I

NASA TECHNICAL MEMORANDUM

NASA TM X- 68203

NASA TM X- 68203

HIGH PRESSURE OXYGEN UTILIZATION BY NASA

by Frank E. Belles
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER proposed for presentation at
Seventy-fourth National Meeting of the American
Institute of Chemical Engineers
New Orleans, Louisiana, March 11-15, 1973

18

E-7370

HIGH PRESSURE OXYGEN UTILIZATION BY NASA

by Frank E. Belles

Aerospace Safety Research and Data Institute
Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

SUMMARY

Although NASA is not one of the country's major oxygen consumers, it uses oxygen under severe conditions including very high flow rates and pressures. Materials for such applications must be carefully selected for compatibility, because susceptibility to ignition increases as operating pressure is raised. Much work is needed, however, to define the selection criteria. Some of the work in this area that is being performed under sponsorship of NASA's Aerospace Safety Research and Data Institute (ASRDI) is described.

INTRODUCTION

Oxygen is a commodity of growing importance with new uses and modes of usage developing at a rapid pace. Production of high-purity oxygen in the U. S. increased tenfold in the past 20 years, from 1 million tons in 1952 to 10 million tons in 1971. Of this increase, a part, was naturally caused by NASA requirements. However, NASA is far from being the major user of oxygen in this country. Of the 10 million tons produced in 1971, NASA used about 75 thousand tons, less than 1 percent.

But when NASA does consume its share, it is likely to be done at a prodigious rate. A Saturn V booster contains 1600 tons of liquid oxygen at launch - not counting that which is in the upper stages - and it is all consumed in the five rocket engines by combustion with kerosene within 3 minutes after launch. This corresponds to 10 tons every second, or about the quantity contained in forty 55-gallon drums.

NASA REQUIREMENTS FOR OXYGEN UTILIZATION

Liquid Oxygen

Although NASA is by no means the country's largest user of oxygen, the conditions of use are severe. Moving liquid oxygen at the rates required by large rocket engines calls for high pressures and high flow velocities. And there are constant upward trends in the pressures required. The engines of the space shuttle orbiter, fueled by liquid hydrogen and oxygen, will operate at a chamber pressure of 3000 psi. This contrasts with the 725 psi chamber pressure used in the upper stage engines of the Apollo and Skylab systems, which operate on the same propellants. This is a large step up in pressure. To attain it will require maximum pressures even higher, up to about 6500 psi in some parts of the shuttle propulsion system.

The reason for adopting higher pressures in the shuttle orbiter is the need to maximize payload. The new system will provide higher performance, and this gain will be reflected as more pounds in orbit. At the same time, every effort has to be made to avoid losing the advantage of higher engine performance to an increase in system weight prompted by the need to contain the new, higher pressures. To hold the weight down and still keep acceptable safety margins will require utmost care and ingenuity in design, in the exploitation of the strength and toughness properties of materials, and in the choice of the materials.

Gaseous Oxygen

The foregoing discussion has dealt with propulsion systems, which utilize oxygen as a liquid. NASA also has requirements for gaseous-oxygen systems that operate at pressures considerably above the range of present industrial practice.

For lunar or space excursions, oxygen must be carried by the astronaut in gaseous form. This is because no source of heat, such as warm ambient air, exists that can be used to vaporize gas from a liquid supply. For extended missions, and for emergency high-demand flows, large amounts of gas have to be carried. The emergency oxygen system carried by astronauts while on the moon exemplifies the requirements. Here, 5.8 lbs. (approximately 70 standard cubic feet of gas) are packed into two spherical vessels, about 6 inches in diameter. The resulting pressure is 6000 psi. This is enough gas to maintain a breathing atmosphere of 5 psia inside the suit for 30 minutes, and at the same time provide for emergency use such as supplemental cooling.

This emergency supply is charged with oxygen at Kennedy Space Center using ground equipment that has been operated at up to 10,000 psi. To the author's knowledge, this is the greatest extreme of oxygen pressure that is presently employed in a functional system.

SAFETY IMPLICATIONS OF HIGH-PRESSURE OXYGEN UTILIZATION

General Considerations

The measures needed to contain high-pressure oxygen and to use it safely are of two kinds: first, those common to any system designed to operate over similar ranges of temperature, pressure, and mass flow; and second, those imposed by the unique chemical properties of oxygen itself. These oxygen-specific requirements can be further characterized in terms of structural and chemical compatibility.

