A Review of the Compatibility of Structural Materials with Oxygen

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Introduction

MORE oxygen is used than all other atmospheric gases combined. About 300 billion cubic feet of oxygen was produced in the U.S. in 1971 and nearly all of it was shipped either as liquid or high pressure gas.[1] During its production, transport, and use, oxygen is in contact with many different materials, virtually all of which will burn. The problem of choosing properly safe, or compatible, materials initiated this review which has the objective of presenting a brief survey of the compatibility of structural materials with oxygen.

A compatible material can be defined as one that will maintain its desirable properties in the presence of oxygen. The oxidation process with bulk materials is either very slow and controllable or violently fast and destructive; incompatibility is usually analogous to the latter. Compatibility with oxygen is, then, a relative quality determined by how readily and to what degree a material will react with oxygen.

Included in this survey is a review of the historical development of compatibility problems and research, a discussion of compatibility testing methods, a summarization of the ignition and combustion research reported in the literature, a discussion of common materials for their relative oxygen compatibility, and an effort to elucidate research areas which would enhance our understanding of the compatibility of bulk materials.

Scope of the Review

That oxygen will readily react with structural materials is obvious with only a cursory glance at accident histories.[2-4] The large amount of energy released when a metal burns is the primary energy source of most serious accidents. The continuously increasing use of oxygen[5] and its more frequent proximity to people in medical, military, aerospace, and oceanographic applications makes safety a more imperative design consideration than ever before.

The past work concerning compatibility of materials with oxygen is characterized by three general inadequacies. The first and probably greatest is the lack of basic research and theoretical attempts to understand the nature of the combustion of bulk materials.[6] Second, is the stop-gap or configuration nature of nearly all the testing that has been done with little attention to the limitation or even definition of many experimental parameters. Third is the classified, proprietary, or other publicly-obscure nature of the results of much of the work. These inadequacies have jointly created a very difficult and complex problem.

The whole problem of ignition and combustion of the many materials that may come in contact with oxygen during its production, transport and use must involve all conceivable energy sources, contaminants in the structure and the oxygen, defects in the structures and the materials, and perturbations in the transferring and transporting procedures. It is reasonable to assume that certain cleanliness and procedural limits will be established and that the number of materials will be kept to a practical limit. Within this context, we have limited this assessment to structural materials, particularly metals, in liquid or

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gaseous oxygen[7] but have considered all energy sources and bulk materials of any surface state (usually clean). The role of contaminants is a crucial one and to assume perfectly clean materials would be to ignore one of the most probable promoted ignition sources. Thus some attention is also directed toward the effect of contaminants.

Only compatibility with oxygen is considered. Fluorine and fluorine-oxygen mixtures, their properties, compatibility, and safety are excellently covered in a book by Schmidt.[8] Compatibility of structural materials with fuels is strictly a chemical problem since both fuel and oxidizer are not naturally present in concentrated form. However, problems do exist with some fuels, e.g., hydrogen, for which several plastics can act as oxidizers.

The category of structural materials should include any material used in pipes, valves, pumps, tanks, etc., which are used in the production, storage, transport, or use of oxygen. Nearly all of the organics and plastics have been rejected for these applications as too readily combustible. Some of the more compatible[4, 9, 10] are used nonstructurally, however, as gaskets, valve seats, lubricants, and the like. This leaves primarily metals as usable structural materials. Ceramics and metal matrix composites will undoubtedly receive more consideration in the future but available relevant data are virtually nonexistent. The combustion of small droplets or particles has also been considered but only for the thermodynamic properties data available.

Combustion of Bulk Materials

The combustion of structural materials, particularly metals, is unique in several ways when compared to gaseous combustion. First and foremost metal combustion is almost always a heterogeneous process; that is, both solid and vapor and frequently liquid phases are present. This complicates the process in many ways. Mass transport of metal and oxidizer to the combustion region may have to be through solid or liquid phases of both the metal and its oxide. This is no longer a simple diffusion process and is probably rate-limiting. Latent heats of phase changes and condensation of the combustion products[11-13] become important as do the thermophysical properties of the combustion products. In some cases, e.g., aluminum oxide,[14] the mechanical behavior of the oxide is critically important. Metals are also characterized by large heats of combustion and, though frequently difficult to ignite, burn violently. The interplay of these properties becomes very complex. For example, the high reactivity of titanium is attributed to the high solubility of titanium oxide in molten titanium.[15] Or, aluminum doesn't ignite until far above its melting point[16] which allows the molten metal to flow away from the heat source—perhaps to a material that will ignite. Or, some polymer combustion products are excellent reducers of protective oxide coatings.[17] This complexity definitely has limited understanding of the combustion process. In fact, the single most important advance in understanding the combustion process since man first became fascinated by fire was probably the rejection of the phlogiston theory and the realization by Lavoisier in the 18th century that oxygen was necessary for combustion.

Generally, investigators have looked at the problem of heterogeneous combustion in two stages: first, the dynamic approach to the point of ignition, and second, a quasi-steady-state combustion process. This distinction is readily made, and the point of ignition is defined to be when the process becomes self perpetuating. Ignition is usually accompanied by the rapid emission of heat and light.

The energy required for ignition is extremely variable and very dependent on the ignition source, the kind of energy which is supplied, and the rate at which it is applied. Most of the research has been safety motivated and concentrates on prevention of the ignition phase. The role of contaminants becomes extremely important since most are more readily ignited and, in turn, can initiate combustion in the metal. Once combustion has begun, the reaction can take many forms from violent fragmentation to self quenching. Much less research has been done on the burning process itself, particularly for bulk materials.

Historical Development

Historically, the impetus for metals or solids combustion research has come from three sources: from the combustion of powders (for mine safety in the early part of this century and for flame temperature enhancement more recently), from the combustion of metal foils and ribbons for a light source in flash bulbs, and from the burgeoning use of oxygen for life support and for a propulsion oxidizer in the aerospace fields.

The initial concern for combustion of powders was from a safety standpoint, primarily in mines,[18] but has concentrated on metal powders[19,20] as they have become more common. This research was significantly extended when the metals' high heat of combustion was utilized for flame temperature enhancement[16] or as an additive to rocket fuels.[21] This has led to a great deal of significant research on combustion of metal particles.[22-26]

The use of metal foils or ribbons as a light source for flash lamps also started very early[27] and has been a continuing stimulus to some research.[28-30] Both of these areas, however, have limited application to bulk materials.

Although the U.S. Bureau of Mines studied the ignition of solid metals as early as 1923[31] in connection with compressor safety, it wasn't until some violent reactions were observed between titanium and oxygen in 1959[15] that significant concern was voiced about the compatibility of metals with oxygen. Since then, the experimental work has taken two principle directions—a large effort of empirical compatibility testing centered around the mechanical impact sensitivity threshold technique[32] and a pursuit of the definition and measurement of an ignition temperature.[33] There has been little basic research and almost no theoretical work. A comprehensive review paper (in 1963) by Markstein[8] deplores the "small research effort" and the "lack of reliable thermodynamic data" as instrumental causes for the lack of understanding. This is still true today and is indicated in both areas by the disparity of impact test results[34] and their lack of correlation with other tests[35] and the unresolved behavior of burning rates[36] or ignition temperature with oxygen pressure.[31,37]

There has been little ignition temperature study since the initial flurry of activity in the early 1960's which was summarized by White and Ward in 1966.[33] Perhaps the only comprehensive studies since then have been one on centrifugal pumps in Germany by Bauer et al.[38,39] and one on the effects of high pressure by Guter[10] mostly on nonmetals.

The few experimental studies of burning rates of larger specimens have all used electrical joule heating of tubes or wires where the energy source stops as soon as combustion or melting breaks the electrical continuity. And all but the often quoted work of Dean and Thompson[40] have measured only the low density and easily combustible metals primarily used as light sources. There are two recent exceptions to this in German studies of burning rates in small elemental metal wires[36,41] and tubes[42] of several German aluminum, copper, and iron alloys. There have been no burning or propagation studies using bulk metals.[43]

Compatibility Test Methods

A test for the compatibility of a material with oxygen basically consists of placing the material in oxygen in the presence of a possible ignition source and observing the reaction as a function of oxygen pressure, temperature, or the ignition energy. The kinds of tests possible are limited only by the ingenuity of selecting possible ignition sources. However, most tests are quite realistic in simulating working conditions and probable ignition sources. Somewhat arbitrarily, these tests are described below by the following ignition categories: mechanical impact, electrical, thermal, acoustic, abrasive, fracture, and configurational, with most of the tests in the first three groups.

There are also many experiments designed to measure some specific thermodynamic property such as the heat of combustion, oxide volume ratio, specific heat, or melting points. Strictly speaking, these are not compatibility tests, but do provide a basis for understanding the potential reactions. Most compatibility tests are concerned principally with ignition, but some are also designed to measure burning rates after combustion has been initiated.

Mechanical Impact

One of the most probable ignition sources is just striking a material in the presence of oxygen—be it dropping a wrench in an oxygen spill, a piece of weld slag impinging a bend in an oxygen pipe line, or simply the closing of a valve. The most common version of this test, developed very early,[44] has resulted in a large amount of data[45–50] and is one of only two ASTM standard tests relating to oxygen compatibility.[32,51] In this test a falling weight imparts a known amount of energy to a striker pin which is in contact with the specimen in the presence of oxygen, and any reaction is noted. It is simple and has the advantage of being adaptable to variable pressures and liquid oxygen.[52,53]

Compatibility by this ASTM test is defined as no reactions out of 20 impacts with the plummet impact energy adjusted to 70 ft-lbs. Key[48] indicated that this go-no-go test has been remarkably successful in rejecting incompatible materials. However, the arguments described in the next paragraph suggest that the poor repeatability inherent in the test may lead to rejection of some compatible as well as incompatible materials. Blackstone and Ku[34] have suggested that this test has also passed some unacceptable materials.

The mechanical impact test procedure has undergone extensive criticism.[34,54–59] The criticism indicates essentially that the statistical procedure of the test is at fault rather than the test apparatus per se. Schwinghamer[53] has refuted some of this criticism. A different statistical approach has been recommended by Jamison[49] as a consequence of this criticism. Instead of accepting a material if it doesn't react in 20 tests at 70 ft-lbs, Jamison recommends that the test be repeated 20 times at different energies to find the energy at which 50% reactions are obtained. This energy (determined from the drop height of the falling weight) is used to indicate the relative impact sensitivity of the material. This method is referred to as the Bruceton or "up-and-down" method of mechanical impact testing. According to Jamison, the "up-and-down" method of impact testing, as an alternative to the go-no-go test, is both efficient and repeatable. That the Bruceton method is more repeatable than the go-no-go test is intuitively reasonable; however, the go-no-go test is less time consuming and therefore is considered more useful as a screening test if the occasional rejection of an acceptable material is permissible.

Blackstone and Ku[34] and Jamison[49] give historical accounts of development of impact testors from the first, described by Lucas and Riehl,[44] to current models. As a result of recent attempts to improve the mechanical impact test it has been suggested that the reaction intensity should also play a major role in material selection in conjunction with the reaction sensitivity. Jamison has pointed out that the improved repeatability of the Bruceton method of impact sensitivity shows that materials are not significantly different in sensitivity. However, he indicates that materials differ widely in intensity since some of them react violently and are totally consumed while others are only slightly charred. It appears that further evaluation may be in order to take advantage of both techniques and to include the intensity of the reaction.

Electrical

Some of the most tragic[60] and extensive[61] oxygen accidents have involved electrical ignition sources from powered electrical circuitry. Ignition tests using electrical ignition are second only to impact tests in frequency, partially due to flash bulb experimentation. Most compatibility data, however, have come from the "flash and fire"[35] test which discharges an electrical arc in the vapor space above a specimen in an oxygen chamber. The specimen temperature is slowly raised while the arc is repeatedly struck until a "flash" or a sustaining "fire" is observed. The temperatures are recorded for these "flash" and "fire" points. The oxygen pressure can also be varied in this versatile test and it permits the study of liquid-specimens as well. This test has been mostly used for organic materials. A modification of this test in which the arc impinges directly on the specimen has also been used[62,63] where the energy in the arc is the primary variable. The generation of static electricity in flowing oxygen systems has been determined to be quite small.[64,65] Another common test uses electrical Joule heating, but this is really, then, a thermal ignition source.

