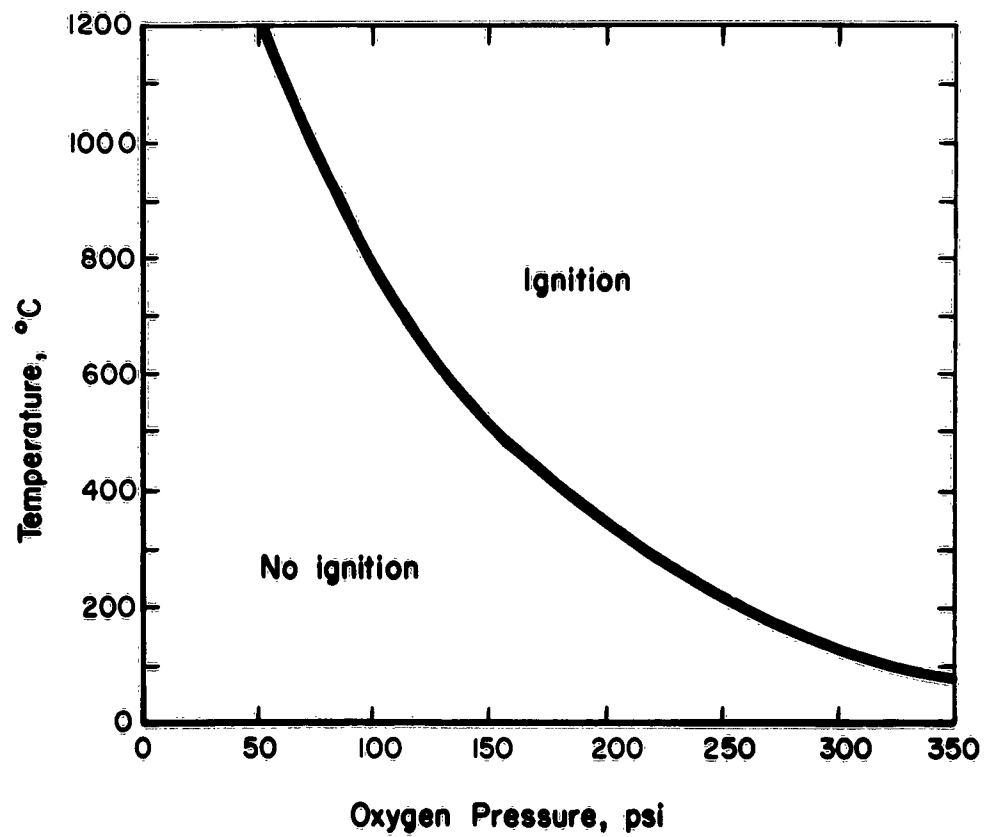


FIGURE 3. EFFECT OF TEMPERATURE ON SPONTANEOUS IGNITION OF RUPTURED TITANIUM IN OXYGEN(15)

The following sections describe reaction sensitivity of materials under conditions similar to those which might be encountered in flight conditions, such as explosive shock during ignition, vibrations, micro-meteoroid puncture, and fluid flow under high pressures and turbulence.

Ignition of Bulk Metals by High Temperature

In the absence of a fresh metal surface, titanium is not easily ignited. The following paragraphs describe bulk metal ignition.

Aerojet-General(16) has studied the autoignition temperatures of a number of common metals when exposed to high-pressure gaseous oxygen. Titanium was found to be the most reactive metal studied, igniting as low as 1000 F below its melting point. (This may not be as serious as it seems, since the melting point of titanium is quite high as compared with other metals. Consider aluminum.)

Experiments were performed using resistance-heated tubes placed in the high-pressure chamber. Heating times of about 2 minutes were used. Thermocouples attached inside the tubes measured the temperature.

The ignition point of titanium varied with the oxygen pressure. In 50 psig O₂, ignition occurred about 250 F below the melting point (about 3000 F), while with 300 psig O₂, ignition occurred about 1000 F below the melting point. In addition, only titanium ignited in an atmosphere of CO₂; at 300 psig, ignition occurred about 250 F below its melting point.

Of other metals tested, it was found that austenitic stainless steels containing 8 per cent or more Ni performed as well as or better than any other. Ignition occurred only at its melting point in 300 and 800 psig O₂. Alloys containing no nickel ignited below the melting point. Aluminum could not be ignited. (Grosse and Conway(17) show that aluminum ignites only above its melting point.) Copper ignited in 300 psig O₂ near its melting point. In 800 psig O₂, Inconel X and Monel failed at about 250 to 500 F below their melting points. Two cobalt-base alloys, Haynes 25 and Multimet, ignited almost explosively at their melting points in 800 psig O₂.

Hill, et al.,(18) report on the ignition of metal cones when heated to high temperature and then exposed to a supersonic blow-down jet, and on wires heated electrically in a static system. They report that under these conditions, titanium, iron, carbon steel, and other alloy steels such as 4130 spontaneously ignite at temperatures below their melting points. On ignition, sufficient heat is generated to cause rapid melting. Inconel, copper, 18-8 stainless steel, Monel, and aluminum could not be made to ignite spontaneously up to the melting point in their equipment (pressures to 800 psi). Magnesium ignited spontaneously in either test at temperatures just above the melting point. Titanium wires were also burned when heated in air or nitrogen.