The first can be disposed of quickly, inasmuch as there is very little information on the subject. A recent survey (ref. 1) called attention to the possibility that crack propagation or fracture in metals might be enhanced in a high-pressure oxygen environment, but found that investigation of this possibility has been sorely neglected. It is also important that some representative nonmetallic materials be checked for degradation of mechanical and/or chemical properties after long-term exposure to high-pressure oxygen.

It scarcely needs to be stated that the case is quite otherwise with respect to chemical compatibility and that there is ample evidence that problems exist. Nor is the extreme reactivity of oxygen a concern only at the very high pressures used in advanced systems. For example, a recent survey (ref. 2) covering the years 1957 to 1971 reported 31 burnouts of pressure regulators on the familiar, seemingly innocuous oxygen cylinders that are charged to maximum pressures of about 2200 psi and are found everywhere. This was far from a complete survey; it covered only regulators from one manufacturer. These cylinders and regulators are handled casually by all kinds of people, many of them quite unaware of the hazard to which they are exposing themselves through their lack of training. Other statistics attesting to the frequency of oxygen fires could also be cited. A common thread that runs through many descriptions of accidents is the element of surprise; the people involved generally thought they had behaved prudently. They simply had not appreciated the extra caution required in handling oxygen. Thus, there is certainly a need for better training. But there is also a need for better criteria to guide the selection of ignition-resistant materials and the establishment of safe operating procedures. The remainder of this paper will review some of the facts pointing up the need for improved criteria, and some of the work within NASA aimed at developing them.

Ignition Susceptibility at High Pressures

One may envision a great many ways in which energy can be added to various parts of an oxygen system rapidly enough, and in sufficient amount, to cause ignition: adiabatic compression, mechanical impact, electric arc, flame, impact of high-velocity particles, and many others. Another obvious hazard is high operating temperature.

No matter what the mode of energy deposition may be, the driving force that results in ignition is an increase in temperature. This increase, whether general or localized in a hot spot, accelerates heat-releasing reactions, and ignition results if the heat cannot be dissipated as fast as it is produced. Hence, the most straightforward way to assess the increased hazards in high-pressure systems is to consider the effects of pressure on the ignition temperatures of various materials.

Figure 1 shows data from several sources (refs. 3 - 7) for seven nonmetallic materials. The three in Figure 1(a) are not generally considered premium materials for oxygen use, although nylon is quite often employed. The other four materials, whose ignition temperatures are plotted in Figure 1(b), are generally regarded as better in the sense that they are less susceptible to ignition in oxygen. The plotted data tend to support this idea, inasmuch as the ignition temperatures in Figure 1(b) are appreciably higher in the high-pressure region represented by the last decade of pressure (1500 to 15,000 psi).

Ignition temperatures are not immutable constants but depend somewhat on the method of measurement. There is a need for more data determined in a consistent manner and covering the range of pressures more fully. Nevertheless, there are several points to be made about the behavior exhibited in Figure 1:

1. The rate of decrease of ignition temperature with the logarithm of the pressure is a characteristic of the material and is much stronger for some than others.

2. Hence, materials selected on the basis of their high ignition temperatures at low pressures may prove relatively unsuitable for use at high pressures.

3. There is relatively little spread from the lowest to the highest ignition temperatures in the high-pressure region; this suggests that the choice of material for high-pressure use may be quite difficult and may have to be aided by other types of tests.

These points are further emphasized by the additional data shown in Figure 2 (refs. 1, 8 and 9; data for mild steel at pressures above 14.7 psia from unpublished Linde work and provided by P. L. Hurning, Union Carbide Corp., Linde Division, Gas Products Production Department, in letter dated November 24, 1970). Here, the ignition temperatures of several metals are plotted against the logarithm of the pressure, and the data for three of the nonmetallics are repeated for comparison. Two alloys show such a strong downward trend that one is led to suspect they will be no more ignition-resistant at high pressures than are the nonmetallics. The same might prove to be true of the stainless steel alloy and of aluminum, but data are lacking to confirm this. Copper, on the other hand, shows a well-defined linear dependence of ignition temperature on the logarithm of the pressure that suggests it is definitely less easily ignited at high pressures than are the nometallics.