Thermal

In reality all ignition sources are thermal sources, but usually the conversion to thermal energy is so rapid that the primary energy form is considered the source. Classed as thermal source tests, then, are bomb tests, promoted ignition, and Joule heating. In the oxygen bomb test[10,63,65] the specimen and a volume of oxygen are enclosed in a bomb whose temperature is slowly raised until ignition is observed. The ignition temperature is recorded. A calorimetric measure of the heat of combustion released can also be obtained from the resulting pressure and temperature excursions. Promoted ignition tests[65] are a variation of this in which the amount of an explosive ignitor necessary to cause combustion is the recorded variable. The energy of the ignitor is readily subtracted from the resulting combustion to obtain the heat of combustion of the specimen.

Electrical Joule heating is the other common thermal source for the testing of metals. A current is passed through the specimen in the presence of oxygen until an ignition temperature is reached. This test is obviously limited to metals and those that ignite before they melt, but since most structural materials are metals, it has resulted in a significant amount of relevant data. Other thermal sources have varied from wood fires and torches[66] to infrared lasers.[67–70]

Acoustic

There are two principal tests in this category; the pneumatic impact and the shock wave. The pneumatic impact test[35] is designed to simulate the adiabatic compression resulting from a rapidly opening high pressure valve. It is usually done just in that manner with a small sample chamber suddenly opened to a high pressure reservoir, and the temperature and pressure reactions noted. These tests use the highest static pressures of all the compatibility tests, exceeding 10,000 psi (70 MN/m^2). Much higher dynamic pressures have been tested using explosive shock waves.[71]

Abrasive

Galling caused by two pieces of metal rubbing was projected as one of the possible causes of an oxygen tank truck accident[72] and there have been a few tests using this technique.[15,38,39,62,73] Also the abrasive effect of fine particles in a flowing oxygen stream has been[65] and is being studied.[74]

Fracture

A highly probable yet seldom observed accident source is fracture. The exposure of a fresh clean surface to oxygen for some metals can cause a violent reaction. Various methods have been used from straight tensile tests[15,37,75] to puncture by bullets[76] or other projectiles. Even the effect of the projectile size and materials has been considered.[77]

Configurational

The final test of oxygen compatibility for any material is whether it will ignite in its final configuration, complete with adjacent materials and possible contaminants. Because of our lack of understanding of the ignition and combustion of materials, most critical applications also undergo an environmental test. Artificial ignition of wire harnesses or clothing, hyperbaric testing of breathing apparatus, and overloading liquid oxygen pumps are all examples of this category. These tests will always be indispensable, especially where safety is of prime concern.

Review of the Literature

Compatibility related research is extensive and scattered, but relatively few papers are directly concerned with the comparison of the oxygen compatibility of bulk materials. Those that are frequently involve several different materials, both ignition and combustion, and often several test techniques. To divide the work by material, property, behavior, or test technique is difficult. Therefore, at the risk of a relevant omission, we have chosen about fifty papers that are broadly concerned with compatibility and discussed them in the loosely defined categories of accidents, experiments, pressure effects, theory, thermophysical properties, and related review papers. The review papers themselves contain hundreds of references for more specific pursuit if desired.

Accidents

Surveys of oxygen related accidents have been conducted recently by Ordin[2] and Johnston[78] for NASA and by McQuaid and Cole[3] for the Navy. Each of these surveys indicates a surprisingly high rate of accidents caused by material incompatibility. The surveys by Ordin and Johnston covered NASA, some Air Force, and some related contractor records. Ordin reported 20% of the mishaps with liquid oxygen and 36% of the mishaps with gaseous oxygen involved material incompatibility. Johnston reported 56% were caused by the presence of oxygen incompatible materials. In many cases more than one factor was involved in the mishaps. For example, procedural errors were involved in 78% of the mishaps and design errors were present in 63% of the mishaps according to Ordin. Even though material incompatibility with oxygen was present in fewer instances than procedural or design error, the percentage due to incompatibility is significantly large, and it is expected to be even higher in high pressure oxygen systems. It is also noted that the accident rate due to material incompatibility in high pressure gaseous oxygen is almost twice that in liquid oxygen.

McQuaid and Cole's survey indicates an accident in a Navy compressed gas system due to spontaneous ignition every four weeks during the period Jan. 1968—May 1971. The survey does not indicate what proportion of these accidents are due to material incompatibility, but it does state that material failure accounts for about half of these accidents; the cause of the other half is unknown. No accidents are attributed to design failure or personnel error. From this information one cannot rule out that a sizeable proportion may be due to material incompatibility.

There are several other small collections of accident histories from the U.S.,[79,80] England[4,81] and Japan[82] most of which conclude that either incompatible materials or collections of contaminants are the major causes of accidents. In addition, there are several detailed accounts of specific accidents, most of which involve liquid oxygen, probably because liquid oxygen accidents tend to be more catastrophic. The accidents in air separation plants[79,83] generally are caused by contaminant accumulation, and tank truck accidents[72,84,85] are more frequently caused by equipment failure or incompatible materials. The Brooklyn truck accident of 1970[72,86] and two Australian accidents[85] were investigated in great detail. The most thoroughly documented accidents were, of course, the two Apollo incidents[60,61] since they were thoroughly instrumented. That they occurred at all, in spite of the extensive precautions necessary for the required high reliability, is a manifestation of the necessity for concern with oxygen compatibility.

Experiments

The experimental research on the ignition and combustion of bulk materials is extremely varied in subjects, techniques, and specimens. Here we discuss chronologically the more general papers that include data on several materials or otherwise contribute to a relative comparison of oxygen compatibility. There are many studies of a specific nature or on nonbulk specimens which are also of value (see for example the many references in Markstein[8] and White and Ward[33]). Data from these papers are also considered in the generalizations and recommendations at the end of this paper, but are not discussed in detail.

In 1923, three decades ahead of any other studies of bulk metal-oxygen behavior, Jakowsky and Butzler[31] undertook a classic study to determine the pressure dependence of the ignition temperature of the metals most frequently used in high pressure oxygen systems: iron, copper, brass, and lead. From this, they hoped to determine the metal most suitable for high pressure oxygen use, i.e., the first compatibility study. They ignited wires inside a pressurized bomb by electrical Joule heating and determined the approximate temperature from resistance vs temperature calibrations of similar wires. Ignition was observed as the severing of the wire and by visual inspection. The lead wire always melted before igniting as did the copper and brass wires at atmospheric pressure. Ignition temperatures decreased with pressure up to 2000 psi with the iron dropping most rapidly. From this they concluded that the copper and brass were better for high pressure applications.

In 1955, Wells[87] reported one of the first comprehensive studies of burn rates for various kinds of steels. In order to improve oxygen torch cutting techniques for the steel industry, he studied the combustion rates of iron bars as a function of the kind of steel, oxygen purity, oxygen flow, and bar diameter. After being ignited by a carbon arc, rotating bars were fed into an oxygen jet at increasing feed rates until they extinguished themselves. The maximum rate which maintained burning was taken as the combustion rate. He found that pure iron burned three times faster than iron with 1% carbon. Diluting the oxygen with about 6% nitrogen also reduced the burning rate by a factor of three. He also determined that the effects of bar diameter and oxygen flow were simply those caused by increased or decreased heat flow.

Hill et al.[88] reported in 1956 on tests in which they placed heated $\frac{3}{8}$ in. (0.95 cm) rods of several materials into a supersonic stream of oxygen. Also electrically heated wires were ignited in static atmospheres of air, oxygen, and nitrogen. Good agreement was found between the experimental data and theoretical ignition temperatures derived from simple heat balance equations. In the static tests they observed effects of local depletion of the oxygen as well as retardation by prior oxidation of the surface. They determined that iron, carbon steels, and other common steels, such as 4130, have spontaneous ignition temperatures below their melting points followed by rapid burning. Inconel,* copper, 18-8 stainless steel, Monel,* and aluminum melted before ignition in the tests performed. Titanium could be burned in air, oxygen, and even pure nitrogen.

In a classic work on the combustion of metals in oxygen published in 1958, Grosse and Conway[16] reported their "skating sun" phenomenon of a region of aluminum combustion floating on a molten pool of aluminum. The basic objective of the work was to develop a technique of producing and utilizing high temperature sources. This they accomplished in an oxygen-powdered aluminum cutting torch with a flame temperature in excess of 3000°C. They also investigated other powders and performed some ignition temperature measurements on bulk metals. This was done by heating a 10 g specimen to a given temperature in an argon atmosphere and then exposing it to a stream of oxygen. Grosse and Conway classify the 17 different metals as those that ignite below or above the melting point and

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* The use in this paper of trade names of specific products is essential to a proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendation by NBS.

relate that to the oxide ratio. They also discuss thoroughly the thermodynamics of metal combustion and the theoretical adiabatic combustion temperature.

An excellent and comprehensive investigation of ignition temperatures was reported in 1959 by Reynolds.[89] He was probably the first to make the strong distinction between ignition and burning and also to correlate preignition behavior with the more thoroughly studied slow oxidation process. The study is primarily a theoretical investigation of various environmental parameters but also includes determinations of several ignition temperatures. He used electrically heated wires in both a static chamber and a high velocity wind tunnel and determined temperatures with an optical pyrometer. Tungsten, tantalum, several titanium and beryllium alloys, and a martensitic stainless steel all ignited near the predicted temperatures. An austenitic steel, copper, nickel, and some nickel alloys melted before igniting. Reynolds also concluded that pressure to 8 atms (0.8 N/m^2) and the shape of the specimen had little effect on ignition temperatures.

Between 1954 and 1961 Harrison[90,91] reported some extensive measurements of the burning rates of small wires of aluminum, iron, magnesium, molybdenum, titanium, and zirconium. The wires were ignited at one end by a small titanium coil and photographed while burning in various oxygen concentrations up to 100% oxygen and 1 atm. Harrison was probably the first to experimentally show the importance of the melting and boiling points of the metals and their oxides. He concluded that the metals could be classified in three broad groups: 1) metals with low boiling points, such as aluminum and magnesium, that burn in the vapor phase; 2) metals with intermediate melting and high boiling points that burn at a molten surface, e.g., iron and titanium; and 3) metals, like zirconium, with refractory oxides which burn to form a solid oxide through which the oxygen or metal vapor must diffuse. He also showed that, at least at low pressures, the burn rate is proportional to the square root of the pressure. There also exists a minimum critical oxygen percentage necessary to support combustion which is different for different materials and increases with wire diameter.

Starting at this time (1959) and extending for a decade, Kirschfeld[3,6,41,92–96] published the results of many different promoted ignition, burning experiments on many different materials: copper, brass, zinc, iron, aluminum, magnesium, cobalt, cast iron, various steels, copper alloys, and nickel alloys. He determined the effects on the burning rates of the diameter of wires and cross sections and surface areas of tubes, wires, and foils. The dependence of the combustion rate on oxygen pressure to 225 atms (22.5 MN/m^2) was determined for many of the materials. Relative burn rates for many of the materials were also discussed. For example, Kirschfeld could not ignite and burn nickel wires up to 200 atm (20 MN/m^2) without twisting or alloying with other metals. Copper and copper alloys burned slowly and with difficulty. High nickel content stainless steels were also slow to burn. The chromium in steel, with its high heat of combustion, tended to enhance burn rates. Low carbon and unalloyed steels and pure iron had combustion rates lower than many of the alloyed steels. Aluminum, magnesium, zinc, and cobalt all burned even more readily. The effect of size and shape of the specimens was a proportionality to the burning cross section.

