MSC-03461

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

DIVISION INTERNAL NOTE

REVIEW OF FACTORS AFFECTING IGNITION OF METALS IN HIGH PRESSURE OXYGEN SYSTEMS

MANNED SPACECRAFT CENTER
HOUSTON, TEXAS
October 28, 1970

Rqt-65331

STRUCTURES AND MECHANICS DIVISION INTERNAL NOTE

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INTRODUCTION

As a result of the Apollo 13 supercritical oxygen tank incident, a literature survey was conducted to determine the availability of data concerning ignition of metals in liquid or high pressure oxygen environments. This paper provides brief summaries of the reported data with emphasis being given to the effects of oxygen concentration; total pressure; convection, including zero gravity; oxygen percentage; and halogenated compounds on ignition.

Supercritical oxygen is carried in spacecraft for three reasons. It is a reactant for the fuel cell power generation system; it provides breathing oxygen for the crew; and it provides drinking water as a by-product of fuel cell operation. Purity of this oxygen is very high as dictated by the requirements for fuel cells. At the start of a mission, the density of supercritical oxygen, which is a single-phase material, is 78 pounds per cubic foot; during the flight the density decreases as oxygen is depleted. A full tank contains 323.45 pounds of oxygen at a pressure of 900±35 psia and a temperature of -325°F. Apollo 13 carried two of these tanks.

Materials in contact with supercritical oxygen in the Apollo oxygen system include both metals and non-metals. Criteria for selection included the results of various tests, based primarily on mechanical impact. One such type is the drop test whereby 72 ft-lbs of energy are imparted against a striker in contact with the specimen submerged in liquid oxygen (LOX) at atmospheric pressure. Another test simulates meteorites puncturing a LOX tank. In some instances, successful usage for thousands of hours also reinforced the confidence in using specific materials.

BACKGROUND

Work has been reported on the ignition of solids, liquids, and gases in various oxygen environments[1-20]. The environment, ignition techniques, ignition energies, and other aspects of ignition in oxygen, have varied widely. Tests described in the literature are so specialized as to make it virtually impossible to define the word "fuel". For example, it is a truism to say that, "Everything burns except metal oxides and water". Schmidt[8], however, points out that firebrick, a mixture of aluminum oxide and silicon dioxide (Al_2O_3 and SiO_2), burns vigorously in gaseous fluorine after preheat with a fluorine-hydrogen torch. He also presents some evidence of reactivity of water vapor which he described as combustion.

Reference 11 indicates that the factors affecting ignition are the following:

1. Composition and physical state of fuel.
2. Composition and physical state of the oxidizer.
3. Pressure, stress, or other internal forces.
4. Gravitational force field.
5. Temperature and enthalpy of container, fuel, and oxidizer.
6. Energy media.
7. System restraints.
8. Surface area, texture, and particle size.
9. Degree of mixing or stratification.
10. Stability or degree of self-degradation.
11. Catalyst.
12. Thermal conductivity.
13. Time.

Montelone[1] relates "possible factors affecting ignition of combustibles in manned spacecraft". These are tabulated in Table I.

IGNITION TEMPERATURES

It is clear that the temperature at which a metal ignites is not a physical or chemical property suitable for tabulation in handbooks since it has been found to involve many variables of environment and configuration. A large majority of materials cannot burn in their solid state. That is, they must absorb energy to produce gases which mix with an oxidizer to produce a flame. Some materials do not require a change to the liquid state and burn by a sublimation process, going directly from a solid to a gas. Others melt, then vaporize to produce a flammable mixture.

The characteristic of the oxidation product also plays a role and, in the case of metals, can be a dominant factor. Some oxides, such as the oxides of chromium, titanium, and aluminum, are hard, tenacious, and heat resistant. Others, such as iron oxide, are porous and therefore virtually useless in inhibiting further oxidation. C. P. Talley[21] reports several rate-limiting steps in the process of burning boron in oxygen.

He points out that while carbon only produces gaseous carbon monoxide and carbon-dioxide, magnesium would yield only solid magnesium oxide, that aluminum would yield only solid or liquid aluminum oxide, and that boron is unique in that the oxide exists in a flame as solid, liquid, and gas over the temperature range produced. He defines five regions of the temperature-pressure plot in which the metal and its oxide have different properties that have an effect on transport of reactants. Talley states that the viscosity and surface tension of the liquid oxide are important in determining rates of burning.

Reynolds[22] investigated a number of structural alloys for aircraft and missile use. He points out that the danger of ignition is increased in regions behind shock waves where temperatures and pressures are exceptionally high. He stresses the difference between ignition and burning. He states, "Ignition is brought about by the exothermal oxidation reaction between the solid metal and its gaseous environment. Consequently, it is believed that the phenomenon of ignition is quite closely related to the relatively slow oxidation that occurs on all metals at low temperatures ("rusting"). Burning, on the other hand, may proceed by any of several mechanisms. It may be a surface reaction or a vapor-phase reaction and occur at some distance from the surface (as in the case of magnesium)". Reynolds' work is with a dynamic gas flow. Table II gives the results of his work. Air and oxygen at pressures of 1 to 7 atmospheres were evaluated. Note that the oxygen content or pressure has no effect on ignition temperatures. Temperatures are given for static air first, then for an airflow of Mach 1.25. The term "brightness" temperature is used to denote the condition at which the exothermic reaction appears to start.