Glasebrook and Montgomery(19) investigated the ignition temperature of copper, brass, and iron in oxygen up to 1700 psi. Copper and brass behaved similarly in that ignition occurred at about 2000 F at atmospheric pressure,

and as the pressure increased, the metal ignited at lower pressure, but the ignition temperature became constant at about 1500 F when the pressure reached 1200 psi. Iron, however, burned at about 1700 F in low pressure, and the ignition temperature continued to drop as the pressure increased. At 1600 psi, the iron ignited at about 1200 F.

To simulate a leak and fire in a missile, hydrogen flowing from a 0.010-inch hole in a titanium disk was ignited and allowed to impinge on a second disk several inches above.⁽⁸⁾ At temperatures up to 2200 F on the top disk and 1800 F on the bottom disk, no burning reaction of titanium was initiated by the surrounding air, although the titanium was severely embrittled. A similar test using aluminum produced only melting of the disks.

In other tests, hydrogen was allowed to burn in and around polyurethane-insulated titanium tanks filled with LH₂ and pressurized to 35 psig. Examination revealed embrittlement but no reaction.

These tests indicate that the temperatures necessary for ignition are higher than would normally occur in space vehicle tank applications, or be permissible for maintenance of structural integrity.

Battelle⁽²⁰⁾ studied and rated several metals for use in high-pressure (7500 psi) gaseous oxygen systems for use at temperatures of -65 to +260 F. Stainless steel Type 316 was rated good with sufficient strength and ductility for pressure-vessel use, having a low oxidation rate and good erosion resistance. Monel has a lower oxidation rate, but is less strong than stainless steel, although it should be adequate where weight is not restricting. Brass has good oxidation resistance in dry, but poor resistance in moist, atmospheres. It is rated poor to fair because of lack of strength. It has only fair erosion resistance. Pure copper is rated very poor because it is too weak for pressure vessels, shows poor retention of physical properties, and has a high oxidation rate after being exposed for long periods of time.

Teflon and Kel-F were found compatible with high-pressure oxygen, while Viton showed questionable compatibility after a limited study. Teflon was found to suffer certain drawbacks due to its cold flow. Kel-F has sufficient strength and rigidity but is not ductile enough for seals. A possible solution may be a compound of both Teflon and Kel-F.

Ignition by Explosive Shock

The sensitivity of materials to reaction when subjected to an explosive shock has been investigated.⁽⁸⁾ The shock was generated by an explosive charge, and transmitted through LOX or GOX to the specimen. In one method, the charge was taped to the outside of a Type 304 stainless steel tube 1-1/2 inch in diameter filled with LOX or GOX. The explosive charge consisted of an M36A1 detonator alone, or with a length of Primacord explosive. The Primacord was 12 inches in length, containing from 50 to 400 grains per foot of explosive. The specimen consisted of two strips 1 x 18 inches suspended in the media. The amount of shock necessary to initiate a reaction was determined for Ti-5Al-2.5Sn, Al-5052-H34, Type 301 stainless steel,

Mg-HK31XA-H24, as well as organic materials Allpax No. 500 and Johns Manville No. 76, and the Primacord itself.

With titanium, a reaction took place generally with no Primacord required, only the force of the detonator. Visual observations of the reaction indicated that in some instances an explosion of the sample occurred when the charge was set off. Otherwise, initial burning, lasting about 1 second, was observed before the explosion. Inspection of the strips indicated that burning proceeded uniformly over most of the surface.

With aluminum, nearly 250 grains of Primacord was required to initiate a reaction similar to but not as extensive as on titanium. When using stainless steel, no reaction was obtained using two 12-inch strips of 400 grains/ft Primacord. A magnesium-thorium alloy reacted with approximately 200 grains of Primacord.

Using fluorocarbon-impregnated gasket materials Allpax No. 500 and Johns Manville No. 76 (1/16 inch thick), only a trace of reaction was noted using 12 inches of 400 grains/ft Primacord with LOX.

To detonate the Primacord explosive itself required 300 to 400 grains/ft Primacord. Water instead of LOX was used, since the explosive contains its own oxidizer.

The reactivity of titanium in LOX was reduced slightly by plating the specimen with electroless Ni and Cu. With copper, a charge of 100 grains of Primacord was required and with nickel about 84 grains.

In a second method of detonation, a 2-inch piece of 400 grains/ft Primacord plus detonator was placed in a stainless steel "cannon" aimed at the 1/8-inch-thick bottom of the stainless steel cylinder. With titanium in LOX, the reaction would occur with the cannon as far away as 2.75 inches (or 0.23 inch for detonator alone). With aluminum, a spacing of 0.48 inch was required in LOX and 0.16 inch in GOX. No reactions occurred with stainless steel or Primacord when the cannon was held against the bottom of the cylinder.

In the third method, a diaphragm of the specimen was used in place of the stainless steel bottom, and the stainless steel cannon was employed. Under these conditions, titanium burned when the mean spacing of the charge from the diaphragm was 2.5 to 3.0 inches for 0.063- and 0.032-inch-thick sheet. With aluminum, the distance for reaction was 0.95 inch for a 0.063-inch thickness and 2.1 inches for a 0.032-inch thickness, both in LOX, or 1.37 inch for a 0.063-inch thickness with GOX. With Primacord, a spacing of 1.55 inches was found to initiate a reaction. No improvement was obtained using nickel or copper electroless coating on titanium.

It is interesting to note, however, that no reaction occurs when a shock is applied by impact to the exterior of titanium containing LOX or GOX. For instance, impact of a titanium tank pressurized to 50 psig with oxygen at room temperature produced no visible reaction in four attempts at the high impact level of 142 foot-pounds. Tests were also made with LOX under atmospheric pressure, and no reaction occurred in four trials at 142 foot-pounds. (8)

In addition, a titanium tube containing LOX was impacted with 70 foot-pounds with no reaction.(9)

No reactions were initiated by an air hammer impacting a stainless steel vessel containing oxygen at 7500 to 8300 psi.(20) Shock loads of 22 to 25 G's were delivered, with up to 100 shocks at 260 F.