RESEARCH ON OXYGEN COMPATIBILITY AT HIGH PRESSURE

In the remainder of this paper, work currently in progress relating to ignition and burning in oxygen will be described. The need to extend such studies to higher pressures is clearly shown by the fact that ignition temperatures go down as pressures go up. Unfortunately, there are no direct correlations known to exist between ignition caused by raising the temperature of the whole sample, and ignition caused by other stimuli. It is hoped that the work in progress may help to reveal such correlations; but, in any event, the work will further define the hazards and the safety criteria to deal with them. It is emphasized that only ASRDI-sponsored work is discussed here; other investigations are under way within NASA, at NBS, and at industrial laboratories.

Ignition Modes

Flow Effects.- Although ignition temperatures are not absolutes, they do indicate the relative ease of ignition and no reasonable person would deliberately operate a high-pressure oxygen system too close to the ignition temperatures shown in Figures 1 and 2. However, high temperatures can occur in other ways. In Figure 2, a line is plotted showing the temperatures reached by adiabatic compression, starting from atmospheric pressure and 70°F. Such temperatures could be approached if a system were abruptly pressurized by opening a valve to a reservoir at high pressure. Although the temperatures shown are maximum ones, and in real systems would be both lower and of relatively short duration, rapid pressurization is clearly a hazardous procedure. Small particles of contaminants, either metallic or nonmetallic; and system components that have low heat capacity and/or heat conductivity, will be especially vulnerable. Their ignition can then kindle more massive components and produce a destructive fire.

A related but different phenomenon is currently under investigation at Lewis Research Center. In realistic gas-flow configurations such as the one shown in Figure 3, large temperature rises can occur in dead-ends during steady flow. This is caused, not by adiabatic compression, but by a resonant process involving repeated shock waves, as outlined in Figure 4. After a few seconds, the temperature can climb to dangerous levels in the gas near the end of the cavity. Temperatures measured for the case of flow from a 1000 psi source, is shown in Figure 5. Experiments with metal chips in the cavity have produced ignition of the chips followed by burnout of the system. This hazard has not been previously appreciated and it is a very real one, inasmuch as dead-end configurations often are built into flow systems or exist in components such as valves, and it is in these cavities that contaminants are apt to collect.

Impact.- Mechanical impact has been long recognized as an ignition hazard in oxygen systems and a test based on the phenomenon is a standard method for screening materials (ref. 10). In this test, a falling weight hits a striker pin resting on the sample. In an effort to extend the significance of such tests from screening to the evaluation of hazards in real systems, the test program outlined in Table I is under way at NASA's White Sands Test Facility (WSTF). A systematic effort is being made to determine the effects of such variables as sample thickness (14-fold range), relative size of striker and sample (100-fold range), and contamination by oil and by grits which may act as stress-concentrators. In some tests, the threshold energy for impact ignition will be carefully determined by varying the weight and drop distance. In others, the effects of presumed sensitizers will be assessed by go-no-go tests at 75 percent of the threshold energy for the clean samples. Because of the large number of runs required to extract the desired information, only three materials are to be studied in the current tests: stainless steel, aluminum, and Teflon.

Another kind of impact has also been recognized as hazardous, especially in gaseous systems, but has received far less attention experimentally. This is the impact of high-velocity particles. Table II outlines a program to be carried out at WSTF that should go a long way toward defining particle-impact hazards in quantitative terms.

Once this is accomplished, the results will undoubtedly affect the specifications for cleaning oxygen systems. As a recent survey shows (ref. 11), various organizations have widely different specifications for allowable particle size and number, none of them based on a realistic assessment of the ignition potential.

Electric Arc.- Figure 6 is a schematic of the apparatus being used at WSTF to determine threshold arc currents for ignition of various materials. The test matrix is shown in Table III. In planning this program, the intention was to evaluate the tolerance of materials to typical malfunctions, such as short circuits or damage to electrical insulation.

The results will help specify current-limiting devices for the protection of electrical equipment exposed to oxygen.

Table IV summarizes some of the early results, obtained with Teflon. These are not threshold currents for ignition, although for the 0.003-inch samples there is a suggestion as to where the threshold may lie. As would be expected, the burning that follows ignition is markedly faster at the higher temperatures and pressures.