A survey of published data on the ignition of metals in oxygen was made by E. L. White and J. J. Ward[23] of Battelle Memorial Institute. This paper relates methods that have been used, experimental values that have been obtained, and the status of theories that permit the calculation of ignition temperatures. They point out that "all metals with the possible exception of gold and platinum, can be expected to ignite in oxygen at some elevated temperature". Also, "alloys of several systems have been shown to ignite in oxygen systems at relatively low temperatures and some, such as the alloys of titanium, zirconium, thorium, uranium, lead, tin, and magnesium, at LOX temperature if some external source of energy input is present".

One low temperature ignition process is the pyrophoric reaction. Ignition can be achieved by quickly exposing powdered metal, without a protective oxide, to air. When the particle size is such that the heat produced by formation of a layer of oxide is sufficient to heat the substrate (a very high surface to mass ratio) to the melting point, the reaction usually proceeds to completion. Sub-micron size particles are most easily ignited. The dramatic reaction is the main reason for the observation of sparks thrown from a grinding wheel, or from a cigarette lighter "flint". In the latter case the alloy involved is a mixture of cerium and iron. This same process can be demonstrated also with nickel, iron, copper, and many other metals if the oxide is first removed from the surface in a reduction reaction, say in heated hydrogen. A simpler technique is to heat a metal-organic salt such as lead acetate. The metal is reduced to its pure form, is powdered, and reacts when poured out of its container after cooling.

Smith[24] describes pyrophoricity as a major problem of the nuclear materials field, stating that "our understanding. . . . is quite inadequate to cope with the broad range of behavior exhibited by pyrophoric metals". He discusses some possible mechanisms while describing a variety of accidents.

A description of magnesium burning is given. From high-speed movies of a magnesium wire burning in oxygen he noted, "that oxidation was accompanied by periodic small localized high-energy explosions, the causes of which are uncertain".

Littman and Church[25] published data on zirconium and titanium "brought rapidly in contact with oxygen". They describe ignition in terms of the pressures tested. They relate, "Spontaneous ignition of clean zirconium in oxygen occurred at room temperature with oxygen pressures of 300 psi and over. . . ." Also, "Oxidized titanium samples ignited at a pressure of about 500 psi oxygen". A wide variety of specimens was used. In the case of zirconium sheet they included some samples which were oxide-free, some etched, some oxidized, some hydrided, some carbided. Sheets "were about 1/2 by 3 inches and varied in thickness from 0.010 to 0.025 inch." Zirconium bar, notched, was a "double-truncated cone with the base of 1/4 inch and the top of 1/8 inch diameter". These bars were tested by breaking in tension and in torsion. Cylindrical rods having a diameter of 1/8 inch were also used. Titanium samples were 0.032 inch of 1/2 inch by 3 inches. Also, zirconium turnings were used in impact tests. Foreign matter in the form of a "few grains of carborundum" was used in impact tests.

An evaluation of thin walled LOX tanks subjected to high stress such as produced by a meteoroid puncture was made by Christian, Chafey, et al[26]. They studied two titanium alloys, type 301 stainless steel, and 2024 aluminum. The titanium was most reactive, igniting in LOX or gaseous oxygen (GOX) in the majority of cases. The stainless steel was not ignited, regardless of the type of test. The aluminum only reacted in one of the eight series of tests; however, in this series it ignited 10 out of 16 times while in contact with LOX. The rapid application of energy precluded measuring any temperature rise. Visible flame was noticeable when there was a reaction, however,

Mellor and Glassman[27] studied the ignition of aluminum and magnesium. They show that the minimum possible ignition temperature of a metal-oxygen system is predictable by a "transition" temperature which is defined as, "the temperature at which the low temperature, generally protective product of such a reaction, becomes non-protective", whether by "melting of the oxide, mechanical stress cracking, or thermal stress cracking".

Kuehl[28] studied ignition of aluminum and beryllium. He showed how the vapor pressure of aluminum and the melting point of the oxide influence ignition. The intersection of these curves, Figure 1, he calls the "critical ignition pressure". Thus, 700 mm is the value for aluminum in oxygen. Glassman[29], summarizing this work, states that "the ignition temperature for aluminum is postulated to be controlled by the oxide melting point at higher pressures and the metal boiling point at lower pressure."

