

Overview

The purpose of this symposium on the flammability and sensitivity of materials in oxygen-enriched atmospheres was to build upon the foundation provided by previous symposia (STP 812, 910, and 986). The aim was to

- provide a reference text on a subject that is not widely addressed in accessible literature,
- build a reference of the concepts and practices used in designing oxygen systems,
- provide a data base to support the use of ASTM Committee G-4 guides and standards, and
- serve as a guide to Committee G-4 members in their future efforts to address the problems of oxygen-use safety.

This volume, in addition to previous symposia proceedings, adds significantly to the available resources on the important subject of the flammability and sensitivity of materials. These resources include the recently published Standard Guide for Evaluating Metals for Oxygen Service (G94) and an ASTM Standards Technology Training course entitled "Fire Hazards in Oxygen Systems" that the Committee G-4 is preparing. Such works, along with the existing body of literature, provide a valuable resource to both the designers and users of oxygen systems. Although much work remains in the areas of materials selection, system design, and maintenance, an excellent foundation has been laid and the structure is taking shape.

This volume comprises four sections. The first section presents five papers on development and evaluation of test methods. The second section, which addresses the ignition and combustion of nonmetallic and metallic materials, is made up of eight papers, and six papers are presented in the third section on the design, analysis, and testing of oxygen components. Five papers on the design, analysis, and testing of oxygen systems comprise the final section. This section includes two papers concerning oxygen fires during surgery, an important field that the Committee G-4 should continue to investigate.

DEVELOPMENT AND EVALUATION OF TEST METHODS

Moffett, Schmidt, Pedley, and Linley investigated the repeatability of the ambient liquid oxygen mechanical impact test (ASTM method D2512). Four nonmetallic materials were subjected to several series of tests conducted at different impact energy levels. The variability in reaction threshold energy level from series to series was found to be within the precision statement of the ASTM method. Using this method, the authors were able to distinguish Teflon and Vespel SP-21 from the more reactive materials but had difficulty distinguishing differences in reactivity between batches or lots of a single material.

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In a second paper by Moffett, Schmidt, Pedley, and Linley, the repeatability of the gaseous fluid impact test (G74) was considered. The authors tested the reactivity of four nonmetallic materials in oxygen over a range of impact pressures. They also investigated the effect of valve opening time and other test variables on the frequency of reaction. The data obtained for each test material varied too much to distinguish other than gross differences in the reactivity of materials. No relationship was found between this variability and the changes in valve opening time and other test variables. The authors recommend that new methods be developed for evaluating the suitability of materials for use in high-pressure oxygen systems.

McIlroy, Zawierucha, and Drnevich examined the effects of testing methodology on the promoted ignition-combustion behavior of two engineering alloys in oxygen. Experimental results were obtained with carbon steel and 316L stainless steel using three promoted ignition-combustion test methods. In the first test method, a 100-mm (4-in.) diameter chamber, static oxygen, and a hydrocarbon oil/iron wire promoter were used. The second test method was similar but the chamber volume was eight times greater than in the first method. In the third test method, the test gas varied from 40 to 99.998 percent oxygen, and the test gases flowed continuously past the test samples. It was found that chamber volume affected the ignition-combustion behavior of carbon steel but had negligible effect on stainless steel. The flow test method proved more severe than the static test methods. The authors recommend further work on evaluating materials at pressures lower than 0.7 MPa (100 psi).

Steinberg, Rucker, and Beeson performed promoted combustion tests on nine structural alloys in a high-pressure oxygen environment. Four methods that have been used to provide a relative flammability ranking of metals were compared, and a new, relative-ranking method was developed. Limitations of the ranking methods were assessed by investigating the effects of changes in test pressure, sample diameter, type of promoter, and sample configuration. Ranking methods that employ velocity as the primary ranking criterion were found to be limited by diameter effects. Methods that use quenching pressure as the ranking criteria were found to be nonselective for metals with similar flammabilities. An overall ranking, with which all methods agree, was chosen.

Yuen developed a data reduction program and ignition model for the analysis of data generated by the NASA White Sands Test Facility frictional heating test system. Data from 15 tests on carbon steel in oxygen were used to demonstrate that the model generates an effective friction coefficient, activation energy, and a reactive flux constant. The Pv product (the mechanical energy that is put into the system) required for ignition was shown to first decrease and then increase with oxygen pressure. The author postulates that at low oxygen pressure, the reactive flux constant was the important parameter controlling the energy required for ignition; at high oxygen pressure, the reduction in friction coefficient caused by formation of oxide was the dominant physical process.