The effects of oxygen pressure bear special mention because Kirschfeld has done more study of this than anybody else. Generally speaking, but with significant exceptions, he finds an approximate square root dependence of the combustion rate on pressure. Some of the exceptions are as follows. Initially, at pressures near 1 atm (0.1 MN/m^2) the burn rates of magnesium and brass decrease with increasing pressure because of the suppression of the vaporization of the magnesium and the zinc in the brass. At intermediate oxygen pressures [16–32 atm (1.6–3.2 MN/m^2)] the burn rates for aluminum and some steels have discontinuities, apparently due to the involvement of different species of oxides. At high pressures, several hundred atmospheres, he also indicates a drastic shift to decreasing burn rates with some metals. This had been predicted by Spalding.[97]

Littman and Church,[37] in 1959, reported on the reactions of titanium and zirconium with oxygen and steam. They used both autoignition and the forming of fresh surfaces by tensile fracture to show that both materials readily react with oxygen. The autoignition temperatures dropped significantly from 1200°C to about 100°C as the pressure was increased to 350 psi (23 MN/m^2).

An often quoted experiment by Dean and Thompson[40] in 1961 used resistance heating of tubes of various metals and alloys in 50, 300, and 800 psi ($\sim$0.3, 2, and 5 MN/m^2) oxygen, carbon dioxide, and a 50-50 mixture of the two. With motion pictures they observed ignition and the extent of burning in eight different stainless steels, six nickel alloys, two cobalt alloys, and aluminum, copper, and titanium. The nickel alloys did not ignite until their high melting points were reached as was also the case with high nickel stainless steels; cobalt and the remaining steels ignited more readily. A copper test section ignited near its melting point only at 300 psi (2 MN/m^2), and an aluminum section melted at a very low temperature and stopped the resistance heating. The titanium was very reactive, even in pure carbon dioxide.

As part of an evaluation of materials and methods for high pressure oxygen systems [to 7500 psi ($\sim$50 MN/m^2)], Baum et al.[64] in 1962 studied the effects of temperature, vibration, shock, storage, flow, and surge on various materials and system components. They chose four metals, 316 stainless steel, Monel, brass, and copper, and several nonmetals for investigation. After an extensive testing program of thermal cycling, shaking and shocking, altering surface properties, eroding with high speed flow and much more, they concluded that among the metals stainless steel and Monel were much more suited to high pressure structural use than brass and copper and that polytetrafluoroethylene (TFE) and polychlorotrifluoroethylene (CTFE) were the best of the nonmetals for valve seat and seal materials.

In a 1963 study to determine the reactivity of titanium subject to various aerospace conditions, Riehl, Key, and Gayle[62] also studied several other metals. Initially they found that various surface coatings on the titanium could reduce but not eliminate its impact sensitivity. They then tested several materials for shock sensitivity by determining the size of ignition cord necessary to cause a reaction in liquid or gaseous oxygen when detonated adjacent to a tube containing a strip of the test material and the oxygen. The materials tested in decreasing order of ignitability were titanium, copper or nickel plated titanium, magnesium, aluminum, the ignition cord itself, fluorocarbon impregnated gaskets, and 304 stainless steel. It should be noted that in this particular test the stainless steel never did ignite and three metals were more shock sensitive than the ignition cord itself. In various semiquantitative puncture and electrical spark tests they concluded that titanium was much more reactive than aluminum or stainless steel.

In another study to evaluate titanium alloys, 301 stainless steel, and 2024 aluminum for liquid oxygen tanks, Christian et al.[75] reported in 1963 on diaphragm puncture, tensile fracture, and simulated micrometeroid puncture tests. The titanium alloys reacted readily with oxygen in many of the tests but appeared to initiate reactions only if the fractures were rapid. Slowly propagating fractures caused by cyclic loads did not cause reactions. Neither the stainless steel nor the aluminum alloy reacted; however, they report that aluminum did react with liquid oxygen in the standard impact test.

Other similar tank rupture tests were reported by Dengler[77] and Stephens et al.[98] These tests included tanks of titanium alloys, 304 stainless steel, 6061 aluminum, and several fiber-reinforced plastics. With projectile rupture only the titanium alloys reacted.

One of the most comprehensive research programs on the compatibility of materials with high pressure oxygen [7500 psi ($\sim$50 MN/m^2)] was published by Nihart and Smith[65] in 1964. In it they discuss previously performed work as well as unpublished work from their laboratory on velocity (particle) impact tests and promoted ignition tests. They also report the detailed results of their oxygen bomb, promoted ignition, and adiabatic compression tests. Besides many thread sealants, lubricants, fluorocarbon plastics, and elastomers, they tested four stainless steels (301, 304, 316, 17-7PH), three nickel alloys (Inconel 600 and X-750 and Monel 400), aluminum, nickel, copper, brass, silver, gold, and lead. In addition they performed some system tests to determine the most important hazards for high pressure oxygen systems. Nihart and Smith report that the relative resistance of metals and alloys to ignition and combustion in 7500 psi ($\sim$50 MN/m^2) oxygen is the same as reported for lower pressures and similar to that reported by Dean and Thompson[40] except for placing aluminum last instead of first. They recommend the nickel alloys and discourage use of aluminum, copper, and stainless steel for high pressures. With reservations, the only plastic recommended for use was a glass-filled TFE. The hazards judged to be most responsible for ignitions in oxygen systems were adiabatic compression and particulate matter loose in the system.

Beginning in 1964 Key et al.[45–48,99,100] have published the results of many years and many thousands of impact tests in liquid oxygen. The authors group the materials tested in the categories of lubricants; sealants and threading compounds; thermal and electrical insulations; plastics, elastomers, and adhesives; gaskets and packing; metals and alloys; and chemicals, solvents, detergents, and miscellaneous. For metals and alloys they generally conclude that all ferrous and aluminum alloys are not impact sensitive but titanium, magnesium, zirconium, indium, and tin alloys are. They also note some unusual effects; for example, adding pigment to the normally unreactive TFE renders it highly sensitive to impact, and chlorofluorocarbon oils and aluminum which are separately insensitive yield a violent reaction to impact when together.

From 1964 until the present, the group at Princeton under Glassman has published a great deal on the ignition behavior of metals. Initially concerned with a spectroscopic investigation of small particle ignition, Brzustowski and Glassman[101,102] determined that aluminum and magnesium burned in the vapor phase. They correlated physical properties, particularly of the oxides, to the burning behavior. They also pointed out the complexity of the process by identifying as many as nine regions dominated by different combustion phenomena. Mellor[14,103] developed a model of heterogeneous ignition emphasizing the role of the oxide behavior and the importance of the oxide volume ratio and correlated it with results for aluminum wires and magnesium ribbons. Laurendau[104] later extended this study to some ten different metallic elements utilizing induction heated wires to determine ignition temperatures and study the role of the oxides.

Kuehl[105,106] in 1965 reported on a study of metal particle ignition and combustion of aluminum and beryllium. In it he also reported some experimental measurements on electrically heated wires and showed that the surface treatment can significantly lower the ignition temperature of aluminum as can burning in water vapor. He also included a good discussion of vapor phase vs molten burning and the role that the oxides play.

Probably the largest variety of materials tested for ignition at high pressures is provided in a study by Guter in 1967.[10] He determined the pressure dependence of the ignition temperature of many materials in a stainless steel bomb capable of 250 atm (25 MN/m^2) and 450°C. The materials were classed in the five groups of lubricants, rubbers, polymers, valve seat materials, and metals and alloys. Generally he found significant reductions in ignition temperature with increasing pressure, and TFE and CTFE were the most ignition resistant of the nonmetals. None of the metals ignited below his maximum temperature of 450°C. However, a drop of oil added to the metal surface ignited at its ignition temperature and raised the local metal temperature enough to cause the metal to ignite.

In a 1968 paper on the inflammability and combustibility of metal tubes in quiet and circulating oxygen, Simon[42] reports the combustion temperature, burn-through times, and the volume of the metal lost for a standard promoted ignition for eleven German alloys. The volume lost for a given amount of igniter material provides a realistic measure of the extent of a reaction caused by the ignition of a contaminant. The copper alloys are much better in this respect than the stainless steels which are better than the high chrome steels, carbon steels, and aluminum alloys.

The ignition temperatures of electrically heated bars of two Russian steels and a nickel alloy were compared by Nesgovorov et al.[107] at pressures up to 1800 psi (12.4 MN/m^2). A linear decrease with pressure was observed with the nickel alloy dropping faster so that at high pressures the steels may be better.

In 1970 Barrere[108] reported the results of photographic and spectroscopic studies of electrically heated and promoted ignition of burning wires of aluminium, magnesium, beryllium, and boron as part of an assessment of particle burning for rocket propellant enhancement. He divides metals generally into volatile and nonvolatile categories to describe the burning and concludes that it is very complex.

In a series of experiments to make more of the test information more relevant to actual use, Bauer et al.[38,39] performed in 1970 and 1971 some fire tests on centrifugal liquid oxygen pumps made of various metals. In addition to generating a wealth of information about safe pump operation, they performed some comparative tests of identical pumps made with impellers and casings of bronze, stainless steels, and aluminum alloys. After artificially seizing the impeller to cause it to rub on the casings and injecting various pieces of metal into the operating pumps, they concluded that bronze casings and impellers provide the greatest security against fire and explosion damage. Stainless steel was second best. Some of the results were quite spectacular; for example, injecting a rusty nail into an aluminum pump caused immediate detonation. The results were not always reproducible, as with tests with bronze casings and aluminum impellers.

In 1971, Keeping[63] reported on a series of tests to rank materials for oxygen compatibility. Three tests were discussed as a review of British testing efforts; a high pressure auto-ignition bomb test, a "pot" test in which a sample was placed in a flowing stream of hot oxygen, and a liquid oxygen impact test. He also discussed several modifications to make the tests more relevant and urged standardization of test procedures. In addition, he reported on a series of promoted ignition tests in which the amount of a standard fuel necessary to ignite the specimen was recorded. The order of decreasing resistance to ignition was copper, Monel, some steels, and titanium. In the course of the tests he noted the hazard of rust contaminants and their highly exothermic reaction with aluminum. He also urged the use of steel sections no less than about 1 mm minimum dimension because of the increased resistance to ignition.

In a series of experiments with oxygen turbo-compressors Naegeli[109] evaluated the effects of various rotor and stator materials when forced to rub and gall at high velocities. He concluded that silver, nickel, and copper are better than the stainless steels even though the steels may be more resistant to ignition. This is principally because in compressor applications local heating is important and the higher thermal conductivities are more desirable.

Pressure Effects

Recent trends in aerospace, military, and commercial use of both liquid and gaseous oxygen point toward use of higher pressure. With this increased use to 10,000 psi (70 MN/m^2) and higher, compatibility considerations are of paramount importance. Deep concern with safety is rightfully prevalent throughout the field. Recently, the authors performed a survey of the compatibility of materials with high pressure oxygen service[110] and its contents are summarized below.

There are considerable high pressure data available, but, in some instances, the inconsistencies produce a confusing picture. The principal sources containing information regarding the

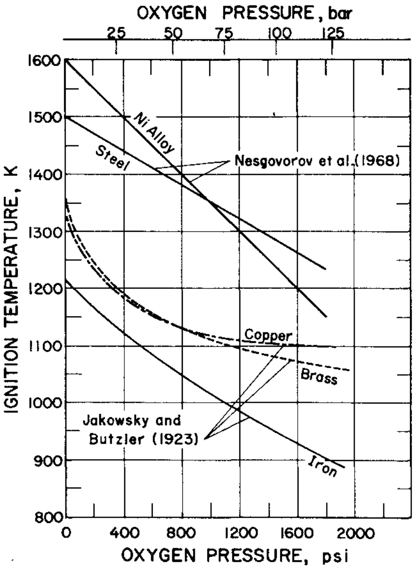

Fig. 1 Ignition temperature of metals as a function of pressure. Data taken from Refs. 31 and 107.

effect of pressure on oxygen compatibility are Attwood,[4] Baum,[64] Dean,[40] Guter,[10] Kimzey,[111] Kirschfeld[36,41,95] and NASA MSC-02681[50] which were discussed previously. An extensive tabulation of test data is contained in Appendix E of NASA MSC-02681. It contains the high pressure compatibility test data of both metals and nonmetals, not just nonmetals as indicated by the title of the source document. The document is periodically updated to include the most recent NASA test data. The sources of oxygen compatibility information include considerable data below 3000 psia (20 MN/m^2) and these data are useful for projections at higher pressures.