Nihart[30] performed "promoted" ignition tests, using a small piece of neoprene to "promote" ignition of the contacting metal foil. He obtained low temperatures for ignition of such a system since he was only measuring the temperature of ignition for the neoprene. This provides a significant flame temperature and assorted free radicals that ignite the metal. He also rates metals according to the amount of neoprene necessary to achieve metal burning. Since this is a measure of the energy to ignite, it is a useful empirical technique for rating materials for use in GOX or LOX.

Grosse and Conway[31] give the factors affecting the ignition temperature of metals as: purity of the metal; gas composition, including moisture content; pressure; velocity or airflow at the surface; state of subdivision; previous history of the metal; and apparatus and technique. They give details on aluminum-oxygen combustion, reporting the surface temperature as the boiling point of the metal (2,500°C), and a flame temperature maximum of 3,500°C. Metals are classified as follows: (1) Ingition temperature at or below the melting point (e.g., magnesium), (2) Ignition above the melting point (e.g., aluminum), and (3) No ignition temperature (e.g., silver, platinum, and mercury). Details on a powdered metal-oxygen torch are given.

Markstein[32] agrees with Reynolds[22] in that the ignition temperature of metals is linked with their low-temperature oxidation properties. He discusses how theories based on this have "been reasonably successful with metals that do not form a protective oxide layer". When protective layers are formed, and particularly if metal and oxide are mutually soluble, ignition is not predictable. Further complications arise, he points out, when the metal is finely subdivided. Markstein emphasizes that, "compared with the present knowledge of combustion of conventional fuels, the burning of metals is as yet poorly understood".

An important study showing that bimetallic alloys have ignition temperatures unlike either metal alone was conducted by Poyarkov[33]. Fifteen alloys were prepared, pulverized, and tested in dry air and in humid air. Data are diven in Table III. Notice that the lowest temperature noted is 510°C, located at 49.1 percent magnesium. The next lowest value is 512°C, with even less magnesium. Both metals in the pure state ignited at higher temperatures. Poyarkov also reported the effect of using air saturated with water at 30°C. He points out that around 565°C, "violent liberation of magnesium vapor begins. After this, ignition occurs which immediately turns into powerful combustion". The 35.9 percent eutectic had the highest reported flame temperature, 2270°K. Poyarkov also noted that when plotting these values on a phase diagram, the slopes parallel the liquidus lines.

EFFECT OF PRESSURE ON IGNITION

Kuehl[28] identifies the critical ignition pressure for aluminum as approximately 700 mm Hg. Above this pressure, the melting point of the oxide is the dominant factor in ignition. This is a physical property not dependent on pressure.

Glassman[29] showed a decided pressure effect. He states, "the ignition temperature of zinc increases with increasing pressure in almost perfect correlation with its boiling point at the respective pressures involved". Reference 35 gives data from 200 torr to 15 atmospheres, substantiating the above statement. Interestingly, it is noted that this plausible effect is different than the effects reported by others.

Hill, et al[34] tested aircraft metals at pressures from one-half atmosphere to 53 atmospheres and concluded that any effect of pressure on oxidation rate was too small to be determined. Using supersonic airflows at Mach 1.4 and 2.0, they ignited iron alloys below the melting point and ignited titanium in air, oxygen, and nitrogen. They could not ignite Inconel, copper, 18-8 stainless steel, Monel, and aluminum at, or close to, their melting points.

Littman and Church[25] reported a decided effect of pressure on spontaneous ignition of clean zirconium and titanium. They also reported ignition of titanium and zirconium when impacted while in liquid oxygen. However, "no ignitions were produced in a gaseous oxygen atmosphere with pressures up to 2000 psi and impacts of the order of 125 ft-lbs".

White and Ward[23] report that, "it appears probable that a definite or an absolute ignition temperature does not exist for a particular metal-oxygen system" and that the "temperatures appear dependent on many factors, some of which are relatively static (e.g., atmosphere, composition, purity, metal surface area, and condition, etc.)". They further state, "an increase in pressure of a gaseous oxygen system tends to promote ignition at lower temperatures or with lower secondary energy inputs".

Reynolds[22] shows that ignition temperature is "essentially independent of ambient temperature and pressure, except insofar as these items influence convective heat transfer". As noted in Table II, pressure is not a factor in ignition of metals for the air and oxygen used, at pressures of from one to seven atmospheres. His plots of temperature versus pressure for nine alloys clearly justify this conclusion.

The scatter in Nihart's[30] work with promoted ignition makes it difficult to establish or refute a pressure effect. One of his conclusions is, "the spontaneous ignition temperatures of the materials tested are essentially the same in 7,500 psi oxygen as in 2,000 psi oxygen".

In summary, it can be stated that any difference in liquid oxygen at 14.7 psia and 1000 psia, as it affects ignition, is probably negligible. The density is different and, since there is more available oxygen at the higher pressure, the burning rate is possibly increased. The ignition temperature is unaffected. The ignition energy for a given piece of metal may vary with pressure, however, no information could be found on this subject.