Fracture.- It is known that titanium will ignite under some conditions when samples are broken in oxygen. Presumably, this is caused by the exposure of fresh, reactive metal, unprotected by an oxide layer. The possibility exists that other metals may also ignite and to investigate this possibility, the apparatus shown in Figure 7 is being used at Lewis Research Center. A pneumatically-driven plunger breaks a metal foil inside a chamber in which tests may be performed at elevated temperatures and pressures.

Table V summarizes the results so far. Only titanium has been found to ignite in these tests, and it does so, at room temperature, at all pressures of pure oxygen above 65 psi. Other tests at temperatures up to 1000°F have not shown any appreciable reduction in this pressure limit. Dilution of the oxygen with nitrogen, on the other hand, greatly increases the pressure required for the fracture-ignition of titanium foils. Figure 8 shows this effect for room-temperature tests.

As shown in Table V, ignition of metal foils other than those made of titanium has not been observed. It is especially interesting to note that aluminum has withstood this test at 1400 psi. However, it is quite possible that results will be otherwise when these apparently safe metals are tested at still higher temperatures and pressures. It should also be noted that, except for the stainless steel, the tests so far have involved pure metals; alloys may respond quite differently.

Burning Rate Studies

The final program of ASRDI-sponsored research to be discussed is one in which the burning rates of nonmetallics are being measured at Lewis Research Center. The objective is to extend such work to higher ranges of oxygen pressure and to correlate the results with literature data obtained at lower pressures and in different geometrical configurations. In the present work, the samples are cylindrical rods oriented with their axes parallel to the direction of flow of high-pressure oxygen. The rods are ignited at the downstream end and are vertical, so that the flame must advance against the flow without assistance from convection.

Table VI compares results for Teflon and nylon at two pressures. At both 300 and 1000 psia, Teflon burns much slower than nylon, and its flame-spread rate varies over a much smaller range in response to changes in flow velocity. Nevertheless, these results again emphasize that Teflon will, indeed, persistently burn in oxygen, and under circumstances that seem extremely unfavorable for flame propagation.

CONCLUDING REMARKS

The intention of this review has been to emphasize the need for engineering criteria that can be used to guide the design and operation of oxygen systems. The degradation of mechanical properties, the susceptibility to ignition by various stimuli, and the resistance to burning, must be quantitatively defined. Some of the work that has been undertaken with these ideas in mind has been described. Such work is an essential adjunct to screening tests which, while they are useful in ranking materials against those already known to be suitable for use on the basis of experience, will tend to become less conclusive as applications are pushed into the high-pressure range where experience is lacking.

REFERENCE LIST

1. Hust, J. G. and Clark, A. F.: A Survey of Compatibility of Materials with High Pressure Oxygen Service. NBS Institute for Basic Standards, Cryogenics Division, Final Report 275.03-72-11, October 1972. (Prepared for Marshall Space Flight Center under NASA Order No. H-92180A.)

2. Lapin, A.: Liquid and Gaseous Oxygen Safety Review, Final Report, Vol. I. NASA CR-120922, June 1972.

3. Guter, M.: Ignition in High Pressure Oxygen. S&T Memo 13/50, British Ministry of Aviation, Reissued February 1967. (First issue, British Ministry of Supply, June 1950.)

4. Stevens, M. R., Fisher, H. D., and Breen, B. P.: Investigation of Materials Combustibility, Fire, and Explosion Suppression in a Variety of Atmospheres. Air Force Aero Propulsion Laboratory AFAPL-TR-68-35, May 1968.

5. Attwood, H. C. and Allen, G. R.: On the Spontaneous Ignition Temperature of Organic Materials in Oxygen. British Ministry of Defence (Aviation Supply) C. P. No. 1172, 1971.

6. Joy, L. A.: Safety Aspects of Using Oxygen in a Hazardous Environment. Aerojet Liquid Rocket Co. Engineering Report No. 037-70, November 1970.

7. Nihart, G. J., et al: Compatibility of Materials with 7500 PSI Oxygen. AD 608260, October 1964.

8. Jakowsky, J. J. and Butzler, E. W.: Oxygen - Oil Explosions; Preliminary Report II, Spontaneous Ignition of Metals in Oxygen Under Pressure. Bureau of Mines RI-2521, September 1923.

9. Reynolds, W. C.: Investigation of Ignition Temperatures of Solid Metals. NASA TN D182, October 1959.

10. American Society for Testing and Materials: Standard Method of Test for Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold Technique). ASTM Designation D2512-70; ANSI Standard Z11.274. ASTM Annual Standards, 1971, Part 18.