The existing high pressure compatibility data can be summarized as follows. The ignition temperatures of metals generally decrease with increasing pressure. However, there are insufficient data available to quantitatively define this pressure dependence for but a few metals over relatively small pressure ranges. Figure 1 illustrates the available ignition temperature data which approach the high pressure range. It is interesting to note that the nickel alloy curve crosses the steel curve, suggesting the possibility that steels may be better suited for high pressure service. No ignition temperature data exist above 2000 psia (14 MN/m^2). There appears to be a definite need for a careful measurement of ignition temperature as a function of pressure up to at least 10,000 psia for some of the more technically important metals. The effect of specimen size and shape should also be investigated.

The burning rate of metals generally increases with the square root of pressure and inversely with cross-sectional area at low pressures, but at higher pressures burning rates decrease, as shown by Kirschfeld.[36,41,95] The nature of this reversal and the pressure at which it occurs are subjects for further study.

The oxygen compatibility of metals under mechanical impact has been extensively studied; however, the repeatability of the data are in question (see compatibility test section). Because of this lack of repeatability, it is difficult to be certain from the available data if metals are more or less sensitive to mechanical impact at higher pressures. The dependence on pressure, according to these data, is, at best, small. On the basis of the impact test data alone, it appears that any of the common metals and alloys, including aluminum and stainless steel, are acceptable for use. However, it is noted that the nickel and copper alloys are less sensitive to mechanical impact than aluminum and stainless steel, in particular.[110]

Other high pressure data such as ignition by electric arc, particle impact, and flash and fire point data are being determined by Stradling[74,112,113] for both metals and nonmetals. Some of these measurements will be at pressures to 10,000 psia ($\sim$70 MN/m^2) and, therefore, will be very useful for material ranking.

The ignition temperatures, as well as the related flash and fire point temperatures of nonmetals generally decrease with increasing pressure up to about 1500 psia (10 MN/m^2). Above this pressure ignition temperatures tend to be independent of pressure. A few typical curves of flash temperature vs pressure are presented in Fig. 2. One should note the close correspondence between flash point and ignition temperature. It can also be observed that the flash points are nearly independent of pressure at 2000 psi, strengthening the conclusion of Nihart and Smith[65] that the ignition temperature is independent of pressure from 2000 to 7500 psia ($\sim$14 to $\sim$50 MN/m^2).

Due to the imprecision of the mechanical impact data on nonmetals it is difficult to readily detect a pressure dependence in sensitivity. Although more compatibility data exist for nonmetals than metals, additional data at high pressures are needed to confirm the pressure dependence of ignition and impact characteristics. A more critical need, however, is the investigation of other nonmetals to find those with the highest oxygen compatibility. Some materials which have probably not been fully explored for oxygen use are the ceramics and composites.

Hust and Clark[110] conclude that "The extension of gaseous and liquid oxygen applications to pressures above 3000 psia is reasonable based on the present data. However, in cases where extremely high reliability is demanded, the extension is considered marginal without further compatibility testing. Considerable compatibility data exist at pressures up to 2000 psia; the sparse compatibility data up to 7500 psia suggest no additional problems will be encountered. However, to obtain high reliability, extensive materials compatibility testing to 10,000 psia will have to be done.

"In high pressure systems the enhancement of existing ignition sources is more important than the decreased ignition temperature of materials. For example, in high pressure applications the effect of adiabatic compression becomes increasingly important, higher flow rates enhance the probability of ignition from friction, impact, static discharge, etc., and reaction intensities increase because of the increased density and availability of O_2. The possibility of ignition due to mechanical failures is also greater.

"There are few compatibility data on most materials above 3000 psia and much is needed. It is also desirable to have more quantitative fundamental data. This requires study of the

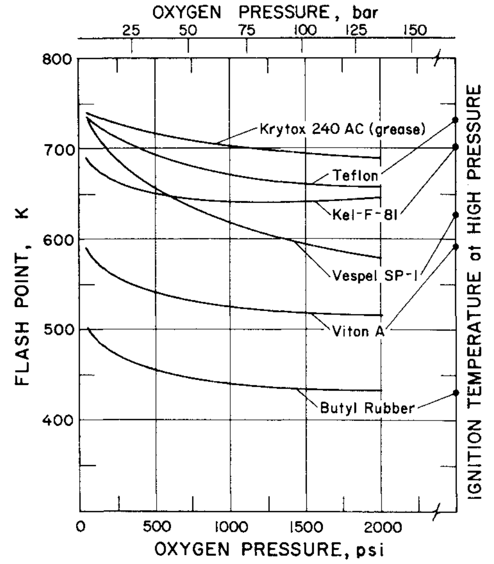

Fig. 2 Flash point temperature as a function of pressure for some nonmetals. Data taken from Refs. 35 and 65. (The use of trade names of specific products is essential to a proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendation by NBS.)

physical phenomena involved and the design of experiments to develop parameters representing these phenomena. There is also a strong need for more engineering compatibility characterization measurements, such as configuration and component tests by manufacturers."

Theory

There is really no comprehensive theory that is directly relatable to relative compatibility but there are several theories concerning ignition of solids and a few models for continuous heterogeneous combustion. Any comparisons between materials would have to be made by adjusting the physical properties contained in a particular model and somehow accounting for the different physical behavior of the different materials and their oxides. Nearly all the theories are based on a heat balance technique and, for ignition, look for the point at which the temperature rise is self-sustaining. Regions of heat deposition and heat removal are defined, and various models differ basically in how detailed this description is. Nearly all ignore possible intermediate chemical reactions or excitations and mass flow and some even ignore the effects of condensation. Because of the interplay of the different melting and boiling points, the solubility and size of the oxides, the heat of combustion and vaporization, the mechanical properties of the oxide, and much more, it is a very difficult task to develop a theory that will describe more than one kind of material. No simple unified theory will probably ever suffice for all materials.

Briefly described below are some of the more recent theoretical works. One older[114] and several more recent reviews[33,115,116] of ignition theories are available for more detailed discussions.

Eyring and Zwolinski[117] were the first to use a simple heat balance between the heat produced by the chemical reaction and that lost by conduction through the oxide coat to obtain a bulk ignition temperature. Hill et al.[88] extended this to include convection and radiation losses because in their experiment conduction losses were small. This is exemplary of the rapid specialization of theories to match specific materials or conditions. Altman and Grant[118] looked at the heat balance around a hot wire used to ignite a rocket propellant. Other specialized considerations are the ignition of single particles by Friedman and Macék[119,120] and Belyaev,[121] ignition of evaporating fuels by Hermance et al.,[122,123] the transition from ignition to burning by Anderson,[124] and a recent concern about the role radiation plays in the ignition of solids by Linan and Williams.[125] Boddington[126,127] has explored the extension of Frank-Kamenetskii's criticality parameter[128] to solid bodies of various shapes to try to predict when they will ignite.

In an early (1956) review of ignition temperatures of solid metals, Reynolds and Williams[114] present a thorough discussion of the many parameters involved in ignition including pressure, temperature, flow, surface state, heat transfer, etc., and the rate limiting factors. They divorce ignition from burning and treat ignition as an extension of slow oxidation. The ignition temperature is defined as the minimum of the time derivative of the temperature, i.e., where the rate of the temperature rise begins to increase. They generate universal curves of temperature, time, and heat flow which agree very well with experiment.

The review of thermal ignition theory by Merzhanov and Averson[116] includes some basic theory by Merzhanov[129-131] and a good discussion of many of the usually ignored effects such as the depletion of the reactants, size effects, and phase transformations.

The review of metal ignition and flame models by Glassman et al.[115] also describes an ignition theory which can help account for the important physical behavior of the reaction products, e.g., oxide coatings. The authors define a transition temperature where the reaction rate becomes independent of time at a constant temperature and relate it to the point where oxide layers become nonprotective. The transition temperature should be a unique value of the metal-oxide system and it is favorably compared with experiments.

Models for steady-state burning behavior are much less prevalent. Markstein[132] probably has the best over-all discussion of the heterogeneous combustion process and whether metals will burn in the vapor phase or from the solid or some combination. Coffin[29] was one of the first to discuss a model for burning to explain his results in burning magnesium ribbons. He assumed magnesium vapor phase burning and a finite reaction zone away from the surface. The burning of solid rocket propellants has been the impetus for calculations by Spalding[97] Belyaev and Bakhman,[121] and Culick and Dehority.[133] Spalding in 1959 predicted the negative pressure dependence at high pressures which was later seen by Kirschfeld.[36] Other discussions varying in the degree of complexity of the interactions considered in the combustion zone are by Lordi and Markstein,[134] Merzhanov,[131] and Henderson[17] who considers polymerization as a possible stage in the burning of aluminum and beryllium.

Thermophysical Properties

Many of the papers already discussed have collections of relevant thermophysical or thermochemical properties. It is beyond the scope of this review to compile and critically evaluate these data, but it should be done.

Probably the best collection of data is in White and Ward[33] a review paper published in 1966 on the ignition of metals in oxygen. They include tables of melting points, boiling points, densities, heats of fusion, and vaporization, vapor pressures vs temperature, thermal conductivities, and specific heats of nearly all the metals and their oxides. Several tables of metal ignition temperatures vs pressure or oxygen dilution for both bulk and fine particles are included in the summary of the work.

Ignition temperatures are collected in several papers, e.g., Mellor.[103] Both Marzani[135] and Guter[10] include ignition temperatures of many nonmetals with the latter including the pressure dependence. Keeping[63] and Brady[73] include properties of some of the oxides and Reynolds and Williams[89] include slow oxidation data and rate constants. Baum et al.[64] show methods and calculations of adiabatic temperature rises, pressure, and temperature relations, and vessel effects. Ignition temperatures, burn rates, and properties from several references are collected by McKinley.[43] Grosse and Conway[16] show an interesting plot of heat of formation of the metal oxides vs atomic number which shows maxima at beryllium, aluminium, titanium, and zirconium and minima at nickel-copper, silver, and gold.

The thermodynamic properties of oxygen are reported by McCarty and Weber[136] and, of course, there are a great deal of data in the *Handbook of Chemistry and Physics*.[137]

Review Papers

There are several review papers that are relevant to considerations of compatibility with oxygen. Many of these have been mentioned already and some have been discussed in detail, such as the theory reviews by Merzhanov and Averson[116] and Glassman et al.[115] and the high pressure review by Hust and Clark.[110]

The slow oxidation of metals which has been related to ignition by Reynolds and Williams is covered by Smeltzer and Perrow[138] and Seybolt.[139] Earlier reviews of the reactivity of metals with oxygen were in 1958 by Reynolds[89] who set out the initial guidelines for compatibility testing, in 1963 by Jackson et al.[15] who considered mostly titanium but many different kinds of tests, and in 1964 a brief summary by Brady.[73] A very thorough review of the ignition of many metals in oxygen was published by White and Ward[33] in 1966. Kimzey[111] reviewed the factors affecting ignition of metals in high pressure oxygen systems in 1970 and McKinley[43] published an excellent review of the experimental work on ignition and combustion of metals in 1971.