It would seem that the difference in the two tests might suggest a basic difference in mechanism. However, the explosive shock experiment can be explained very simply by the proposed mechanism. It is believed that in the explosive shock experiment, shock waves are produced and focused on the specimens in the center. Stresses, both compression and tensile, are set up on the metal, which tend to rupture the surface. The fresh surface reacts and produces an almost instant reaction with the oxygen compressed by the shock wave. In the case of the external impact, the shock waves are dissipated by the surrounding metal and fluid. Higher energy levels which rupture the surface, would be expected to initiate a reaction. (See section below on ignition by puncture.)

Ignition by Electric Discharge

The possibility of ignition of titanium by an electric spark has received limited study at MSFC.(8) Potential spark sources exist in a missile system from electronic devices such as level indicators, and from buildup of static charges during fluid flow.

A spark was transmitted either by a steel needle momentarily touching a grounded sample enclosed in flowing gaseous oxygen, or by using a 45 degree pointed sample in place of the needle and touching a grounded steel plate. The results were variable depending on the thickness of sample, extent of confinement, oxygen flow rate, and point of impingement of spark. Titanium reacted at spark energies between 1 to 10 joules; the lower spark energies were found for samples 0.005 inch thick. Higher energies were required for 0.007 and 0.010-inch-thick samples. Neither aluminum nor steel ignited with a 10-joule spark.

Battelle(20) studied electrostatic charges under flow conditions. High-pressure gas, generally 12,000 to 16,000 psi, was released (up to 8 seconds flow time) through a brass orifice of 5-mil diameter. The electrostatic charge and temperature was picked up on a probe at the outlet from the orifice. Voltages ranging from -0.19 to a maximum of only + 0.80 volt and temperatures up to 154 F were picked up. Such electrostatic charges were considered insignificant by themselves. Glasebrook and Montgomery(19) showed that larger electrostatic charges were observed when either dust or moisture was present. It is recommended that flow equipment be grounded whenever possible.

Ignition by Puncture

Puncture by Bullet Under LOX

Bendix Aviation Corporation's Pioneer Central Division investigated the use of titanium for LOX bottles, or converters.⁽²¹⁾ The converter must pass the standard gunfire test, which consists of firing a 50-caliber armor-piercing incendiary bullet through plywood to get tumbling action on impact. The titanium converter was filled with dry LOX and was not pressurized prior to impact. On impact, a huge flash was observed, and a violent reaction occurred, resulting in the fragmentation of the vessel. Fusion and burning was noted on the fracture faces of some of the pieces. The reaction did not propagate, and not all the LOX was consumed.

Stainless steel (Type 304L) converters do not shatter unless they are faulty or have defects at the grain boundaries. They do exhibit tearing, however. When stainless steel bottles filled with liquid N₂ or LOX are hit with a nonincendiary bullet, only a hole is made.

Bendix has also investigated the effect of impurities in the LOX on the gunfire test. Bendix believes that the water content is very important. It found that, when a vessel containing LOX, plus ice as an impurity, is hit by an incendiary bullet, more damage occurs than when water is absent.

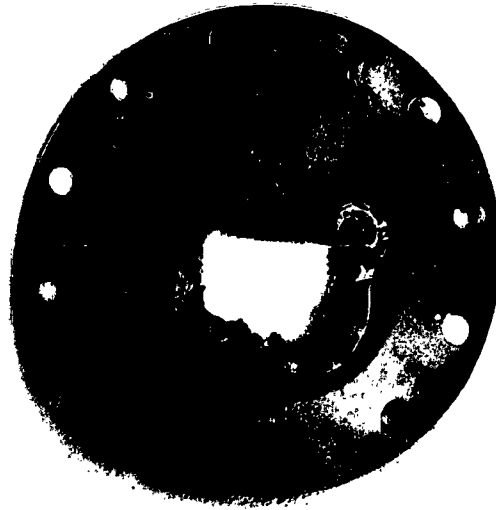
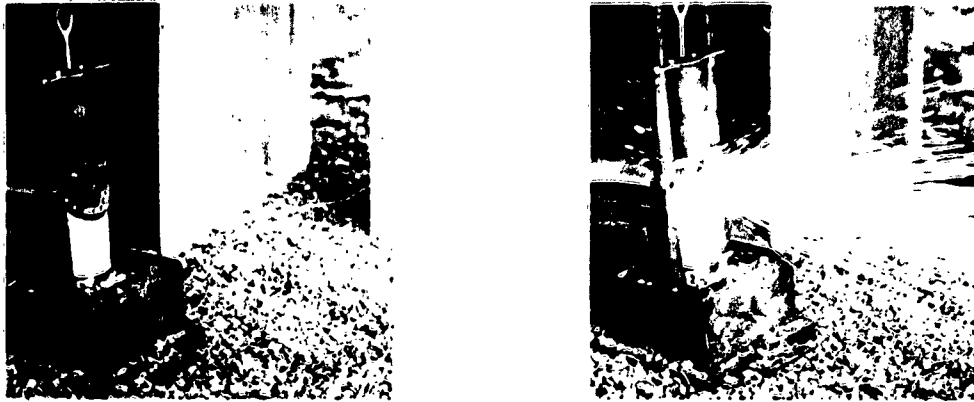
Bullets and steel darts were fired into tanks of Ti-5Al-2.5Sn filled with LOX.⁽⁸⁾ With darts, flashes occurred 3 times and sustained burning once. With bullets, the titanium tank exploded. A similar test using aluminum produced only clean holes.