IGNITION AND COMBUSTION OF MATERIALS

Nonmetals

Lockhart, Hampton, and Bryan compared the oxygen compatibility rankings of eleven nonmetallic materials using six different test methods: the standard liquid oxygen mechanical impact test (ASTM D2512), an enhanced liquid oxygen impact test, the standard pressurized gaseous mechanical impact test (ASTM G86), the standard pneumatic impact test (ASTM G74), autogenous ignition temperature via pressurized DSC, and heat of combustion (ASTM D2015). The rankings were found to vary depending upon the test method. When the results of all the tests were considered, it was determined that the better materials were PTFE, filled PTFEs, and fluoroelastomers.

Wharton, Nolan, and Swindells studied factors that affect spontaneous ignition temperatures (SITs) of nonmetallic materials in gaseous oxygen. Previous work by these authors was extended to encompass more materials and to investigate the effect of contamination on SITs. Standard bomb test results were found to depend strongly on testing parameters and on the chemical composition of the test specimen. Hydrocarbon-grease contamination of PTFE caused a dramatic reduction in the SIT when the degree of contamination was above a critical level. The critical amount of contaminant required for ignition was found to depend on heating rate and the degree to which the sample was subdivided.

Currie, Irani, and Sanders examined the oxygen pressure regimes at which silicone greases can be used safely. The BS 3N 100 high-pressure oxygen ignition test was used to evaluate SITs of a variety of silicone greases in oxygen at various pressures. Variations in composition and additives present in greases did not affect the SIT in pure oxygen. Consequently, the authors do not feel it is necessary to test silicone greases in the future, and they will apply a safe maximum working pressure limit of 1.0 MPa (145 psi) for their use.

Metals

Zawierucha, McIlroy, and Drnevich investigated the promoted ignition-combustion behavior of five engineering alloys that may be encountered in or considered for use in gaseous oxygen applications. In this investigation, alloys in the rod configuration were evaluated under both flowing and static conditions. Static tests were conducted in a vessel of the same volume as the apparatus used in the joint ASTM/CGA/NASA metals test program (see STP 986) and also in a larger vessel. Oxygen-nitrogen gas mixtures with purities ranging from approximately 40 to 99.7 percent at pressures of 0.79 to 34.6 MPa (115 to 5000 psi) were used in this comparative study. A number of metallurgical variables and concerns were identified which may influence the results of metals flammability tests. The authors found two major deficiencies in the oxygen compatibility area: the lack of data comparing different heats in which the chemical composition for a single alloy can vary significantly, and the lack of comparative data on different mill forms of engineering alloys.

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Sato obtained data on the upward fire-spread rates in oxygen along rods made from six pure metals and ten steels. The rods, which varied in diameter from 1 to 3 mm (0.04 to 0.12 in.), were tested in commercially pure oxygen at pressures ranging from 0.1 to 10 MPa (14 to 1450 psi) at initial test sample temperatures ranging from ambient to 1273 K (1832 °F). The author found that tin and titanium burned in the same manner as aluminum. Fire-spread rates along the titanium rods were greater than those along the aluminum rods. Steels burned in the same manner as iron, and the fire-spread rate of carbon steel decreased with increasing carbon content. For stainless steels, fire-spread rates along thinner rods were greater than those for mild steel; however, for thicker rods the fire was sometimes extinguished during spreading when the oxygen pressure was low. Fire-spread rates of various stainless steels were similar.

Werley, Slusser, and Zabrenski studied the combustion of 17 metals using a pressurized oxygen index test. The tests explored upward propagation against a small downward gas flow at pressures to 10.3 MPa (1500 psig). The metals were ranked according to flammability limits obtained in two different ways: using the pressurized oxygen index (the minimum oxygen concentration necessary to sustain combustion of the solid at a fixed pressure after positive ignition) and using the threshold pressure (the minimum pressure necessary to sustain combustion at a fixed oxygen concentration after positive ignition). The effect of melt drainage patterns, sample configuration (rod versus tube), and heat treatment on the flammability of 304 stainless steel were considered. The authors review the use of these and other data to support increased usage of 304 stainless steel.

Benz, Steinberg, and Janoff examined upward combustion in oxygen of a liquid-phase burning metal to obtain a combustion model. These authors evaluated the effects of varying the pressure and rod diameter on the rate-limiting processes for combustion of 316 stainless steel. The rate-limiting steps for upward combustion of 316 stainless steel rods were found to depend on two factors: incorporation and mass transport of oxygen in the molten mass and heat transfer between the molten mass and the rod. Both of these rate-limiting steps were found to depend on rod diameter, with small rods depending on convective heat transfer and larger rods depending on oxygen incorporation and mass transport in the molten mass.