The first review of combustion research which included solids was prepared in 1946 by A. D. Little, Inc.[140] Grosse and Conway[16] also discussed previous work in their paper on the

Table 1 Thermal data on metals and alloys[a]

Materials	Ignition temp K	Melting temp K	Boiling temp K	Melting temp of oxide(s) K	Boiling temp of oxide(s) K	Thermal conductivity at 300 K (W/cmK)	Thermal diffusivity at 300 K (cm^2/s)	Heat of combustion (J/g)	Oxide volume ratio
Elements									
Aluminum	> 1000	933	2720	2323	3800	2.2	0.91	31,000	~1.3
Beryllium	~2500	1356	2750	2820	~4300	1.6	0.44	68,000	0.7[b]
Copper	1300	1360	2855	1503–1600	...	4.0	1.15	2,400	1.71
Gold	does not ignite	1336	2980	...	...	3.1	1.24	8	...
Iron	1200	1812	3160	1693–1870	...	0.8	0.23	7,000[b]	2.23
Magnesium	900	923	1390	3075	3350	1.6	0.90	25,000	0.81
Manganese	...	1517	2314	2058	3400	0.23	0.063	7,000	1.25
Molybdenum	1023	2890	5100	1070–2880	1530–	1.4	0.63	6,100	~3.3
Nickel	1730	1730	3110	2230	...	0.6	0.15	4,000	1.64
Silver	does not ignite	1233	2450	...	...	4.0	1.61	140	...
Tantalum	1550	3270	5700	2073	...	0.6	0.26	5,600	2.54
Tin	1140	505	2960	1353–2200	...	0.6	0.39	2,400	1.32
Titanium	~1600	1950–2070	3550	1920–2400	3000–3300	0.18	0.076	16,000[b]	1.73
Zinc	1170	693	1181	2250	...	1.25	0.46	5,300	1.44
Zirconium	1670	2125	4650	2960	...	0.43	0.23	12,000	1.56
Copper alloys									
Berylco 25[c]	1133–1144	1144–1255				0.24–0.38	~0.38	...	
Brass 70/30	1273	1183				1.26	0.39	3,600	
Nickel alloys									
Inconel[c]	1620	1670				0.11	0.040	4,700	
Hastelloy[c]	1600	1640				0.11	0.040	5,000	
Monel[c]	1520	1600				0.25	0.066	3,400	
Iron alloys									
Cr steel	1420	1670				0.30	0.085	7,700	
Stainless steels (300–400)	1400–1670	1670				0.15	0.043	8,000	
Carbon steel	1370	1780				0.80	0.23	7,500[b]	
Titanium alloys									
Ti-6Al-4V	~1600	1803–1908				0.066	0.027	16,000[b]	
Ti-8Mn	1610	1775				0.11	0.051	16,000[b]	
Nonmetals									
TFE	750	~600				0.002	~0.001	1,100	
CTFE	700	~500				0.002	~0.001	1,500[b]	
Polyethylene	450	~400				0.004	0.002[b]	9,000	
Nylon[c]	475	~500				0.003	0.002[b]	7,000	

[a] Most data taken from Refs. 16, 33, 43, 89 and 115.

[b] Approximated.

[c] The use of trade names in this paper of specific products is essential to a proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendation by NBS.

combustion of metals in oxygen. Probably the best reviews of the combustion of metals and the heterogeneous combustion process are by Markstein[8,132] in 1962 and 1967. Essenhigh[141] also considers heterogeneous combustion in 1967 and Axworthy and Evers[142] in 1971 reviewed the postignition combustion behavior of metals in high pressure oxygen systems and discuss what should be measured to characterize it.

In other reviews Gordon et al.[24] and Friedman[22] cover techniques for combustion research, Cochran et al.[143] review the combustion research in zero-gravity, and Pelouch[144] considers the safety aspects in design for oxygen systems.

Several texts are also worth mentioning as possible reference sources. These are the *Fundamentals of Combustion* by Strehlow,[145] *Heterogeneous Combustion* edited by Wolfhard et al.,[146] *High Temperature Oxidation of Metals* by Kofstad,[147] and *The Electrical Aspects of Combustion* by Lawton and Weinberg.[148]

Relative Compatibility of Materials

Virtually all of the metals, with the possible exceptions of gold and platinum, will react with oxygen at some temperature and pressure, yet some are consistently more difficult than others to ignite or to maintain burning. Ideally, it would be possible to rank the various materials for compatibility but it is only possible for a given set of conditions. In a different application this ranking could be totally different, as the disparity of some of the test results indicate.

McKinley[43] has taken an excellent approach in ranking materials only for a specific test and has done so for eleven references. The relative position of a material in the ranking will be different for different tests. The order for electrical ignition of a wire, for example, ranks aluminum first while a promoted ignition test ranks it last. Choosing a material, then, entails evaluating the test method closest to approximating the actual application conditions.

Another way of analyzing relative compatibility is to formulate an equation for a compatibility index with variable weighting factors. The equation is dependent on the physical properties of the materials and the magnitudes of the weighting factors are based on the particular application. For example, the compatibility index could be defined as being proportional to ignition temperature, thermal diffusivity, impact energy necessary to react, mass, etc., and inversely proportional to the heat of combustion, operating temperature and pressure, flow velocities, etc. Then there would have to be several weighting factors for different systems to evaluate potential ignition sources, risks, exposure to oxygen, damage effects, etc. It cannot be overstressed that a compatibility index is very arbitrary but may well suffice for comparisons for a given specific application.

It is possible, however, to discuss the general behavior of a group of materials in the presence of oxygen in hopes of providing some guidance where there is wide range of choice. Some general characteristics of the compatibility of some of the more common structural materials, mostly alloy classes, are described below. The relevant physical properties of the base metals, for some of the alloys, and some other materials are shown in Table 1.

Nickel and copper alloys

Nickel and copper alloys are generally the most compatible metals available for oxygen use. The high nickel alloys and nickel copper alloys are difficult to ignite and even more difficult to keep burning.[40,63] They show a definite quenchant behavior[40,88,89] probably due to low heats of combustion and high thermal diffusivity so that the heat is carried away rapidly. Nickel-copper alloys are being used more and more for safety in high pressure applications in spite of the added cost.

Stainless steels

Those stainless steels with high nickel content are generally better for use with oxygen. Austenitic steels are also better than martensitic. Low carbon and low alloy steels begin to behave more like iron which is more readily ignited and burns faster but occasionally will quench itself with slag.[88] The stainless steels, as a class, have relatively high ignition temperatures[33] and in some tests show quenchant behavior if they do ignite.[41] With their excellent mechanical properties the stainless steels are frequently the best balance between cost and safety.

Aluminum alloys

Aluminum alloys are widely used in oxygen systems and have an impressive safety record. Several accidents have involved aluminum burning but are usually ignited by some other source.[72,79,83] Aluminum, however, is classed generally with the other light metals with relatively low ignition temperatures, high heats of combustion, and violent fragmentation when it does burn.[54,93,95,105] Aluminum alloys will frequently melt before igniting[14,40] and can flow away from the heat source which would hinder any reaction. It could stop the reaction, but may cause hot, molten aluminum to flow to another part of the system. The low cost and weight per unit strength of aluminum alloys, however, have led to common use in oxygen systems.

Titanium alloys

These light, strong alloys are commonly used in aerospace applications but are very reactive with oxygen and are seldom used with it. A fresh surface of titanium will react violently[15] and its alloys pass few of the compatibility tests.[62] These facts coupled with a relatively low ignition temperature and high heat of combustion virtually exclude it from use.

Other metals

Nearly all the other metals suffer from low ignition temperatures and ready combustion once ignited. Basically, all the light alkali metals, the transition metals (except Cu, Ni, and perhaps Co), the rare earths, and the transuranium elements[149-151] have shown undesirable behavior with oxygen. Notable exceptions are the noble metals which are virtually inert but limited by their high cost.

Nonmetals

Very few nonmetals are used structurally with oxygen systems. Two notable exceptions are polytetrafluoroethylene (TFE) and polychlorotrifluoroethylene (CTFE). Compared to metals these materials are highly combustible[10] but are the best of what is available. TFE and CTFE are more compatible than other organic materials because they are highly fluorinated with the strong fluorine-carbon bond. Generally, the more halogenated (particularly with fluorine) a hydrocarbon is, the safer it will be with oxygen.

The search for highly compatible materials for use with oxygen is far from over. Nonmetals are urgently needed. Some materials which have probably not been fully explored are the ceramics and composites.

Recommended Selection Procedure

To assist in choosing a properly safe material we have outlined some considerations and guidelines as follows. Obviously one should first select materials which physically fulfill the mechanical demands of the component considered. These materials can then be analyzed to select the most chemically compatible material. This selection process often can be based upon the material ranking of a given compatibility test. Or it may be based upon the concensus of the material ranking recommendations found in the literature, as is also frequently advocated. However, we believe that both of these suffer from two serious drawbacks: 1) no consideration is given to the uniqueness of the particular demands of the application in question, and 2) the materials ranking recommendations based upon the results of individual investigations often are highly contradictory, due to the specialized nature of the test and the biased interpretation of the results. A case in point is the wide disparity in the ranking of aluminum and stainless steel reported by various investigators.[40,65,93,95] We believe the material selection process should be accomplished by matching the particular demands of the equipment component with the materials best satisfying these demands. Material selection on this basis assumes the existence of several types of compatibility and physical properties data for these materials. For example, if a component is likely to be impacted but not likely to be in a high temperature environment, major consideration should be given to materials with a low impact sensitivity before considering their ranking according to ignition temperature. The importance of equipment design should not be ignored. For example, the introduction of slow opening valves and heat sinks, whenever possible, will reduce the probability of ignition by adiabatic compression.

The following is a priority sequence of guidelines that can be followed when selecting materials for oxygen use in the presence of ignition sources. Of course any considerations must include the effects of possible contaminants in the system. 1) Eliminate ignition—select a material which is least likely to ignite under the operational conditions. 2) Prevent continued reaction—select a material which tends to quench the reaction after ignition. 3) Reduce the rate of reaction—select materials which react as slowly as possible after ignition to permit the control of the reaction.

The first guideline is most likely satisfied by selecting the material with highest ignition temperature but is also affected by the presence of oxide coatings or the possibility of intermaterial reactions. For example, it has been reported and discussed by Key,[46,48] Ordin,[2] and Keeping[63] that chlorofluoro compounds may react strongly with aluminum under shear forces. This reaction may be sufficient to ignite aluminum in the presence of oxygen. Iron rust according to Keeping[63] significantly lowers the ignition resistance of aluminum in oxygen. Materials with a high thermal diffusivity are better in dynamic systems since local energy impulses will result in less pronounced hot spots than with low diffusivity materials. In a static system high thermal conductivity materials are more desirable for essentially the same reason. Materials whose melting point is higher than the ignition temperature should be free of sharp edges. The presence of sharp edges may result in hot spots for ignition. If the ignition temperature is sufficiently above the melting point, sharp edges will probably be smoothed by melting before ignition occurs. This has been reported to be the case for aluminum by Keeping.[63] At high pressures the prevention of ignition should be the principal goal because any reaction will probably be catastrophically destructive.

The second guideline, selecting a material which tends to quench itself, is influenced by several factors. The heat of combustion is the most important. If it is sufficiently low, the heat may be conducted away rapidly enough to quench the burning. The reaction products may also interfere with continued oxidation. For example, slag buildup has been reported to have a quenching effect in iron.

The materials portion of the third guideline, select slow burning materials, is affected by essentially the same factors. However, one can also utilize good design to slow down the reaction. For example, one might insert a nickel-alloy pipe section in a predominantly stainless steel pipe. The nickel alloy section, having a lower reaction intensity, would either quench or slow a reaction propagating along the pipe. The shape and size of components at strategic points in a system can be significant in controlling a reaction. Thermal anchoring of potentially reactive components to a cold heat sink can also be useful in curtailing a burn. A rapid operating system to shut down the oxygen supply may prevent extensive damage, unless the initial burn occurs with explosive violence. Limiting the oxygen availability by restricting oxygen flow where possible is desirable for control purposes.

The balancing of these considerations on top of the normal design criteria provides a tough problem indeed. We hope that by enumerating some of them we have aided future safe design. Much more data, however, would be of help.

Future Research

To be able to specify those materials that are compatible with oxygen under all conceivable conditions that could occur would require an understanding of all oxidation phenomena that would be legendary. However, the application of academic research capabilities to basic combustion coupled with a correlated series of empirical testing programs could come close to achieving this goal. Such a program would have to include a wide range of work: for example, generation and collection of all the thermodynamic data for all states of metals and their oxides, exploration of new materials of construction such as composites and new modes of use such as slush or solid oxygen, development of a series of materials screening tests, and evaluation of the contaminant-component interaction to the point of being able to specify minimum potential energy levels for interaction. This is obviously beyond the scope of any single effort on a nonemergency basis. Three areas of work should be considered as a beginning: existing information, empirical testing, and basic research.