High-speed movies of the titanium tank bullet test disclosed that rapid and violent combustion occurred immediately on penetration, showering burning titanium over the area. Some burning particles exploded in flight. The reaction appeared to subside, but several tenths of a second after puncture, a powerful detonation occurred.

Mechanical Puncture

Both GD/A⁽¹³⁾ and MSFC⁽⁸⁾ have investigated the conditions in which titanium will react when punctured in contact with LOX and gaseous oxygen. A titanium diaphragm was attached to a container which was pressured by oxygen. MSFC placed the diaphragm in the bottom so it would be covered completely, when LOX was used, and the diaphragm was punctured from below. GD/A placed the diaphragm on an angle with an outlet at the top to maintain LOX in contact while puncture was made from the top by a drop-weight machine. See Figure 4.

Results from MSFC show that titanium will react with gaseous oxygen when punctured by a pointed rod or knife edge at pressures as low as atmospheric. Table 2 reports the data for Ti-5Al-2.5Sn using a pointed rod. At 35 to 40 psig pressure, 49 reactions were observed in 57 trials with Ti-5Al-2.5Sn varying from 0.010 to 0.032 inch thick.



122

FIGURE 4: Sequence photographs of falling-weight type mechanical puncture of 0.016 inch Ti-6Al-4V diaphragm. The sharp chisel point is about to pierce the diaphragm in the left photo. The photo at the right was taken 1/20 second later. It shows the titanium burning with a spectacular emission of brilliant sparks. The chamber contained gaseous oxygen at 30 psig. Energy of puncture was 45 ft-lb. In the photograph below is shown a 0.028 inch Ti-5Al-2.5Sn diaphragm which was partially burned in a similar test.

(Courtesy of J. E. Chafey, General Dynamics/Astronautics(13)

TABLE 2. EFFECT OF PRESSURE ON TITANIUM DIAPHRAGM
REACTIVITY ON PUNCTURE(8)

Oxygen Pressure, psig	Total No. Tests(1)	Reactions	
		Sustained Burning	Flashes
25	1	1	-
20	1	1	-
15	4	2	2
10	2	1	1
5-6	2	1	1
0(2)	5	2	2

(1) Using 1/8-inch-diameter pointed tool and 0.010-inch-thick Ti-5Al-2.5Sn, gaseous oxygen at room temperature.

(2) Slight positive gas flow.

Ti-13V-11Cr-3Al reacted 3 times plus 1 flash in 6 trials; thus it may be slightly less sensitive.

No reactions in 47 trials were obtained with Al 2014-T6 and 6061-T6 at pressures to about 50 psi. HK31 magnesium gave 1 faint flash out of 20 trials at pressures from 40 to 100 psig. No reactions were obtained with gaseous oxygen at 35 to 40 psig and a temperature of -297 F for Type 301 stainless in 10 trials or Allpax 500 Fluorolube in 5 trials.

GD/A reports quite similar results, i.e., some reactions occurred even at atmospheric pressure with Ti-6Al-4V, Ti-5Al-2.5Sn, and Ti-75A; 71 reactions were obtained in 115 tests using a conical penetrator and 1/4- and 1-inch chisel in the 10 to 50 psig range. The larger chisel seemed to give a higher incidence of severe burning. Also, a nonsparking beryllium-copper tool seemed to decrease the sensitivity.

The incidence of reaction was decreased by diluting oxygen with helium. With 25 per cent or more helium, the occurrence of the reaction was prevented. No reaction occurred using gaseous hydrogen when titanium, aluminum, or stainless steel were punctured. No reactions occurred with stainless steel or aluminum with oxygen.

Using LOX, GD/A obtained reactions 12 out of 15 times with Ti-5Al-2.5Sn and Ti-6Al-4V, when the system was pressurized at 30 psig. MSFC reports 20 out of 21 reactions with Ti-5Al-2.5Sn under pressures of 35 to 40 psig. No similar reactions occurred with aluminum or stainless steel.

MSFC reported⁽⁸⁾ that Lewis Research Center fired 7/32-inch steel and Nylon pellets in 0.025-inch titanium panels exposed to LOX. Violent explosions result with both type of pellets.

Both GD/A and MSFC state that, on the basis of their studies, titanium is not recommended for construction of thin-walled LOX tanks for space vehicles. Also, GD/A does not recommend use of titanium for thin-walled gaseous oxygen vessels.

Simulated Micrometeoroids

Because of the reactions caused by penetration and the possibility of penetration by meteoroids in space, simulated micrometeoroids were fired into titanium containing LOX. MSFC⁽⁸⁾ employed GD/A to perform these experiments⁽¹³⁾, and Utah Research and Development Company⁽²²⁾ aided in those performed in vacuum.

GD/A fired steel pellets (0.1 to 0.2 g) through the air at velocities of 9,100 to 15,900 ft/sec to penetrate titanium, aluminum, or stainless steel diaphragms at each end of a cylinder pressurized to 20 or 60 psig. With Ti-6Al-4V and Ti-5Al-2.5Sn, 0.025, 0.016, and 0.014 inch thick, the back diaphragm ignited 15 out of 16 times and the front over half of the time with either LOX or gaseous oxygen at room temperature. See Figure 5. Control tests using 60 psig N₂ or air at atmospheric pressure gave no reactions. In 8 trials using Al-2024-T3 (0.016 inch), and 7 trials using Type 301-XFH stainless (0.010 inch) with 60 psig LOX, and GOX, no reactions occurred. However, slight oxidation was observed around some penetrations on aluminum.