EFFECT OF CONVECTION ON IGNITION

Reynolds[22] analytically found a decided convective effect on ignition temperature. He states, "the dependence of the ignition temperature on convection and radiation heat transfer rate predicted by the analysis is extremely interesting. It is found that the ignition temperature depends only on the magnitude of these transfers and not upon their direction with higher heating or cooling rates giving higher ignition temperature. No experimental data are available either to substantiate or to repudiate this result".

Work in zero gravity flammability[36] included a variety of metallics and non-metallics ignited by a heated nichrome wire in 5 psia oxygen and other hypobaric atmospheres. Two significant effects were noted - one is that 20 gage nichrome wire, heated electrically, ignited in several of these tests (approximately 3 percent) but did not burn to completion. The other is that Teflon appeared to be ignited easier in this environment than in one-g, perhaps because the heat from the wire was more effective in pyrolyzing this polymer. These were in fact propagation tests and ignition energies were not measured. Quantitative data of this type will not be available until such experiments can be performed on board orbiting spacecraft.

Two other metals were ignited. One was a commercial grade magnesium alloy chosen for its ease of ignition. The other was stainless steel sponge. Both readily ignited in zero gravity.

The significant difference between metals and non-metals from the point of view of convection is that metals do not produce large volumes of gaseous combustion products. Therefore, there should be no blanketing effect that would prevent oxygen flow or inhibit a steady-state reaction. In fact, higher temperature should result in zero-g, increasing burning rates, as the convective heat loss is eliminated.

During orbital coast of a spacecraft at a nominal zero gravity condition, the supercritical oxygen inside a tank may be undergoing convective flow. Operation of interior heaters does not, naturally, cause a flow because of density changes that are imparted. There are three methods of generating convective flow; these include: the operation of a "fan" designed to stir the material and compensate for stratification, the withdrawal of material (a very minor effect, dependent on the geometry of the outlet), and a back-flow of oxygen into the tank from whatever cause (an unlikely event).

EFFECT OF OXYGEN PERCENTAGE

As was noted in the section on the effect of pressure, a variety of opinion exists in the literature on the ignition effect from pure oxygen versus a mixture of gases. Again, Reynolds[22] takes the view that the ignition temperature is the same in oxygen as in air. His data substantiate this view. White and Ward[23], as stated earlier, say that the "dilution of oxygen with an inert material, gaseous or liquid, tends to reduce sensitivity of metals in oxygen systems". Hill, et al[34], testing with static oxygen and dynamic airflow, did not attribute any significance to the oxygen content. Nor did Glassman[27]. Kuehl[28] saw no effects from pure oxygen versus mixtures of oxygen and argon on the ignition of aluminum. Certainly the vapor pressure and melting point of the oxide are unaffected by the gas composition. For beryllium and aluminum, however, water vapor markedly depressed the ignition temperature. Both argon and water vapor gave reduced burning rates compared with oxygen for both aluminum and beryllium. Littman and Church[25] compared oxygen with oxygen-helium mixtures and obtained ignition of zirconium at lower total pressures as the oxygen content increased from 73 percent to 100 percent. In this work, an oxygen content below 73 percent appears to preclude ignition with the techniques employed. The effect of water was different in that when "zirconium strips ignited in oxygen were allowed to burn down into a pool of water, they reacted with the water, but the reaction was eventually quenched". Studying the effect of water, Littman and Church ignited "a 1/4-inch zirconium bar instead of the 0.020 inch strip. The bar was ignited. . . .and it was allowed to burn in water to a depth of about three inches. The bar was completely consumed, indicating that massive shapes of zirconium, once ignited, are not quenched by immersion in water".

Friedman and Macek[37], studying the combustion of aluminum, conclude "that ignition occurs only upon melting of the oxide layer (m.p. 2300°K) which coats the particle. The process of ignition is not affected by the moisture content of the hot ambient gas and only slightly by its oxygen content".

Coffin[38], burning magnesium ribbon, showed the influence of diluting the oxygen atmosphere with argon, nitrogen, and helium. He showed increases in burning rates by the addition of water vapor.

The effect of carbon dioxide was studied by Rhein[39] who ignited metal powders in pure carbon dioxide gas. He reported results with lithium, beryllium, calcium, magnesium, boron, aluminum, cerium, Mischemetall, titanium, zirconium, thorium, uranium, manganese, and chromium. This work was a study related to the "planetary atmospheres of Venus or Mars". Aluminum, for example, ignited at 360° and 420°C for ultra fine powder, 0.03 micron size.

Poyarkov's work[33] with alloys of aluminum and magnesium is worth noting in this regard, especially his observation of the "violent liberation of magnesium vapor" noted when samples were heated to 565 - 570°F. This addition to the atmosphere could have an effect on ignition of the heated metal. His humid air data showed lower ignition temperatures.

The combustion of titanium in nitrogen has been reported[40] at temperatures above 802°C. The same source gives ignition of titanium in carbon dioxide above 550°C.