11. Bankaitis, H. and Schueller, C. F.: ASRDI Oxygen Technology Survey, Volume II, Cleaning Requirements, Procedures, and Verification Techniques. NASA SP-3072, 1972.

IGNITION BY MECHANICAL IMPACT[(a)]

DETERMINATION OF ENERGY THRESHOLDS

MATERIAL	THICKNESS, IN.			STRIKER PIN-SAMPLE BEARING AREA			PRESSURE, PSIA			TEMPERATURE, °F		
METALLICS	0.01	0.07	0.140	0.1a^2	1a^2	10a^2	100	1000	5000	-250	70	1000
STAINLESS STEEL	X	X	X	X	X	X	X	X	X	X	X	X
STAINLESS STEEL W/NONIGNITIBLE GRIT	X			X	X	X		X			X	
STAINLESS STEEL W/CUTTING OIL FILM	X			X	X	X		X			X	
STAINLESS STEEL W/LUBRICATING OIL FILM[b] NOTE[c]	X				X			X			X	
NONMETALLICS	0.001	0.01	0.10	0.1a^2	1a^2	10a^2	100	1000	500	-250	70	1000
TEFLON	X	X	X	X	X	X	X	X	X	X	X	X
TEFLON W/NONIGNITIBLE GRIT		X		X	X	X		X			X	
TEFLON W/CUTTING OIL FILM[b]		X			X			X			X	

[a]ENERGY LEVELS - 100 TO 1200 FT-LB/IN.^{2}
[b]SIMILAR TESTS TO BE PERFORMED USING OTHER CONTAMINANTS.
[c]SIMILAR SERIES OF TESTS WITH ALUMINUM.

CS-65848

TABLE I

IGNITION BY PARTICLE IMPACT (ABRASIVES)

DETERMINATION OF ENERGY THRESHOLD

METALS -
STAINLESS STEEL, ALUMINUM, MONEL, INCONEL, PHOSPHOR BRONZE, BRASS

NONMETALS -
TEFLON, VITON, VESPEL SP-21

THICKNESS (IN.) -
0.1, 0.5, 1.0

DIAMETER (IN.) -
0.5 & 2 TIMES ABRASIVE JET DIAM

VELOCITY, FT/SEC -
100, 300, 500, 1000

PRESSURE (PSIA) -
100, 1000, 5000

ABRASIVES -
SAND, WELD SCALE (SIZES - 0.001 & 0.0001 IN.)

CS-65841

TABLE II

E-7370

IGNITION BY ELECTRIC ARC
DETERMINATION OF ENERGY THRESHOLDS[a]

MATERIAL	THICKNESS, IN.			PRESSURE, PSIA			TEMPERATURE, °F		
METALLICS	0.01	0.070	0.140	100	1000	5000	-250	70	1000
STAINLESS STEEL	X	X	X	X	X	X	X	X	X
MONEL	X				X				
PHOSPHOR BRONZE	X				X				
NONMETALLICS	0.001	0.01	0.10	100	1000	5000	-250	70	b
TEFLON	X	X	X	X	X	X	X	X	X
VITON			X		X			X	
HIGH TEMP INSULATION		X			X				X

[a]ARC - 0.1-20.0 AMPS; DURATION UP TO 2 SEC.
[b]MAX TEMP - 500° F OR USE TEMP + 50%.

CS-65842

TABLE III

IGNITION BY ELECTRIC ARC TEFLON

THICKNESS, IN.	TEST CHAMBER		ARC CURRENT, mA	RESULTS	BURN TIME, SEC
	PRESSURE, PSIA	TEMPERATURE, °F			
0.003	100	70	250	2 PARTIAL BURNS (SELF-EXTINGUISHING)	1.5
				2 TOTAL BURNS	
	1000	70	250	NO BURN	
	100	500	175	TOTAL BURN	1.0
	1000	500	150	TOTAL BURN	.5
.010	100	70	225	TOTAL BURN	3.0
	1000	70	200	TOTAL BURN	1.5
	100	500	200	TOTAL BURN	1.25
	1000	500	150	TOTAL BURN	1.0
.100	100	70	250	TOTAL BURN	6.0
	1000	70	200	TOTAL BURN	5.0
	100	500	200	TOTAL BURN	4.0
	1000	500	150	TOTAL BURN	3.0