Existing Information

As was indicated in the review of past work, there are a great deal of uncorrelated data available in the literature, and no time or effort should be wasted in attempting to sort out the many different tests and their multiplicity of parameters. However, considerable basic thermophysical properties data are available, some of them hidden in the compatibility tests but most available in chemical or combustion research journals and handbooks. These include the melting point, boiling point, density, heat of fusion, heat of vaporization, specific heat, heat of formation, heat of ionization, vapor pressure, thermal conductivity, ignition temperatures, oxygen and oxide solubility, oxide volume ratios, and oxidation states for all the metals, their oxides, and other potential structural materials. These data are necessary for any comparison with theoretical predictions, comparisons between materials, and a prerequisite for experimental design. Therefore, they should be collected, critically evaluated, and published in a form useful for design engineers and research scientists.

The other aspect of existing information that can be utilized is a correlation of presently operational test apparatus. In order to do this, a set of well characterized, standard research materials could be established to be provided to any group willing to run tests on them and disclose their results. With the proper choice of materials, say several metals and some nonmetals, a wide range of comparisons could be made with the elimination of the troublesome materials and preparation parameters. This program, at a minimal cost, would provide several beneficial results. First, it would generate an interest in the whole problem of compatibility and encourage an awareness of work going on in the whole field. It would also allow extension of any group's capabilities and confidence in its results. Also, it could rapidly indicate those tests or kinds of tests that are consistent as well as those that are obviously not. These materials would then provide a basis for comparison with any new tests.

Empirical Testing

Empirical testing of candidate materials in configurations closely approximating their potential use is obviously the most practical approach and has a definite application in this problem. To provide an accident situation involving oxygen transport, a structural material must not only ignite but continue to burn to sufficiently weaken the structure. In contrast to this, a space application may be aborted with ignition only, since component reliability is synonymous with personnel safety.

For this reason, a wide ranging and comprehensive research program on the ignition of materials should be undertaken. Several major categories of ignition sources can readily be defined and standard test materials could be examined in each. Some ignition sources have been well covered but could be looked at again with the same test materials for good correlation. The role of contaminants is a crucial one for ignition and should always be included. (A major effort along these lines has been initiated by the Aerospace Safety Research and Data Institute of NASA.)

For an accident situation, ignition is almost always assumed and the propagation of burning is what determines the nature of the accident. Some materials have been shown to be difficult to burn and in some cases even show a quenchant behavior, probably due to their large heat capacities, small heats of combustion, and the role of their combustion products. Nearly all of the research done on burning rates has been with small wires, ribbons, or tubes. Therefore, research into the burning behavior of bulk materials with minimum dimensions of the order of 1 cm should be done. This would involve ignition of different shapes of bulk samples of structural materials in an attempt to understand the role of the mass, shape, surface state, and environment in the propagation of combustion. The idea would be to look for parameters that by design could aid in quenching any reactions. (A small effort along this line has been initiated at NBS.)

Basic Research

As was indicated earlier, the biggest problem in the compatibility of materials is the lack of basic understanding of the heterogeneous combustion process. This is not only because there has been no urgent practical need for it in the past, but also because its inherent high combustion rates and high temperatures make it very difficult to study. It has been suggested[132] that a good way to study combustion would be to slow the combustion process down by oxygen deprivation; thus, only part of the energy needed to sustain combustion would be supplied by the heat of combustion of the burning materials. The additional energy would be supplied by an external source. (An effort encompassing this is also underway at NBS, utilizing an infrared laser as the supplemental energy source.) New sophisticated techniques such as mass spectrographic analysis, spin resonance, Raman scattering, or scanning electron microscopes can be used to identify chemical species or oxidation or ionization states of the reactants. An integral part of the effort should be an analytical study of relating slow oxidation[139,147,152] to combustion behavior as suggested by Reynolds.[89]

Other areas of basic research which should be explored are ignition and combustion theory (e.g., how big and how hot a spot is necessary), alteration of mechanical properties (particularly fatigue and crack propagation) in an oxygen environment, long term interaction with contaminants (metallic or oxide whisker, crack, or third compound formation), stress corrosion and the role of defect structures, thermo-mechanical oxide behavior, and electronic behavior in the heterogeneous combustion process.

Of particular interest, because it can be documented as accident causes,[2,86,153] should be the effect of an oxygen environment on the fatigue properties of the structural materials used in oxygen systems. Both the maximum design stress and the flaw size rejection during initial nondestructive testing are critically dependent on this knowledge. The fatigue behavior of a pressurized oxygen container is very critical, particularly if the pressure is cycled, yet very little work has been done.[64] Crack growth enhancement has been reported for a titanium alloy by Jackson et al.[15] and the absence of any enhancement for a nickel alloy has been reported by NASA.[154] This is an area of investigation that has been sorely neglected.

All in all, there is a great deal that can yet be done.

Note added in Proof: A significant and thorough effort to collect, evaluate, and summarize oxygen safety information, identify safety problem areas, and initiate necessary research has been underway for several years at the Aerospace Safety Research and Data Institute (ASRDI) at NASA Lewis Research Center. Since submission of this manuscript several of their efforts have resulted in publications which are not included in the References and, in fact, supersede Refs. 2 and 144. The ASRDI output includes several papers on compatibility, safety, cleaning requirements, accidents, fluid properties, ignition and combustion which are nicely summarized in Ref. 155.

References

[1] "Industrial Gases: A Markets/Management Portrait," *Cryogenics and Industrial Gases*, Vol. 6, Jan./Feb. 1972, pp. 15–23.

[2] Ordin, P. M., "Mishaps with Oxygen in NASA Operations," TMX-67953, Nov. 9–11, 1971, NASA.

[3] McQuaid, R. W. and Cole, E. L., "A Survey of Compressed Gas System Casualties Due to Spontaneous Ignition during the Period 1 Jan. 1968-31 May 1971," Rept. 28-148, May 1972, Naval Ship and Research and Development Center, Bethesda, Md.

[4] Attwood, H. C. and Allen, G. R., "On the Spontaneous Ignition Temperature of Organic Materials in Oxygen," CP 1172, 1971, Aeronautical Research Council Current Paper, Ministry of Defense, London, England.

[5] Flynn, T. M. and Smith, C. N., "Trends in Cryogenic Fluid Production in the United States," *Advances in Cryogenic Engineering*, Vol. 17, Plenum Press, New York, 1972, p. 1.

[6] Markstein, G. H., "Combustion of Metals," *AIAA Journal*, Vol. 1, No. 3, March 1963, pp. 550–562.

[7] "Commodity Specification for Oxygen," CGA Specification G 4.3, 1966, CGA, Inc., New York.

[8] Schmidt, H. W., *Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems*, NASA SP-3037, 1967.

[9] Breed, L. W., Wiley, J. C., Jr., and Key, C. F., "Partly Fluorinated Lubricating Oils and Greases for Use as Lox-Compatible Lubricants," *Industrial and Engineering Chemistry Product Research and Development*, Vol. 9, March 1970, pp. 53–56.

[10] Guter, M., "Ignition in High Pressure Oxygen," AD 648-612, RR/D 1312, 1967, British Oxygen Co. Ltd., London, England.

[11] Courtney, W. G., "Condensation During Heterogeneous Combustion," *11th International Symposium on Combustion*, Combustion Institute, Pittsburgh, Pa., 1967, pp. 237–244.

[12] Hermsen, R. W. and Dunlap, R., "Nucleation and Growth of Oxide Particles in Metal Vapor Flames," *Combustion and Flame*, Vol. 13, 1969, pp. 253–261.

[13] Wolfhard, H. G., Glassman, I., and Green, L., eds., *Heterogeneous Combustion*, Pt. IV, Academic Press, New York, 1964, pp. 667–671.

[14] Mellor, A. M. and Glassman, I., "A Physical Criterion for Metal Ignition," NASA, A 65-11057, Oct. 1964, Western States Section/The Combustion Institute, Pittsburgh, Pa.

[15] Jackson, J. D., Boyd, W. K., and Miller, P. D., "Reactivity of Metals with Liquid and Gaseous Oxygen," DMIC Memo 163, Jan. 1963, Batelle Memorial Institute, Defense Metals Information Center, Columbus, Ohio.

[16] Grosse, A. V. and Conway, J. B., "Combustion of Metals in Oxygen," *Industrial and Engineering Chemistry*, Vol. 50, April 1958, pp. 663–672.

[17] Henderson, C. B., "A Proposed Combustion Scheme for the Gaseous Oxidation Reactions of Beryllium and Aluminum," *Combustion Science and Technology*, Vol. 1, 1970, pp. 275–278.

[18] Cassel, H. M. and Liebman, I., "The Cooperative Mechanism in the Ignition of Dust Dispersions," *Combustion and Flame*, Vol. 3, Dec. 1959, pp. 467–476.

[19] Hartmann, I., "Recent Research on the Explosibility of Dust Dispersions," *Industrial Engineering Chemistry*, Vol. 40, 1948, pp. 752–758.

[20] Jacobson, M., Cooper, A. R., and Nagy, J., "Explosibility of Metal Powders," Rept. RI 6516, 1964, U.S. Bureau of Mines, Washington, D.C.

[21] Davis, A., "Solid Propellants: The Combustion of Particles of Metals Ingredients," *Combustion and Flame*, Vol. 7, 1963, pp. 359–368.

[22] Friedman, R., "Experimental Techniques for Solid-Propellant Combustion Research," *AIAA Journal*, Vol. 5, No. 7, July 1967, pp. 1217–1223.

[23] Friedman, R. and Macék, A., "Combustion Studies of Single Aluminum Particles," *9th International Symposium on Combustion*, Academic Press, New York, 1963, pp. 703–712.

[24] Gorden, A. S., Drew, C. M., Prentice, J. L., and Knipe, R. H., "Techniques for the Study of the Combustion of Metals," *AIAA Journal*, Vol. 6, No. 4, April 1968, pp. 577–583.

[25] Nelson, L. S., "Combustion of Metal Droplets Ignited by Flash Heating," *11th International Symposium on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1967, pp. 409–416.

[26] Nelson, L. S., Rosner, D. E., Kurzius, S. C., and Levine, H. S., "Combustion of Zirconium Droplets in Oxygen/Rare Gas Mixtures–Kinetics and Mechanism," *12th International Symposium on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1969, pp. 59–70.

[27] Lenze, F., *Chemisches Zentralblatt*, Vol. 1, 1931, p. 2388.

[28] Fassell, W. M., Jr., Gulbransen, L. B., Lewis, J. R., and Hamilton, J. H., "Ignition Temperatures of Magnesium and Magnesium Alloys," *Journal of Metals*, Vol. 3, July 1951, pp. 522–528.

[29] Coffin, K. P., "Some Physical Aspects of the Combustion of Magnesium Ribbons," *5th International Symposium on Combustion*, Reinhold Publishing Corp., New York, 1955, pp. 267–276.

[30] Nijland, L. M. and Schröder, J., "Generation of Light by Fluorine Reactions in Flash Lamps," *Phillips Research Reports*, Vol. 21, 1966, pp. 304–321.

[31] Jakowsky, J. J. and Butzler, E. W., "Preliminary Report II, Spontaneous Ignition of Metals in Oxygen under Pressure," Serial No. 2521, Sept. 1923, Bureau of Mines, Washington, D.C.

[32] "Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold Technique)," ASTM Designation D 2512-70, 692, 1970, American Society for Testing and Materials, Philadelphia, Pa.

[33] White, E. L. and Ward, J. J., "Ignition of Metals in Oxygen," Rept. DMIC-224, Feb. 1966, Defense Metals Information Center, Batelle Memorial Inst., Columbus, Ohio.

[34] Blackstone, W. R. and Ku, P. M., "An Assessment of Impact Test Techniques for Determining the Fire or Explosion Hazards of Materials Exposed to Liquid Oxygen," *Materials Research and Standards*, Vol. 11, June 1971, pp. 30–35.