Gordon, et al[41], reported on various effects of ignition of metal particles based on ignition techniques employed. They say that, "the greatest area of ignorance in metal combustion is the identification of reaction products and their properties as a function of temperature and composition of the environment.

IGNITION ENERGIES

Hartmann[42] measured the minimum ignition energy of metal powder both as a dust cloud and a dust layer. His values are extremely low, comparing very well with hydrocarbon solids (see Table IV). Values with foil or other metal geometries, although not available, are undoubtedly much greater. Most measurements of ignition energy in the literature are directed towards combustible gas mixture or solids (e.g., ignition of pyrotechnic or propellants). A novel system using a laser pulse to apply a finite, measurable quantity of energy has been described for use with metals [41,43,44]. Other tests, simulating nuclear blast radiant effects, use pulses from an electric arc.

Qualitative tests to learn if ignition would occur were reported by Christian, et al[26]. White and Ward[23] relate several other types of tests for titanium in contact with oxygen. These include "drop-weight type" tests for producing high impact energy to provide ignition. Ignition attempts by explosive shock, by puncture, by machining or galling, and by tensile rupture were noted. Situations that did not produce ignition were: mechanical impact on the outside of a LOX container (as high as 140 ft-lb), rapid pressurization (250 pressurization cycles of 0 to 1500 psi in 0.6 second and back to zero in two seconds), LOX compression in a hydraulic cyclinder (by application of 70 ft-lb of energy from a dropped weight), dilution by liquid nitrogen (above 70 percent), vibration (200 cycles per second at 20 g's with a 0.03-inch double amplitude), slosh vibration (10 minutes in a Rotap machine), ultrasonic energy (400-watt, 25-kc magnetostrictive transducer for 15 minutes using 10, 25, and 63 mil thick coupons), sonic energy (150 dB acoustic pressure level for 210 seconds), a simulated loose equipment in LOX test (2-inch cubes of 321 stainless steel, rough cut, and placed in a Ti-5Al-2.5Sn tank of LOX at 35 to 40 psig and vibrated in a Rotap machine for 15 minutes), loose equipment in GOX (same as before except for the use of steel balls impacted to 20 mils depth. White and Ward[23] show no reaction of aluminum in LOX at 72 ft-lb. Christian, et al[26] showed a reaction of 2024 aluminum in LOX in "compressive impact" tests but not from tensile tests or puncture tests in GOX or LOX.

EFFECT OF HALOGENATED COMPOUNDS

The interaction of halides with oxygen modifies metal ignition considerably. According to Schmidt[8], "when metals are exposed to fluorine, one of two chemical effects can be expected to occur, i.e., either film formation or corrosion". No exception could be found to this statement. Apparently all metals react with fluorine to some extent. Godwin and Lorenzo[45] studied ignition of metals in fluorine using two techniques to determine ignition temperatures. Results, reported by Schmidt[8] give ignition temperatures for seven metals. All are lower than for oxygen, Table II.

The fluoride non-metallics are very important aerospace materials. They are not very radiation resistant, but their oxygen compatibility is excellent. For this latter reason they are used as structural plastics and electrical insulation, even inside supercritical, high-purity LOX tanks. Schmidt[8] reports that, "polytetrafluorethylene $(C_2F_4)n$ begins to dissociate at about 842°F. Beach[46] reports on hundreds of tests studying compatibility of Teflon with many fuels and oxidizers, with most results classed as "satisfactory", "suitable for use", "not affected", and "compatible for long term application". He gives Nihart's spontaneous ignition temperature in oxygen as 413°C and 469°C for two different types of Teflon in oxygen at 2000 psi and

410°C and 465°C for the same configurations at 7500 psi. Liquid oxygen impact tests by the Liquid Propellant Information Agency, NASA-MSFC, Plastics Technical Evaluation Center, and the Office of the Director of Defense Research and Engineering are quoted.

Key[47] reports insensitivity of both FEP and TFE Teflon at impacts to 10 kgM (72 ft-lb). When in contact with metals, however, TFE, adhesive, and aluminum foil reacted two of three times in LOX with 10 kgM impact. TFE and copper reacted 5 of 40 times. Key[47] also reported no reaction with copper in LOX. Thus, it appears that a synergistic effect has been found involving a metal and TFE.

Messina[48] studied compatibility of perfluorinated lubricants with various metals. He tested metals at high shear by rotating a rounded, one-quarter inch diameter dowel in a one-half inch diameter cavity. Approximately three grams of test lubricant were evaluated by rotating the dowel at 1760 RPM under a load of 1000 psi for one minute. Explosive reactivity was noted with some formulations, according to the metal pairs selected. In this test metal particles are produced along with high temperatures. Tests were performed in air.