Stoltzfus, Benz, and Homa investigated the Pv product (the product of the contact pressure and surface speed) required for the frictional ignition of 16 alloys. Alloys containing large amounts of nickel were found to have the greatest resistance to ignition. The effect of the coefficient of friction on ignition was evaluated and was found to have a major effect on the ignition of alloys. The authors conclude that in environments where frictional heating is the dominant ignition source, alloys must be selected on the basis of data from frictional heating tests.

DESIGN, ANALYSIS, AND TESTING OF OXYGEN COMPONENTS

Christianson and Plante designed an ignition-resistant valve for

use at high flow rates in high-temperature and high-pressure oxygen environments. A valve used in these environments is susceptible to ignition by particle impact (as demonstrated by the ignition and combustion of an oxygen flow control valve during qualification testing at the White Sands Test Facility). The authors' design and testing processes resulted in a valve that met all established design parameters when tested under normal and worst-case conditions. They conclude that adherence to general design parameters such as careful design of the gas flow path, appropriate selection of ignition-resistant materials, and configurational testing at worst-case operating conditions can ensure safe and reliable oxygen components.

Newton, Langford, and Meyer investigated the ignition containment capability of 12 oxygen regulators subjected to promoted ignition. Oxygen regulators were preset to 0.55 MPa (80 psi) and connected to a system that permitted a flow rate of 1966 cc/s (250 scfh) and contaminated with hydrocarbon oil. The regulators' inlet passages were then pressurized to 15.2 MPa (2200 psi) with gaseous oxygen, and the oil was ignited with an electrical spark. The hydrocarbon flame was allowed to propagate with the oxygen flow throughout the regulator. The test articles were monitored by video to document their ability to contain the internal combustion. Reactions ranged from complete containment for one two-stage regulator to extensive burning and explosive energy release for several other single- and two-stage regulators.

Barthelemy, Delode, and Vagnard studied the ignition and burning of oxygen regulators and considered the influence of test equipment and procedure on the results obtained. The conditions that lead to ignition by "adiabatic compression" were investigated. How such ignitions occur and how they can be prevented were considered. The influence on ignition characteristics of the materials of construction and of the internal design of regulators was also considered. The authors determined that although European and international standards for regulator testing exist, these standards are neither sufficiently precise nor reliable enough to produce consistent results. The authors indicate that conflicting results were obtained when various laboratories performed regulator tests using these procedures. The authors also conclude that "aluminum pressure regulators can be safely used in oxygen service equally well as brass regulators." This conclusion is based upon tests in which aluminum and brass-bodied regulators were ignited internally. Test results are shown indicating that both regulators burned through. Others take exception to the conclusion. It is argued that the observation made by the authors that aluminum and brass regulators can be safely used when clean, and that both can yield equal results when ignited, does not support a conclusion that they are equally safe. A question for discussion of the controversial conclusion is presented.

Janoff, Bamford, Newton, and Bryan investigated the ignition of PTFE-lined flexible hoses by rapid pressurization with oxygen. Stainless steel, braided, flexible hoses lined with PTFE were exposed to high-volume pneumatic impact tests. The objective of the testing was to characterize the ignition mechanism by determining the effects on ignition of impact pressure, pressurization rate, and volume upstream

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and downstream of the hose. Ignitions occurred at impact pressures well below the working pressure of the hoses and at pressurization rates easily obtained with manually operated valves. The hoses ignited at the downstream end, and the fire propagated back toward the source of fresh oxygen. The addition of stainless steel hardline downstream from the hose prevented ignitions at all pressures and pressurization rates. Internal observations revealed evidence of shock ionization of the oxygen prior to ignition. The authors indicate that, although adiabatic compression of the oxygen is the most likely source of thermal energy for ignition, shock ionization of the oxygen may play an important role in the ignition mechanism by decreasing the activation energy necessary to kindle the reaction.

Irani, Currie, and Sanders extended their previous work (presented in STP 986) by examining five candidate elastomeric materials that could be used in high-pressure oxygen. Actual service conditions were simulated, and the effects of gas pressure, temperature, and moisture content on the materials were systematically studied. Test data were interpreted with respect to the structure and strength of the materials.