[35] Pippen, D. L. and Stradling, J. S., "Techniques for Determination of Flash and Fire Points and Impact Sensitivity of Materials in a Gaseous Oxygen Environment," *Materials Research and Standards*, Vol. 11, June 1971, pp. 35–44.

[36] Kirschfeld, L., "On the Burning Rate of Metals in Oxygen to 200 Atmospheres Pressure," *Metallwissenschaft und Technik*, Vol. 21, Feb. 1967, pp. 98–101.

[37] Littman, F. E. and Church, F. M., "Reactions of Metals with Oxygen and Steam," AEC R. and D. Rept., Aug. 1960, SRIA-29, Stanford Research Institute, Menlo Park, Calif.

[38] Bauer, H., Wegener, W., and Windgassen, K. F., "Fire Tests on Centrifugal Pumps for Liquid Oxygen," *Cryogenics*, Vol. 10, June 1970, pp. 241–248.

[39] Bauer, H., Klein, G. K., Wegener, W., and Windgassen, K. F., "Fire Tests on Centrifugal Pumps Handling Liquid Oxygen—Part 2," *Cryogenics*, Vol. 11, 1971, pp. 469–476.

[40] Dean, L. E. and Thompson, W. R., "Ignition Characteristics of Metals and Alloys," *Journal of American Rocket Society*, Vol. 31, July 1961, pp. 917–922.

[41] Kirschfeld, L., "Combustibility of Steel and Cast Iron in Oxygen at Pressures of up to 150 atms.," *Archiv fur den Eisenhüttenw*, Vol. 39, 1968, pp. 535–539.

[42] Simon, W., "The Inflammability and Combustibility of Metal Tubes in Quiet and Circulating Oxygen," *Stahl und Eisen*, Vol. 88, Oct. 3, 1968, pp. 1090–1097.

[43] McKinley, C., "Experimental Ignition and Combustion of Metals," *CGA—Oxygen Compressors and Pumps Symposium*, Atlanta, Ga., 1971.

[44] Lucas, W. R. and Riehl, W. A., "An Instrument for Determination of Impact Sensitivity of Materials in Contact with Liquid-Oxygen," *ASTM Bulletin*, Vol. 244, Feb. 1960, pp. 29–34.

[45] Key, C. F. and Riehl, W. A., "Compatibility of Materials with Liquid Oxygen," TMX-985, Aug. 1964, NASA.

[46] Key, C. F., "Compatibility of Materials with Liquid Oxygen II," TMX-53052, May 1964, NASA.

[47] Key, C. F., "Compatibility of Materials with Liquid Oxygen III," TMX-53533, Nov. 1966, NASA.

[48] Key, C. F., "Compatibility of Materials with Liquid Oxygen IV," TMX-53773, Aug. 1968, NASA.

[49] Jamison, H. H., "Development of a Gaseous Oxygen Impact Testing Method," *Materials Research and Standards*, Vol. 11, June 1971, pp. 22–27.

[50] "Non-Metallic Materials Design Guidelines and Test Data Handbook, Revision C," MSC-02681, Feb. 1972, NASA.

[51] "Flammability of Plastics Using the Oxygen Index Method," ASTM Designation D 2863-70, 719, May 1970, American Society for Testing and Materials, Philadelphia, Pa.

[52] Key, C. F., "An Apparatus for Determination of Impact Sensitivity of Materials in Contact with Liquid and Gaseous Oxygen at High Pressures," *Materials Research and Standards*, Vol. 11, June 1971, pp. 28–51.

[53] Schwinghamer, R. J., "Impact Sensitivity of Materials in Contact with Liquid and Gaseous Oxygen at High Pressure," *CGA—Oxygen Compressors and Pumps Symposium*, Atlanta, Ga., Nov. 1971.

[54] Reynales, C. H., "Compatibility of Materials with Oxygen," Rept. D 81-444, Oct. 1958, Douglas Aircraft Co. Inc., Long Beach, Calif.

[55] Reynales, C. H., "Selection of Lubricants and Thread Compounds for Oxygen Missile Systems," *Advances in Cryogenic Engineering*, Vol. 6, 1961, pp. 117–129.

[56] Staph, H. E., Baber, B. B., Ku, P. M., and Weatherford, W. D., "Survey of Lubricant Compatibility Test Methods for Missile Systems," DDC-AD 292 130, Technical Documentary Rept. ASD TDR 62-190, Jan. 1962, Southwest Research Institute, San Antonio, Texas.

[57] Burmeister, L. C., Loser, J. B., and Sneegas, E. C., "Advanced Valve Technology," NASA SP-5019, 1967.

[58] Blackstone, W. R., "Development of an Improved Gaseous Oxygen Impact Test System," N70-32875, July 1970, NASA.

[59] Jamison, H. H., "Development of a Method for Qualifying Spacecraft Materials Used in Pure Oxygen," MSC-01553, Oct. 26, 1970, NASA.

[60] "Apollo 204 Accident," Senate Rept. 956, 90-2-2, Jan. 1968, U.S. Senate, Washington, D.C.

[61] "Apollo 13 Mission Report," MR7, May 1970, NASA.

[62] Riehl, W. A., Key, C. F., and Gayle, J. B., "Reactivity of Titanium with Oxygen," N 63 19264, Rept. TR R-180, Nov. 1962, NASA.

[63] Keeping, W. O., "Compatibility of Materials with Oxygen," *CGA—Oxygen Compressors and Pumps Symposium*, Atlanta, Ga., 1971.

[64] Baum, J. V., Goobich, B., and Trainer, T. M., "An Evaluation of High Pressure Oxygen Systems," AMRL-TDR-62-102, Sept. 1962, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

[65] Nihart, G. H. and Smith, C. P., "Compatibility of Materials with 7500 psi Oxygen," DDC-AD 608 260, AMRL-TDR-64-76, Oct. 1964, Union Carbide Corp., Tonawanda, N.Y.

[66] Holyer, N. F., "Aluminum High Pressure Oxygen Cylinders—Safety Tests," Rept. 3505, Sept. 1964, British Oxygen Co. Ltd., London, England.

[67] Nelson, L. S., Richardson, N. L., and Prentice, J. L., "Apparatus for the Production and Ignition of Metal Droplets with a Pulsed Laser," *Review of Scientific Instruments*, Vol. 39, 1968, pp. 744–747.

[68] Deming, J. L., Weber, J. H., and Luh, C. T., "Ignition of Exothermic Solid-Phase Reactions by a Laser Pulse," *Combustion and Flame*, Vol. 14, 1970, pp. 375–380.

[69] Prentice, J. L., "Combustion of Pulse-Heated Single Particles of Aluminum and Beryllium," *Combustion Science and Technology*, Vol. 1, 1970, pp. 385–395.

[70] Prentice, J. L., "Experimental Burning Rates of Single-Laser Ignited Beryllium Droplets," *Combustion Science and Technology*, Vol. 3, 1971, pp. 287–294.

[71] Bell, L. E., English, W. D., Murata, K. K., Pohl, S. W., and Tiner, N. A., "A Shock Sensitivity Tester for Liquid Propellant-Structural Material Systems," *Materials Research and Standards*, Vol. 11, June 1971, pp. 16–53.

[72] "NTSB Report: LOX Tanker Accident," *Cryogenic and Industrial Gases*, Vol. 6, July/Aug. 1971, pp. 19–25.

[73] Brady, E. W., "Compatibility of Metallic Materials with Liquid Oxygen," DDC-AD-459 269, Rept. DVR-64-459, Oct. 1964, Aerojet General Corp., Sacramento, Calif.

[74] Stradling, J., "Ignition by Abrasives," NASA TP-WSTF-193, 1971, White Sands Test Facility, White Sands, N. Mex.

[75] Christian, J. L., Chafey, J. E., Hurlich, A., Watson, J. F., and Witzell, W. E., "Compatibility of Metals and Cryogenic Liquids," *Metals Progress*, Vol. 83, 1963, pp. 100–103, 122, 124.

[76] Stepka, F. S., Dengler, R. P., and Morse, C. R., "Investigation of Catastrophic Fracturing and Chemical Reactivity of Liquid Filled Tanks When Impacted by Projectiles of High Velocity," N66-82375, TMX-52063, Nov. 1964, NASA.

[77] Dengler, R. P., "An Experimental Investigation of Chemical Reaction Between Propellant Tank Material and Rocket Fuels or Oxidizers When Impacted by Small High-Velocity Projectiles," N 64-17152, TN-D-1882, Aug. 1963, NASA.

[78] Johnston, R. S., "High Pressure Oxygen Systems Survey," MSC Apollo 13 Investigation Team Final Rept., Panel 8, May 1970, NASA.

[79] Cowles, S. W., "Oxygen Fires," *Safety in Air and Ammonia Plants (AIChE)*, Vol. 8, 1966, pp. 19–20.

[80] Reider, R., "The Influence of Accidents in the Continuing Development of Cryogenic Procedures," *2nd International Cryogenic Engineering Conference*, Brighton, England, May 7–10, 1968.

[81] Weber, U., "Explosions Caused by Liquid Oxygen," *Chimie Industrie*, Vol. 90, 1963, pp. 178–183.

[82] "Survey of Accidents in the Air Separation Plants," NASA Technical Translation F 13, 388, *Journal of Ammonium Sulfate Engineering*, Vol. 17, Nov. 1964, pp. 1–122.

[83] Boyne, W. J., "Liquid Oxygen Disposal Vessel Explosion," *Safety in Air and Ammonia Plants (AIChE)*, Vol. 8, 1966, pp. 7–11.

[84] Pinney, G. G., "Oxygen Trailer Fire," *Safety in Air and Ammonia Plants (AIChE)*, Vol. 4, Sept. 1961, pp. 49–50.

[85] Kilmartin, J., "Two Liquid Oxygen Explosions," *Fire Journal*, Vol. 65, 1971, pp. 15–24.

[86] Feinburg, I. J. and Passaglia, E., "Investigation of LOX Tank—Truck Explosion and Fire," unpublished NBS Report, National Bureau of Standards, Washington, D.C.

[87] Wells, A. A., "The Iron-Oxygen Combustion Process—Study Related to Oxygen Cutting," *British Welding*, Vol. 34, Sept. 1955, pp. 392–400.

[88] Hill, P. R., Adamson, D., Foland, D. H., and Bressette, W. E., "High Temperature Oxidation and Ignition of Metals," TM RML 55L236, March 1956, NASA.

[89] Reynolds, W. C., "Investigation of Ignition Temperatures of Solid Metals," TN D-182, Oct. 1959, NASA.

[90] Harrison, P. L., "The Combustion of Titanium and Zirconium," *7th International Symposium on Combustion*, Butterworths, London, 1959, pp. 913–919.

[91] Harrison, P. L. and Yoffe, A. D., "The Burning of Metals," *Proceedings of the Royal Society, London*, Vol. A261, Jan. 6, 1961, pp. 357–370.

[92] Kirschfeld, L., "Combustion of Metals in Oxygen," *Angewandte Chemie*, Vol. 71, 1959, pp. 663–667.

[93] Kirschfeld, L., "Combustion Rates of Light Metal Wires in Oxygen," *Metallwissenschaft und Technik*, Vol. 14, March 1960, pp. 213–219.

[94] Kirschfeld, L., "Combustion Rates of NE—Heavy Metal Wires in Oxygen," *Metallwissenschaft und Technik*, Vol. 14, Aug. 1960, pp. 792–796.

[95] Kirschfeld, L., "Combustion Rates of Light Metal Wires in High Pressure Oxygen," *Metallwissenschaft und Technik*, Vol. 15, Sept. 1961, pp. 873–878.

[96] Kirschfeld, L., "Influence of Geometric Form on the Combustion Rate of Sheet Metal in Oxygen," *Archiv fur den Eisenhüttenw*, Vol. 33, Sept. 1962, pp. 617–621.

[97] Spalding, D. B., "The Theory of Burning of Solid and Liquid Propellants," *Combustion and Flame*, Vol. 4, 1960, pp. 59–76.

[98] Stephens, H. R. and Walker, K. E., "Safety in Small-Scale High Pressure Experiments," *Industrial and Engineering Chemistry*, Vol. 49, 1957, pp. 2022–2025.