The Douglas Aircraft Company[49] in 1958, reviewed manufacturers literature in selecting lubricants for oxygen equipment. They noted such statements of caution as: halogenated compounds, "are not recommended for aluminum thread applications. The extremely high localized temperatures of minute seizures and/or welding of aluminum have been known to cause a chemical reaction between oils and aluminum parts such as piston rings, pipe threads, and screw threads subject to high frictional heat, may be hazardous". The chemical composition of halogenated lubricants includes linear polymers of chlorotrifluorethylene. As pointed out in NASA-MSC Flight Safety Bulletin 19-3 of September 20, 1966[50], this polymer, containing both chlorine and fluorine bonds, appears to be worse then the completely fluorinated lubricants. Key and Riehl[51] pointed out this anomaly in 1964.

An accident caused by a reaction of barium powder and trichlorotrifluoroethane is reported by Kamm [52]. One condition was that "the degree of thermodynamic instability of metals and halogenated hydrocarbons is generally unrecognized by the technical community. Manufacturer's literature relative to the so-called "chemically inert" compounds may be misleading". This same report recommended, "mixtures of alkali and alkaline earth metals with any halogenated hydrocarbon must be recognized as an explosion hazard". A NASA-MSC Flight Safety Bulletin, 18-3, describes this accident, listing all elements in Group I, II, and III of the Periodic Table as applicable. Common metals in these classes include magnesium, aluminum, copper, silver, gold, zinc, cadmium, and beryllium. Kamm 's[52] accident report includes a laboratory investigation by Rocketdyne (Artz). Table V summarizes his work showing that barium and lithium are the most reactive, with aluminum rated as the third most reactive.

The decomposition of polytetrafluoroethylene (PTFE) was studied by Fenimore and Jones[54]. They show elemental fluorine as one product of pyrolysis, suggesting that it plays a role by rapidly reacting with the PTFE Monomer. This work also shows some characteristic of the decomposition product by the damage to probes used to collect gas samples. Quartz was "attacked by the gas" and "an alumina probe was also eaten away by the flame". A measure of flame temperature showed a maximum of approximately 1300°F (1128°C). This is considerably lower than other reported ignition temperatures of aluminum. Since a flame involving PTFE in oxygen appears to be capable both chemically and thermally, of attacking the aluminum oxide, it would probably initiate ignition of aluminum, which would then propagate simply an aluminum-oxygen reaction.

The question of halogenated compounds reacting with aluminum in the presence of oxygen has caused the Douglas Company[49] to recommend "the elimination of the aluminum cup or liquid oxygen receptacle in the impact testing machine". Also, "a re-evaluation of impact levels of various materials should be conducted using a stainless steel cup".

Inhibiting action has also been reported. Gordon and Salmon[55] have a patented method for reducing the sensitivity of liquid oxygen by the addition of a halogenated hydrocarbon consisting of one or three carbon atoms and one or more fluorine atoms. A range of from 0.5 to 50 MOL percent is indicated in some instances and 25 MOL percent, or less, for other cases. They stress the need for solubility in the liquid oxygen, a boiling point relatively high compared with the boiling point of the liquid oxygen, a vapor pressure in the vapor space above the solution of halogenated hydrocarbon and liquid oxygen--not greater than about one micron, and that it be relatively inert with liquid oxygen.

The reactivity of various chlorinated solvents with LOX was reported[56]. Several halogenated solvents reacted explosively with liquid oxygen; methylene chloride 1,1,1-trichloroethane, trichloroethylene, chlorinated "dye penetrants No. 1 and No. 2". Carbon tetrachloride exploded "only mildly" with LOX and trichlorotrifluoroethane (TF) did not explode.

The flammability of the TFE monomer in oxygen was investigated by Colwell, Wachi, and Green[57] of Aerospace Corporation. Flame temperatures over 2300°K are reported. Data for various fuel-oxidizer mixes are given.

Clogston[58] gives data on various reactions of powdered aluminum and magnesium in chlorinated hydrocarbons. He gives times for pressure rises in sealed containers to reach certain values. Aluminum was found to be more reactive than magnesium.

Rhein[59] has placed sufficient reliability on the reaction between a metal and a halogen to propose a "spacecraft chemical heater" utilizing this approach. His choice, based on weight and the necessity for hypergolic ignition is powdered lithium as the fuel and liquid ClF_5 as the oxidizer. This reaction gives 4.469 kilocalories per gram.

CONCLUDING REMARKS

The literature available prior to the Apollo 13 incident indicates that little work has been performed on electrically induced ignition of metals. Much work has been done on impact ignition, particularily in LOX environments; however, much of the data are not directly usable due to the wide variety of experimental techniques employed. Sufficient work has been performed to permit the following observations:

1. The ignition temperature of a metal in LOX is independent of pressure, convection, and oxygen percentage.

2. The effect of halogen impurities on the ignition temperature of metals cannot be determined from existing data.

3. Ignition temperatures, like boiling points, or melting points, appear to be depressed by the addition of impurities.

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TABLE I

Combustible

1. Composition
    - Structure
    - Physical properties
    - Chemical properties
2. Physical State
    - Gas
    - Liquid
    - Vapor
    - Aerosol (mist)
    - Solid
    - Dust
    - Aerosol (dust)
3. Geometry
4. Orientation