GD/A observed reactions even when the titanium panel was sandwiched between Al-2014-T3 (all 0.016 inch thick) or Type 301-XFH stainless (0.010 inch thick).

Utah Research⁽²²⁾ employed a diaphragm arrangement in its vacuum tests. The vacuum chamber was at approximately 250 microns Hg, and the oxygen pressure was maintained at 60 psig. Steel spheres, 1/16 inch diameter, traveling at a speed of 10,000 to 20,000 ft/sec were used for puncture. Diaphragms of Ti-6Al-4V and Ti-5Al-2.5Sn were used in one run with LOX and two with O₂ at room temperature. All diaphragms burned. No reaction occurred with Type 301 XFH (0.010 inch) or Al-2024-T3 (0.016 inch) diaphragms.

In other tests at a velocity of only 610 to 650 ft/sec, 3 out of 4 penetrated titanium diaphragms burned.

For comparison, no reactions occurred with titanium pressurized with hydrogen at 60 psig using the high-speed pellets.

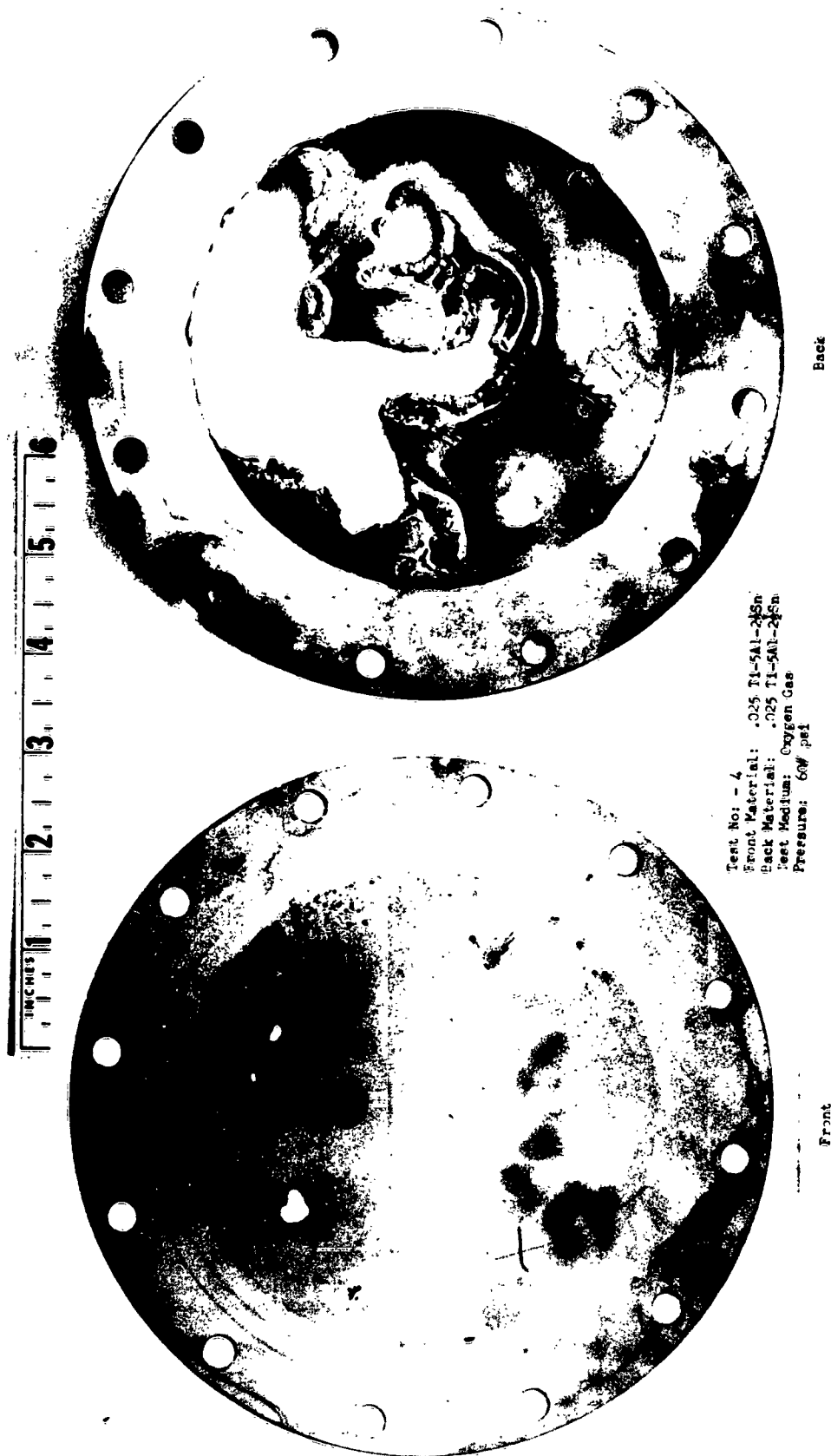


FIGURE 5. SIMULATED MICROMETEOROID PUNCTURE TEST SHOWING BURNED TITANIUM DIAPHRAGMS
(Courtesy of J. E. Chafey, General Dynamics/Astronautics(13)

Pressure

Two titanium tanks filled with LOX and surrounded by LN₂, and one filled with LOX and surrounded by air at ambient temperature, withstood 250 rapid pressure cycles without failure.⁽⁸⁾ The pressure rose almost instantly to 1500 psig, and leveled out to 1000 psig, all within about 0.3 second, and maintained 1000 psig for approximately 0.6 second or longer before dropping to 0. The entire cycle required less than 2 seconds.