CS-65849

TABLE IV

METALS TESTED IN 100% OXYGEN

METAL	TEMP, ^0F	PRESSURE, PSI	IGNITION	REMARKS
ALUMINUM	80	1000	NO	
ALUMINUM	80	1400	NO	
COLUMBIUM	80	UP TO 900	NO	
TANTALUM	80	UP TO 900	NO	
TITANIUM	80	65	YES	TOTAL OF 47 RUNS WERE MADE
STAINLESS STEEL - 304	80	UP TO 900	NO	
VANADIUM	80	383	NO	
ZIRCONIUM	80	70-90	NO	

CS-65843

TABLE V

E-7370

BURNING RATE STUDIES

PRESSURE, PSIA	MATERIAL	OXYGEN GAS VELOCITY, FT/SEC	FLAME SPREAD RATE, FT/SEC
300	TEFLON	1.0 TO 3.5	0.002 TO 0.004
	NYLON	.7 TO 15.0	.008 TO 0.350
1000	TEFLON	.4 TO 5.0	.008 TO 0.018
	NYLON	.4 TO 5.0	.030 TO 1.32

TABLE VI

CS-65840

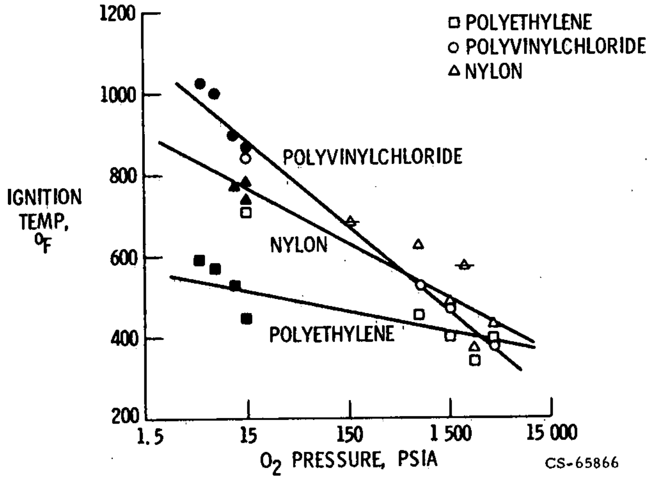


Fig. 1a - Effects of pressure on ignition temperatures of non-metallic materials in 100% oxygen atmosphere.

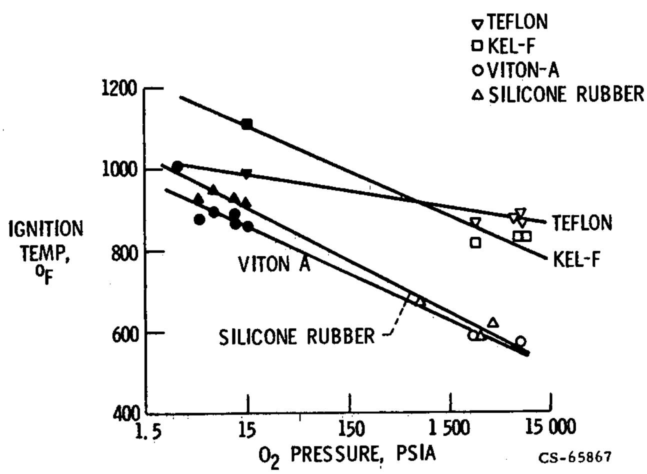


Fig. 1b - Effects of pressure on ignition temperatures of non-metallic materials in 100% oxygen atmosphere.