Gunaji, Stoltzfus, Schoenman, and Kazaroff investigated the effects of surface treatments on the tribological characteristics of Monel K-500 being rubbed in high-pressure oxygen. Seven surface treatments were evaluated at ambient and 6.9 MPa (1000 psi) oxygen pressures. The sample temperatures during tests at ambient oxygen pressure were significantly higher than during tests at 6.9 MPa (1000 psi) oxygen pressure. Ion-implant treatments reduced the average coefficient of friction, but this effect was eliminated when the contact pressure was increased from 5 to 20 kN/m² (20 to 200 psi). Total sample wear was greater at 6.9 MPa (1000 psi) than at ambient oxygen pressure except when chrome was present. Electrolyzed chromium dramatically increased the total sample wear of Monel K-500; other surface treatments affected sample wear only slightly. The authors indicate that although some useful observations could be made from the data generated using this test apparatus, a different method must be developed to allow a more sensitive assessment of the effects of surface treatments on the tribological characteristics of metals.

DESIGN, ANALYSIS, AND TESTING OF OXYGEN SYSTEMS

Barter and Hillen investigated incidents in, and problems associated with, oxygen systems. It was found that in the initial design of oxygen systems, the oxygen compatibility of materials forming the component parts was important. In addition, contamination of systems resulting from frequent use was found to introduce serious risk factors. It was determined that the designer must be made aware of potential contaminants and how they may affect system safety. Valve designs that were particularly sensitive to system contaminants were identified. The authors suggest that design philosophy should address sensitivity to contamination and design codes should identify and prohibit "poor practice." Finally, the authors indicate that the severity of gaseous oxygen fires is intimately related to the period of oxygen flow; thus, the authors recommend automatic shut-off devices that

operate under abnormal flow conditions. The authors considered one such device and some of its limitations.

Santay examined the use of quantitative fault tree analysis to evaluate systems for oxygen service. A scenario was proposed: In the event of a process plant upset, systems not normally intended for use in oxygen might be suddenly subjected to an oxygen-enriched atmosphere. If the upset condition occurred frequently, a conservative approach would be to design all components as if they were normally in oxygen service. As an alternative, the probability of the upset condition could be calculated to quantitatively assess the risk and recommend corrective measures to further reduce the risk. Quantified fault tree techniques could be used to determine a system's compatibility when exposed to oxygen in this manner. An example of the application of such an analysis was considered. The author concludes that although fault tree quantification alone is not the answer to assessing a system's compatibility, it should become part of a complete scientific and engineering approach to establishing safe oxygen system design.

Simpson, Wolf, and Schiff measured the effect of helium dilution of oxygen on the flammability of endotracheal tubes. The results of oxidant index tests using helium diluent were compared to the results of oxidant index tests using nitrogen diluent. Data for endotracheal tubes made from four materials were compared. The helium dilution values differed from the corresponding nitrogen dilution values by as much as 20 percent. The authors conclude that the common clinical practice of using helium rather than nitrogen as an oxygen diluent in potentially flammable situations does not increase patient safety.

Bruley and Lavanchy investigated fires that have occurred during surgery of the head and neck. They concentrated on oxygen- and nitrous oxide-enriched fires, the common medical devices that act as ignition sources, and the combustible substances that are present during surgery. The authors summarized a comparative evaluation of surgical draping materials, which included testing for flame-spread rates and ignitability in standard atmospheres. They also considered the oxygen-enriched atmosphere phenomenon of surface fiber flame propagation on reusable surgical textiles. The authors recommend methods of minimizing the risk of surgical fires, including special precautions for preventing surgical laser fires.

Hokkanen investigated the concept that oxygen-enrichment in foam insulation for liquid-nitrogen transfer lines constitutes a potential fire hazard. The author measured oxygen levels inside two types of foam insulation by analyzing samples of gas from the innermost layer of foam on a liquid nitrogen transfer line. Oxygen levels above 30 percent were detected. The oxygen percentage decreased at a rate that was dependent on the insulation ventilation. It was found that long-range effects could be expected in systems operating over long time periods. A substantial part of the foam could then be affected by diffusion of oxygen-rich gas into the cells of the foam and by the large number of cells that opened as a result of thermal cycling.

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These papers confirm that the objectives of the Symposium were met. The papers presented here (in conjunction with previous symposia volumes) provide a previously unavailable reference of oxygen system design concepts and practices. These volumes provide a data base that supports the use of ASTM Committee G-4 guides and standards. In addition, they serve as a guide to committee members in their future efforts to address the problems of safe oxygen use.

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