Battelle⁽²⁰⁾ studied surge conditions caused by the sudden release of 10,000 to 16,000 psi oxygen into a small stainless steel receiver. Instantaneous pressures of 5000 to 8300 psi were recorded in the receiver with no indication of reaction. A bulk temperature rise of the receiver was 21 to 42 F. The gas temperature rise could have been of the order of 150 F or more.

In the use of a pressure regulator, a sudden surge of 16,000 psi oxygen (above the rated 10,000 psi) caused a violent reaction which burned out the stainless steel regulator. This reaction seemed to center around a porous stainless steel filter and a neoprene "O"-ring.

Battelle⁽⁹⁾ simulated the simple application of hydraulic pressure of LOX against titanium by impacting a hydraulic cylinder containing LOX and a titanium sample, and by impacting directly a hardened ball placed over a pocket of LOX on titanium. No reactions were obtained at the 70 foot-pound level.

Flow Through an Orifice

Leakage of oxygen at 100 psig pressure through an orifice in a titanium disk could not be made to cause a reaction.⁽⁸⁾ LOX was also squirted through a titanium orifice using a hydraulic cylinder, with no apparent reaction.⁽⁹⁾

Using materials other than titanium, Battelle⁽²⁰⁾ studied the high-velocity flow of high-pressure gaseous oxygen through both metals and plastics. Pressures as high as 12,000 psi were released through orifices of 0.005 to 0.013 inch. No reactions were obtained with stainless steel, Monel, brass, copper, Kel-F, or Teflon. Erosion was a problem due to entrained particles. Stainless steel and Monel had good resistance while the others had fair to poor resistance. Teflon was somewhat weak, and cold flow caused the orifice to close. Stainless steel and Monel are considered good materials of construction; of the plastics, a combination of Teflon and Kel-F would be desired for ductility and strength.

Simulated Loose Equipment in LOX Tank

The effect of components breaking loose and vibrating in a LOX tank during flight was simulated.⁽⁸⁾ A 2-inch cube of Type 321 was rough cut with a power hack saw and placed in a Ti-5Al-2.5Sn tank. The tank was

filled with LOX and pressurized with 35 to 40 psig oxygen. The tank was then vibrated in a "Rotap" machine (used for vibrating powders into sized fractions on sieves). After about 15 minutes, the LOX evaporated, and the cube rattled around in gaseous oxygen. Examination of the tank showed a surface peppered with only minute dents and no reaction indicated. Similar results are reported⁽⁹⁾ on compressive impact studies. Steel balls were impacted up to 20 mils deep into a titanium sample with no reactions.

Vibration

High vibration levels, as associated with space vehicles, were studied. Vibration tests⁽⁸⁾ of LOX-filled tanks, made with up to 200 cycles per second at 20 G's with a 0.03-inch double amplitude, caused no reactions.

In other experiments, a "sloshing" vibration was investigated using a LOX-filled tank in a Rotap machine for 10 minutes in each of 5 tests. In a similar test, the top vent port was left open and tapped lightly by the machine as dense vapors passed over the impact area. No reaction occurred.

In experiments with gaseous oxygen⁽²⁰⁾, vibrations of 600 to 840 cps were applied to copper, brass, stainless steel, and Monel containers. The temperature of the system varied from room temperature to 280 F and the pressure varied with temperature from 5000 to 11,000 psi. Various contaminants such as organics (2 to 8 drops of hexane, pentane, decane), aluminum and steel chips, Teflon, Kel-F, and Viton O-rings were placed in the vessels for vibrations up to 360 minutes. No reactions were obtained under these conditions.

Acoustic Energy

Ultrasonic

Titanium coupons were placed in LOX and subjected to ultrasonic energy from a 400-watt, 25-Kc magnetostrictive transducer.⁽⁸⁾ Three runs using disks 0.010, 0.025 and 0.063 inch thick, for 15 minutes' duration produced no reaction.

Sonic

Two 0.010-inch-wall titanium tanks filled with LOX and pressurized to 50 psig were located 8 feet from a rocket motor.⁽⁸⁾ A 4000-pound-thrust LOX-kerosene rocket engine was fired to produce a 150 db acoustic pressure level. Four tests for a total of 210 seconds produced no reactions.

CONCLUSIONS

Of the more common metals and alloys considered for missile and space applications, only titanium and zirconium have exhibited catastrophic reactions with liquid and gaseous oxygen. Carbon steel, stainless steel, nickel alloys, copper alloys, aluminum, magnesium, tantalum, columbium, and molybdenum are considered nonreactive in LOX and GOX under conditions which initiate violent reactions with titanium.

Since reactions have been observed under a wide variety of conditions, it is strongly recommended that the use of titanium in oxygen systems be severely restricted. Furthermore, any consideration of the use of titanium in such systems should be predicated on the basis of a thorough investigation under actual service conditions.