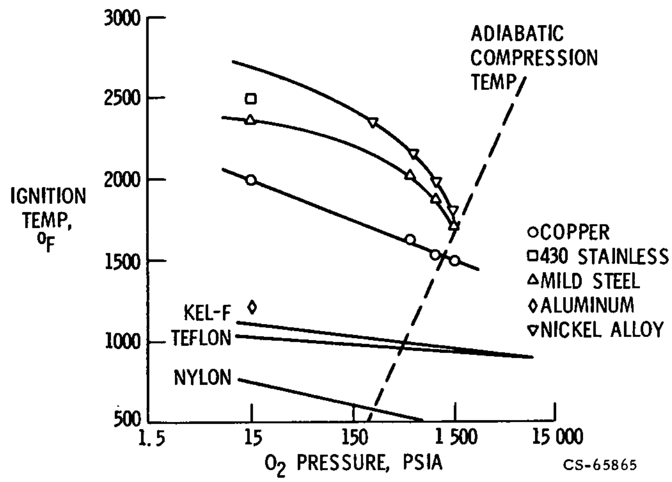
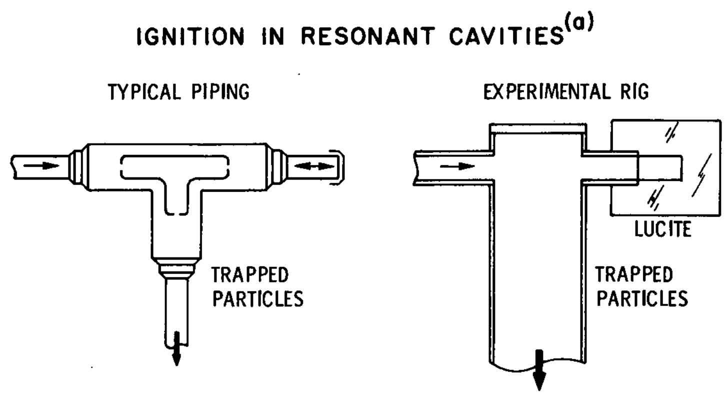


Fig. 2 - Effects of pressure on ignition temperatures of metals in 100% oxygen atmosphere.

E-7370



[a]VARIABLES INCLUDE TUBE SIZE, PRESSURE, METALS, & NONMETALS.

CS-65846

Fig. 3

RESONANCE TUBE IGNITION – INTERNAL FLOWS

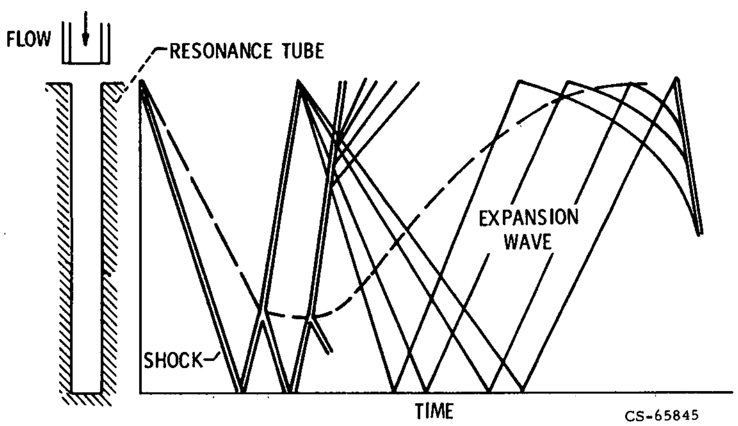


Fig. 4

RESONANCE TUBE IGNITION

TEMPERATURE IN RESONANT CAVITIES

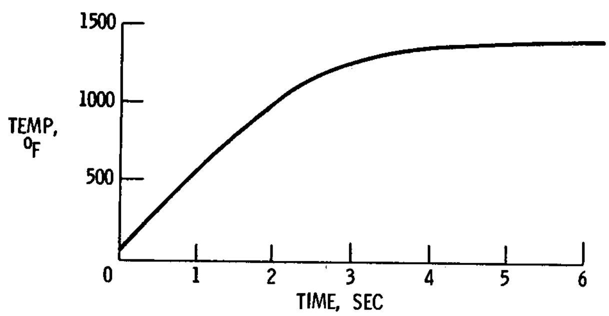
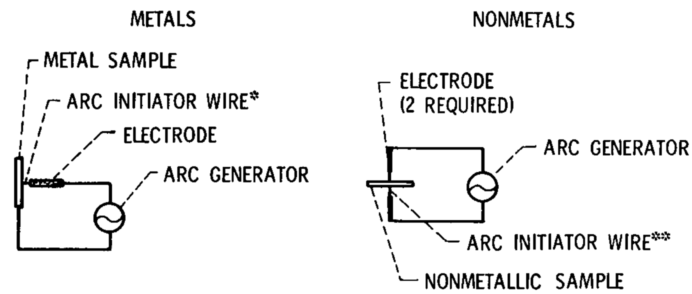


Fig. 5

CS-65839

IGNITION BY ELECTRIC ARC



*SHORT CIRCUIT CURRENT DETERMINED BY ARC INITIATOR WIRE DIAM.
**SHOULD ARC INITIATOR CONCEPT BE UNSUCCESSFUL, A HIGH VOLTAGE SPARK WILL BE USED TO INITIATE THE ARC.