[99] Key, C. F. and Gayle, J. B., "Effect of Liquid Nitrogen Dilution on LOX Impact Sensitivity," *Journal of Spacecraft and Rockets*, Vol. 3, No. 2, Feb. 1966, pp. 274–276.

[100] Key, C. F. and Gayle, J. B., "Preliminary Investigation of Explosive Hazards of Solvents in Contact with Liquid Oxygen," Internal Note P and VE-M-65-3, April 1965, NASA.

[101] Brzustowski, T. A. and Glassman, I., "Spectroscopic Investigation of Metal Combustion," *Progress in Astronautics and Aeronautics, Vol. 15, Heterogeneous Combustion*, edited by H. G. Wolfhard et al., Academic Press, New York, 1964, pp. 41–74.

[102] Brzustowski, T. A. and Glassman, L., "Vapor Phase Diffusion Flames in the Combustion of Magnesium and Aluminum, I and II," *Progress in Astronautics and Aeronautics, Vol. 15, Heterogeneous Combustion*, edited by H. G. Wolfhard et al., Academic Press, New York, 1964, pp. 75–158.

[103] Mellor, A. M., "Heterogeneous Ignition of Metals: Model and Experiment," Aerospace and Mechanical Sciences Rept. 816, 1967, Princeton University, Princeton, N.J.

[104] Laurendeau, N. M. and Glassman, I., "Ignition Temperatures of Metals in Oxygen Atmospheres," *Combustion Science and Technology*, Vol. 3, 1971, pp. 77–82.

[105] Kuehl, D. K., "Ignition and Combustion of Aluminum and Beryllium," *AIAA Journal*, Vol. 3, No. 12, Dec. 1965, pp. 2239–2247.

[106] Kuehl, D. K. and Zwillenberg, M. L., "Investigation of the Ignition and Combustion of Metal Wires," NAS 7-353, UARL F910336-24, May 1967, United Aircraft Research Lab., East Hartford, Conn.

[107] Nesgovorov, L. Y., Prozorov, U. A., and Cholin, V. G., "Experimental Determining of Minimum Ignition Temperatures of Metallic Materials in the Presence of Gaseous Oxygen," *Latvijas PSR Zinatnu Akademijas Vestis, Fizikas un Tehnisko Zinatnu Serija*, Vol. 1, 1968, pp. 70–75.

[108] Barrere, M., "Recent Experimental Results on the Combustion of Aluminum and Other Metals," AGARD Conference Proceedings No. 52, 1970, pp. 20–21.

[109] Naegili, J. P., "What Triggers Oxygen Turbo Compressor Fires?," *CGA—Oxygen Compressors and Pumps Symposium*, Atlanta, Ga., 1971.

[110] Hust, J. G. and Clark, A. F., "A Survey of Compatibility of Materials with High Pressure Oxygen Service," *Cryogenics*, Vol. 13, June 1973, pp. 325–336.

[111] Kimzey, J. H., "Review of Factors Affecting Ignition of Metals in High Pressure Oxygen Systems," MSC-03461, TMX-67201, Oct. 1970, NASA.

[112] Stradling, J. S., "Ignition by Electrical Arc," NASA TP-WSTF-192, 1971, White Sands Test Facility, White Sands, N. Mex.

[113] Stradling, V. S., "Ignition by Single Mechanical Impact," NASA TP-WSTF-194, 1971, White Sands Test Facility, White Sands, N. Mex.

[114] Reynolds, W. C. and Williams, J. J., "An Investigation of the Ignition Temperatures of Solid Metals," NASA N-108826, TND-182, Oct. 1959, Stanford University, Stanford, Calif.

[115] Glassman, I., Mellor, A. M., Sullivan, H. F., and Laurendeau, N. M., "A Review of Metal Ignition and Flame Models," AGARD Conference Proceedings 52, 1970, pp. 19–41.

[116] Merzhanov, A. G. and Averson, A. E., "The Present State of the Thermal Ignition Theory: An Invited Review," *Combustion and Flame*, Vol. 16, 1971, pp. 89–124.

[117] Eyring, H. and Zwolinski, B. J., "The Foundations of Reaction Rate Theory and Some Recent Applications," *Record of Chemical Progress*, Vol. 8, 1947, pp. 87–102.

[118] Altman, D. and Grant, A. F., Jr., "Thermal Theory of Solid-Propellant Ignition by Hot Wires," *4th International Symposium on Combustion*, edited by L. Bernard, The Williams and Wilkins Co., Baltimore, Md., 1953, pp. 158–161.

[119] Friedman, R. and Macék, A., "Ignition and Combustion of Aluminum Particles in Hot Ambient Gases," *Combustion and Flame*, Vol. 6, 1962, pp. 9–20.

[120] Macék, A., Friedman, R., and Semple, J. M., "Techniques for the Study of Combustion of Beryllium and Aluminum Particles," *Heterogeneous Combustion*, edited by H. G. Wolfhard, I. Glassman, and L. Green, Jr., eds. Academic Press, New York, 1964, pp. 3–16.

[121] Belyaev, F. and Bakhman, N. N., "Theory of Burning of Powders and Solid Rocket Propellants (A Review)," *Combustion, Explosion and Shock Waves*, Vol. 2, 1966, pp. 3–17.

[122] Hermance, C. E., Shinnar, R., and Summerfield, M., "Ignition of an Evaporating Fuel in a Hot Oxidizing Gas, Including the Effect of Heat Feedback," *Astronautica Acta*, Vol. 12, March 1966, pp. 95–112.

[123] Hermance, C. E., "Variable Density and the Theory of Gas Phase Ignition of Solids," *Astronautica Acta*, Vol. 16, Feb. 1968, pp. 35–36.

[124] Anderson W. H., "Model of Transient Ignition in Self-Sustained Burning," *Combustion Science and Technology*, Vol. 5, 1972, pp. 75–81.

[125] Linan, A. and Williams, F. A., "Radiant Ignition of a Reactive Solid with In-Depth Absorption," *Combustion and Flame*, Vol. 18, 1972, pp. 85–97.

[126] Boddington, T., "The Growth and Decay of Hot Spots and the Relation Between Structure and Stability," *9th International Symposium on Combustion*, Academic Press, New York, 1963, pp. 287–293.

[127] Boddington, T., Gray, P., and Harvey, D. I., "Thermal Theory of Spontaneous Ignition: Criticallity in Bodies of Arbitrary Shape," *Royal Society, London—Philosophical Transactions*, Vol. 270, 1971, pp. 467–495.

[128] Frank-Kamenetskii, D. A., *Diffusion and Heat Exchange in Chemical Kinetics*, N. Thon, translator, Princeton University Press, Princeton, N.J., 1955.

[129] Merzhanov, A. G., "On Critical Conditions for Thermal Explosion of a Hot Spot," *Combustion and Flame*, Vol. 10, 1966, pp. 341–348.

[130] Merzhanov, A. G., "Thermal Explosion and Ignition as a Method for Formal Studies of Exothermic Reactions in the Condensed State," *Combustion and Flame*, Vol. 11, 1967, pp. 201–211.

[131] Merzhanov, A. G., "The Theory of Stable Homogeneous Combustion of Condensed Substances," *Combustion and Flame*, Vol. 13, 1969, pp. 143–156.

[132] Markstein, G. H., "Heterogeneous Reaction Processes in Metal Combustion," *11th International Symposium on Combustion*, Combustion Institute, Pittsburgh, Pa., 1967, pp. 219–234.

[133] Culick, F. E. L. and Dehority, G. L., "An Elementary Calculation for the Burning Rate of Composite Solid Propellants," *Combustion Science and Technology*, Vol. 1, 1969, pp. 193–204.

[134] Lordi, A. and Markstein, G. H., "Steady State First-Order Reaction at an Infinite Plane Surface to which Reactant Diffuses from a Point Source," *International Journal of Heat and Mass Transfer*, Vol. 11, 1968, pp. 355–359.

[135] Marzani, J. A., "Spontaneous Ignition of Solid Materials at Elevated Pressures," Report, Oct. 1968, Eastern Section Combustion Institute, University of Massachusetts, Amherst, Mass.

[136] McCarty, R. D. and Weber, L. A., "Thermophysical Properties of Oxygen from the Freezing Liquid Line to 600 R for Pressures to 5000 psia," TN 384, July 1971, National Bureau of Standards, Boulder, Colo.; also Roder, H. M. and Weber, L. A., *ASRDI Oxygen Technology Survey, Vol. I: Thermophysical Properties*, NASA SP-3071, 1972.

[137] Weast, R. C., ed., *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio, 1972.

[138] Smeltzer, W. W. and Perrow, J. M., "Oxidation of Metals," *Industrial and Engineering Chemistry*, Vol. 53, April 1961, pp. 319–324.

[139] Seybolt, A. U., "Oxidation of Metals," *Advances in Physics*, Vol. 12, 1963, pp. 1–43.

[140] Little, A. D., "A Summary of the Status of Research on the Mechanism of Combustion," AD 634-867, Oct. 1946, Applied Physics Lab., Silver Spring, Md.

[141] Essenhigh, R. H., "On the Inter-Influence of Classical Heterogeneous Combustion Research and Related Aerospace Problems," *11th International Symposium on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1967, pp. 291–308.

[142] Axworthy, A. E. and Evers, W. H., "Post Ignition Combustion Behavior of Structural Metals in High-Pressure Oxygen," Rept. RPP-885, Feb. 1971, Rocketdyne, North American Rockwell, Los Angeles, Calif.

[143] Cochran, T. H., Petrash, D. A., Andracchio, C. R., and Sotos, R. G., "Burning of Teflon Insulated Wires in Supercritical Oxygen at Normal and Zero Gravities," N71-17896, TM-X-2174, Feb. 1971, NASA.

[144] Pelouch, J. J., Jr., "Oxygen Technology Survey: Metals and Alloys," NASA Lewis Research Center, Cleveland, Ohio (to be published).

[145] Strehlow, R. A., *Fundamentals of Combustion*, International Textbook Co., Scranton, Pa., 1968.

[146] Wolfhard, H. G., Glassman, I., and Green, L., Jr., eds., *Heterogeneous Combustion*, Academic Press, New York, 1964.

[147] Kofstad, P., *High-Temperature Oxidation of Metals*, Wiley, New York, 1966.

[148] Lawton, J. and Weinberg, F. J., *Electrical Aspects of Combustion*, Clarendon Press, Oxford, 1969.

[149] Schnizlein, J. G., Pizzolato, P. J., Porte, H. A., Bingle, J. D., Fischer, D. F., Mishler, L. W., and Vogel, R. C., "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Thorium, Zirconium, Plutonium and Binary Alloys," ANL 5974, April 1959, Argonne National Lab., Argonne, Ill.

[150] Mouradian, E. M. and Baker, L., "Burning Temperatures of Uranium and Zirconium in Air," *Nuclear Science and Engineering*, Vol. 15, 1963, pp. 388–394.

[151] Leibowitz, L., Baker, L., Schnizlein, J. G., Mishler, L. W., and Bingle, J. D., "Burning Velocities of Uranium and Zirconium in Air," *Nuclear Science and Engineering*, Vol. 15, 1963, pp. 395–403.

[152] Pilling, N. B. and Bedworth, R. E., "The Oxidation of Metals at High Temperatures," *Proceedings of the Royal Society, London*, Vol. 29, 1923, pp. 529–582; see also *Chemical and Metallurgical Engineering*, Vol. 28, 1922, p. 72.

[153] Cataldo, C. E., "H-1 Engine LOX Dome Failure," X 65 17071, TM-X53220, March 1965, NASA.

[154] NASA, Panel 1—Apollo 13 Investigation Team, "Investigation of Crack Growth Threshold of Inconel 718 Exposed to High Pressure Oxygen," N 71-1995, Vol. 3, 1970, NASA, pp. 401–406.

[155] Mandel, G. and Mckenna, P. J., "Abstracts of NASA-ASRDI Publications Relevant to Aerospace Safety Research," TM X-71428, Sept. 1973, NASA.