Environment

1. Oxidizer
    - Composition and properties
    - Physical state
2. Inert Material
    - Composition and properties
    - Physical state
3. Other Contaminants
    - Composition and properties
    - Physical state
4. System
    - Pressure
    - Volume
    - Temperature
    - Relative humidity
    - Containment material
5. Acceleration
6. Other Materials
    - Proximith
    - Configuration
    - Orientation
    - Physical properties
    - Chemical properties

Ignition Sources

1. Electrical
    - Arcing
    - Inductive sparks
    - Electrostatic sparks
2. Hot Surfaces
    - Frictional sparks or heating
    - Impact sparks or local heating
    - Heated walls, surfaces
    - Heated wires
    - High shear rates
    - Compression of sharp vibration points
3. Heated Gases, Vapors
    - Hot Jets (pilot flame)
    - Adiabatic compression
    - Shock waves
    - Gases and metallic vapors (from material penetrations micrometeroids)
4. Chemical
    - Hypergolic offgases, condensed liquid, etc.
    - Pyrophoric dusts - metallic or nonmetallic produced from continued contact of materials
    - Thermite reactions caused by intimate contact of a metal and metal oxide; e.g., aluminum and rust.
    - Catalysis promoting rapid reactions
5. Electromagnetic Emission
    - Heating by ultrasound radio frequency, radar, microwave, infrared, light, etc.
    - Catalysis by light, ultraviolet, X-ray

TABLE II

IGNITION TEMPERATURES OF SOLID METALS

Metal	Ignition Temperature, °F	Gas	Pressure, atm.
Mild Steel	2,240 to 2,330[a]	Air	1-7
Tungsten	2,270 to 2,350[a]	Air	1-7
Tantalum	2,260 to 2,340[a]	Air	1-7
Titanium alloy:			
RC-70	2,880 to 2,960[a]	Air, O_2	1-7
RS-70	2,890 to 2,940[a]	Air, O_2	1-7
RS-110-A	2,860 to 2,910[a]	(C), O_2	1-7
RS-110-BX	2,850 to 2,920[a]	(C), O_2	1-7
Stainless Steel:			
430	2,460 to 2,490	(C), O_2	1-7
302	(b)	Air, O_2	1-7
Copper	(b)	Air, O_2	1-7
Nickel	(b)	Air, O_2	1-7
Nickel alloys:			
Inconel	(b)	Air, O_2	1-7
Inconel X	(b)	Air, O_2	1-7
Beryllium alloys:			
Berylco 10	1,750 to 1,760	Air, O_2	1-7
Berylco 25	(b)	Air, O_2	1-7

(data from Reynolds[22])

Note:

(a) - Brightness temperature
(b) - Melts before igniting
(c) - Does not ignite in air

TABLE III - SELF-IGNITION TEMPERATURES

(Al-Mg Powders in Air)

Percent Mg in Al	Self-ignition temp., °C	
0	694	
9.5	565	515(A)
25.1	550	
35.9	527	
37.5	527.4	505(A)
38.5	526	
42.2	512	
43.6	517	
47.0	512	
49.1	510	485(A)
55.2	519	
65.8	527	
70.6	534	
91.8	548	
100.0	579	

(data from Poyarkov[33])

NOTE: A - air is humid

TABLE IV - MINIMUM EXPLOSIVE CONCENTRATIONS AND MINIMUM ENERGY REQUIRED FOR IGNITION OF METAL POWDERS BY ELECTRIC SPARKS

Powder	Minimum energy (millijoules)		Minimum Concentration (mg./liter)
	Dust cloud	Dust layer	
Aluminum, atomized	15	2.5	40
Aluminum, stamped	10	1.5	35
Antimony	-	-	420
Dowmetal	80	8	20
Iron, hydrogen reduced	80	160	105
Iron, carbon reduced	320	-	120
Iron, carbonyl	20	80	250
Magnesium, atomized	120	40	10
Magnesium, milled	40	8	20
Magnesium, stamped	20	1	20
Manganese	80	3	125
Silicon	80	-	100
Tin	160	-	190
Thorium	5	0.004	75
Thorium hydride	3	0.006	80
Titanium	10	0.008	45
Titanium hydride	60	1.6	70
Uranium	45	0.004	60
Uranium hydride	5	0.032	60
Vanadium	60	-	220
Zinc	650	-	480
Zirconium	5	0.001	40
Zirconium hydride	60	0.064	85
Ferrosilicon (88% Si)	-	-	425
Ferrotitanium, low-carbon	-	-	140
Magnesium aluminum (50-50)	80	20	50

(data from Hartmann[42])

TABLE V

MINIMUM IMPACT SENSITIVITY HEIGHT (inches)

(5-lb Ball)