Some of the conditions found to initiate reactions with titanium are as follows:

- (1) Impact of the titanium surface in contact with LOX. Impact energies as low as 10 to 20 foot-pounds give a high incidence of reactions, which may or may not propagate catastrophically. The presence of grit, dirt, and metallic particles increases the possibility for reaction. Abrasion and galling usually cause some nonpropagating reactions.
- (2) Tensile rupture of the metal. Propagating reactions starting at the fractured face have been observed at gaseous oxygen pressures of 50 to 100 psi over the temperature range -250 F to room temperature and above. It is believed that both a fresh surface and gaseous oxygen must be present for a reaction to take place.
- (3) Puncture by external means. Extremely violent reactions in both GOX and LOX have been observed for titanium samples pierced by (a) bullets, (b) high-velocity particles simulating a meteoroid, (c) knife edges, etc.
- (4) Explosive shock. The energy transferred to titanium by a mild explosion outside a container is sufficient to initiate a violent reaction of a specimen suspended in LOX or GOX.
- (5) Electrical spark. An electrical discharge of the order of 1 to 10 joules depending on the thickness of the titanium can cause a reaction.

It should be pointed out that no completely effective procedures or treatments are known to prevent the reactivity. Metallic coatings of

copper, nickel, and aluminum give some protection under certain conditions of impact, as do some types of corrosion inhibitors. However, all these treatments are effective only so long as a fresh titanium surface is not exposed.

Reactions with titanium have not been observed under conditions where a fresh surface and gaseous oxygen are not present even when the titanium is severely deformed by machining, broken in fatigue, indented by blows, or subjected to severe vibration.

REFERENCES

- (1) Extract of DMIC internal memorandum, "LOX-Titanium Reaction at Aerojet-General Corporation" (February 20, 1959).
- (2) Extract of DMIC internal memorandum, "ABMA Results With Titanium-LOX" (July 16, 1959).
- (3) Beane, George A., "Results of Impact Testing of Titanium With Liquid Oxygen", WADC TN-59-175 (April, 1959).
- (4) Extract of DMIC internal memorandum, "Preliminary Data on the Reaction Sensitivity of Titanium and Oxygen" (August 14, 1959).
- (5) Extract of DMIC internal memorandum, "LOX-Titanium Impact Studies at Convair Astronautics" (March 16, 1959).
- (6) Extract of DMIC internal memorandum, "Titanium-LOX Sensitivity at Convair Astronautics" (December 30, 1959).
- (7) Extract of DMIC internal memorandum, "ARTC Committee Meeting on LOX-Impact Testing, Project 18-58" (October 20, 1959).
- (8) Riehl, W. A., Key, C. F., and Gayle, J. B., "Reactivity of Titanium With Oxygen", NASA, George C. Marshall Space Flight Center, Presented at the Society of Aerospace Materials and Process Engineers National Meeting (November 15, 1962).
- (9) Jackson, J. D., Miller, P. D., Boyd, W. K., and Fink, F. W., "A Study of the Titanium-Liquid Oxygen Pyrophoric Reaction", Battelle Memorial Institute to Wright Air Development Division, WADD TR 60-258 (March, 1960).
- (10) Extract of DMIC internal memorandum, "Tests of Titanium Impact Properties in LOX" (August 3, 1959).
- (11) Jackson, J. D., Miller, P. D., Boyd, W. K., and Fink, F. W., "A Study of the Mechanism of the Titanium-Liquid Oxygen Explosive Reaction", Battelle Memorial Institute to Aeronautical Systems Division, ASD TR 61-479 (September, 1961).
- (12) Vorobyev, A. A., Kalugin, V. F., Kramskov, B. V., and Glubokov, Ye. S., "A Method of Cladding Titanium and Its Alloys", Byulleten Izobretenii, No. 19, 13 (1960), Class 7a, 8, No. 132171 (654963/22 of February 17, 1960).
- (13) Chafey, J. E., Witzell, W. R., and Scheck, W. G., "Titanium-Oxygen Reactivity Study", General Dynamics/Astronautics to George C. Marshall Space Flight Center, Contract No. NAS 8-2664 (July 2, 1962).
- (14) Littman, Fred E., and Church, Frank M., "Reactions of Titanium With Water and Aqueous Solutions", Stanford Research Institute to Union Carbide Nuclear Company, Final Report AECU 3825 (June 15, 1958).

- (15) Littman, Fred E., and Church, Frank M., "Reactions of Metals With Oxygen and Steam", Stanford Research Institute to Union Carbide Nuclear Company, Final Report AECU-4092 (February 15, 1959).
- (16) Dean, L. E., and Thompson, W. R., "Ignition Characteristics of Metals and Alloys", Aerojet-General Corporation, Journal of the American Rocket Society, 31, 917-923, No. 7 (July, 1961).
- (17) Grosse, A. B., and Conway, J. B., "Combustion of Metals in Oxygen", Ind. Eng. Chem., 50 663 (1958).
- (18) Hill, P. R., Adamson, David, Foland, D. H., and Bressette, W. E., "High-Temperature Oxidation and Ignition of Metals", Langley Aeronautical Laboratory, NACA RM L55L23b (March 26, 1956).
- (19) Glasebrook, A. L., and Montgomery, J. B., "High Pressure Laboratory", Ind. Eng. Chem., 41 (10), 2368-73 (October, 1949).
- (20) Baum, J. V., Goobich, B., and Trainer, T. M., "An Evaluation of High Pressure Oxygen Systems", Battelle Memorial Institute to 6570th Aerospace Medical Research Laboratories, AMRL-TDR-62-102 (August, 1962).
- (21) Extract of DMIC internal memorandum, "Titanium-LOX Studies at Bendix Aviation Corporation, Pioneer Central Division, Davenport, Iowa" (February 15, 1960).
- (22) Lee, T. W., "Micrometeoroid Impact Study", Utah Research and Development Company, Salt Lake City, to General Dynamics/Astronautics (January 17, 1962).