VARIABLES INCLUDE

- TEMPERATURE - -250, 70° F, 1000° F
- PRESSURE - 100, 1000, 5000 PSI
- CURRENT - 20.5, 0.5 AMPS
- MATERIAL THICKNESSES
- MATERIALS - S. S., MONEL, BRONZE, TEFLON, VITON

CS-65844

Fig. 6

FRACTURE IGNITION RIG

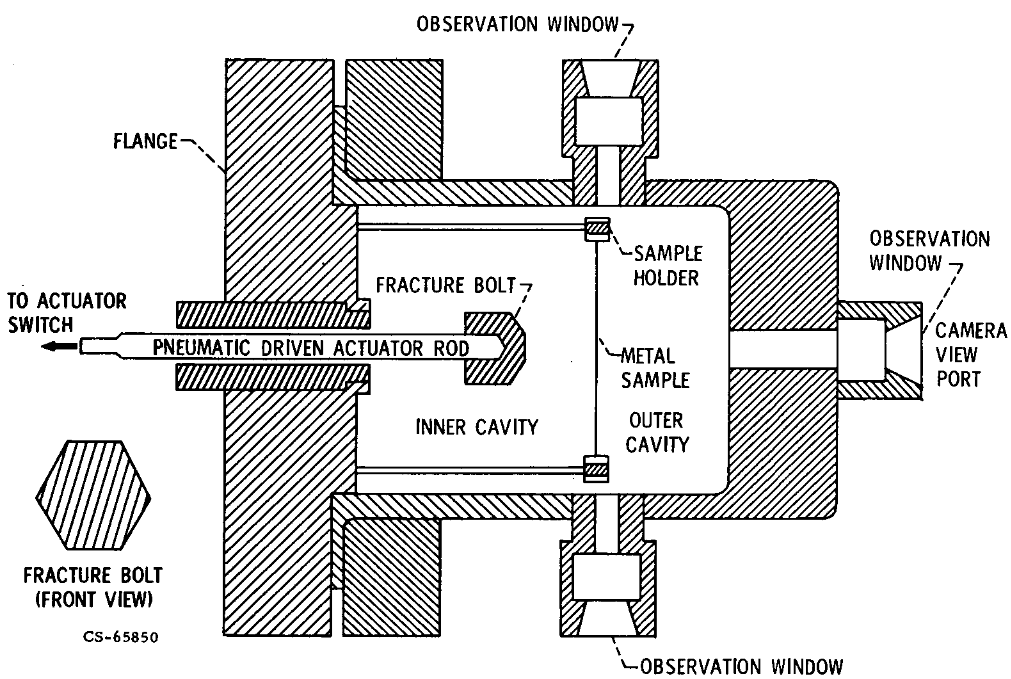


Fig. 7

E-7370

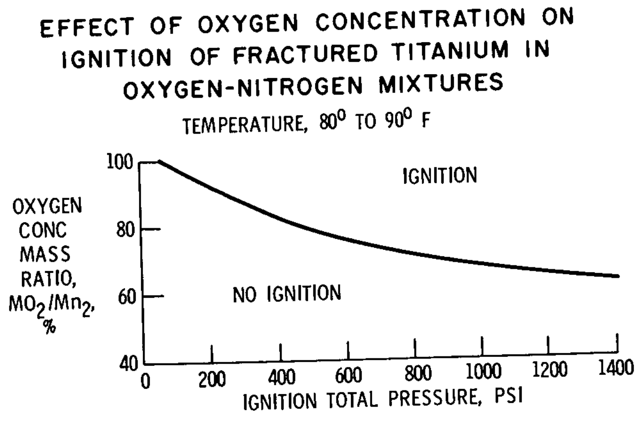

EFFECT OF OXYGEN CONCENTRATION ON IGNITION OF FRACTURED TITANIUM IN OXYGEN-NITROGEN MIXTURES
TEMPERATURE, 80° TO 90° F
IGNITION
NO IGNITION
OXYGEN CONC MASS RATIO, MO2/Mn2, %
100
80
60
40
0
200
400
600
800
1000
1200
1400
IGNITION TOTAL PRESSURE, PSI
CS-65838

Fig. 8