SOLVENT	METAL									
	Al Powder	Mg Powder	Ti Powder	Ba Shavings	Li Shavings	Be Powder	BeH_2 Powder	Al Filings	Mg Filings	B Powder
Freon MF	F,50	0	0	X,20 F,15	X,50 F,40	0	0	0	0	0
Freon TF	F,50	0	F,50	X,10 F,4	X,20	0	0	0	0	0
Carbon Tetrochloride	X,50	F,50	0	X,15 F,10	X,18	F,50	0	0	0	0
Trichloroethylene	0	F,50	F,50	X,15 F,13	X,25	F,50	0	0	0	0
Perchloroethylene	0	0	0	X,20 F,15	X,30	0	0	0	0	0
1,1,1 Trichloroethane	0	0	0	0	0	0	0	0	0	0

X,Number - Height in inches at which detonation occurred.

0 - No reaction at 50 inches.

F,Number - Height in inches at which flash or heavy sparking occurred

(data from Kamin[52])

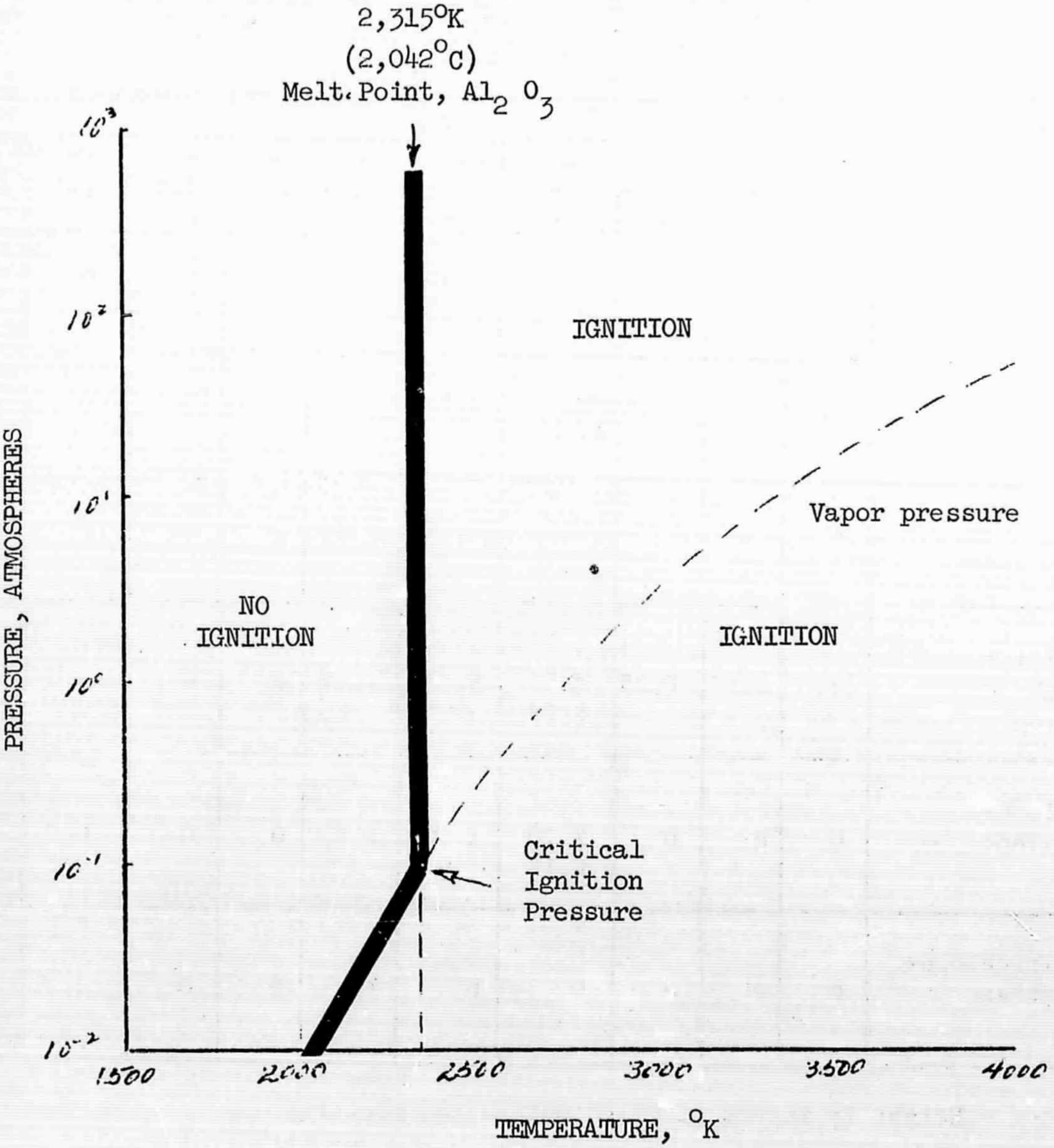

FIGURE 1. VAPOR PRESSURE OF ALUMINUM

(From Ref. 28)