LIST OF DMIC MEMORANDA ISSUED
DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio

Copies of the technical memoranda listed below may be obtained from DMIC at no cost by Government agencies and by Government contractors, subcontractors, and their suppliers. Others may obtain copies from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

A list of DMIC Memoranda 1-117 may be obtained from DMIC, or see previously issued memoranda.

DMIC Memorandum Number	Title
118	Review of Recent Developments in the Metallurgy of High-Strength Steels, July 21, 1961, (AD 259986 \$0.50)
119	The Emittance of Iron, Nickel, Cobalt and Their Alloys, July 25, 1961, (AD 261336 \$2.25)
120	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, July 31, 1961, (AD 261293 \$0.50)
121	Fabricating and Machining Practices for the All-Beta Titanium Alloy, August 3, 1961, (AD 262496 \$0.50)
122	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, August 4, 1961, (AD 261292 \$0.50)
123	Review of Recent Developments in the Technology of Beryllium, August 18, 1961, (AD 262497 \$0.50)
124	Investigation of Delayed-Cracking Phenomenon in Hydrogenated Unalloyed Titanium, August 30, 1961, (AD 263164 \$0.50)
125	Review of Recent Developments in Metals Joining, September 1, 1961, (AD 262905 \$0.50)
126	A Review of Recent Developments in Titanium and Titanium Alloy Technology, September 15, 1961, (AD 263167 \$0.50)
127	Review of Recent Developments in the Technology of Tungsten, September 22, 1961, (AD 263888 \$0.50)
128	Review of Recent Developments in the Evaluation of Special Metal Properties, September 27, 1961, (AD 263994 \$0.50)
129	Review of Recent Developments in the Technology of Molybdenum and Molybdenum-Base Alloys, October 6, 1961, (AD 264291 \$0.50)
130	Review of Recent Developments in the Technology of Columbium and Tantalum, October 10, 1961, (AD 264983 \$0.50)
131	Review of Recent Developments in the Technology of High-Strength Stainless Steels, October 13, 1961, (AD 264984 \$0.50)
132	Review of Recent Developments in the Metallurgy of High-Strength Steels, October 20, 1961, (AD 265135 \$0.50)
133	Titanium in Aerospace Applications, October 24, 1961, (AD 266927 \$1.50)
134	Machining of Superalloys and Refractory Metals, October 27, 1961, (AD 268081 \$1.00)
135	Review of Recent Developments in the Technology of Nickel-Base and Cobalt-Base Alloys, October 31, 1961, (AD 266004 \$0.50)
136	Fabrication of Tungsten for Solid-Propellant Rocket Nozzles, November 2, 1961, (AD 268311 \$0.75)
137	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, November 8, 1961, (AD 266469 \$0.50)
138	Review of Recent Developments in the Technology of Beryllium, November 16, 1961, (AD 267079 \$0.50)
139	Review of Recent Developments in the Technology of Tungsten, November 24, 1961, (AD 268082 \$0.50)

LIST OF DMIC MEMORANDA ISSUED
(Continued)

DMIC Memorandum Number	Title
140	Review of Recent Developments in Metals Joining, December 6, 1961, (AD 268312 \$0.50)
141	The Emittance of Chromium, Columbium, Molybdenum, Tantalum, and Tungsten, December 10, 1961, (AD 269784 \$1.25)
142	Effects of Moderately High Strain Rates on the Tensile Properties of Metals, December 18, 1961, (AD 270167 \$1.00)
143	Notes on the Forging of Refractory Metals, December 21, 1961, (AD 271030 \$1.50)
144	Review of Recent Developments in Titanium Alloy Technology, December 29, 1961, (AD 269209 \$0.50)
145	The Use of Nickel-Base Alloys in the Rotating Parts of Gas Turbines for Aerospace Applications, January 11, 1962, (AD 271174 \$0.75)
146	Magnesium-Lithium Alloys - A Review of Current Developments, February 6, 1962, (AD 272683 \$0.75)
147	An Evaluation of Materials for Rocket-Motor Cases Based on Minimum-Weight Concepts, March 8, 1962, (AD 273297 \$1.00)
148	The Emittance of Ceramics and Graphites, March 28, 1962, (AD 274148 \$2.50)
149	Methods of Strengthening the Ultrahigh-Strength Steels, April 2, 1962, (AD 275041 \$1.00)
150	Compilation of Tensile Properties of High-Strength Alloys, April 23, 1962, (AD 275263 \$1.25)
151	Compatibility of Propellants 113 and 114B2 with Aerospace Structural Materials, April 27, 1962, (AD 275427 \$0.50)
152	Electron-Beam Welding of Tungsten, May 21, 1962, (AD 276283 \$0.50)
153	Brazing and Bonding of Columbium, Molybdenum, Tantalum, Tungsten and Graphite, June 11, 1962
154	The Effects of Decarburization on the Properties of Ultrahigh-Strength Steels, June 18, 1962
155	The Effects of Solutes on the Ductile-to-Brittle Transition in Refractory Metals, June 28, 1962
156	Properties of Mar-Aging Steels, July 2, 1962
157	A Compilation of the Tensile Properties of Tungsten, September 11, 1962
158	Summary of Briefings on Refractory Metal Fasteners, October 8, 1962
159	Nondestructive Testing of Solid-Propellant Rocket Motors, October 24, 1962
160	Identification of Microconstituents in Superalloys, November 15, 1962
161	Electron Microscopic Fractography, December 21, 1962
162	Report on Meeting to Review Maraging Steel Projects, December 28, 1962