IGNITION OF METALS IN HIGH PRESSURE OXYGEN

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Abstract

A description of an experimental facility used to determine the ignition and combustion characteristics of metallic materials is described. The results obtained for aluminum 6061, 302 stainless steel, and the nickel alloy--N$\emptyset$6625--are given.

Introduction

For a number of years, accidents involving the sudden ignition and combustion of metals in contact with liquid and gaseous oxygen have occurred. These accidents have occurred to many users of liquid and gaseous oxygen. Some of the accidents have resulted in injury and/or death to personnel close to the accident.

During the development of the Space Shuttle main engine, several major failures occurred due to the sudden ignition and combustion of metallic materials in contact with liquid and gaseous oxygen. As these failures were analyzed it became apparent that data on the ignition and combustion characteristics of many materials was either limited or not available.

To alleviate this problem, a program was initiated at the National Bureau of Standards, by the George C. Marshall Space Flight Center to determine the ignition and combustion characteristics of specific alloys in high pressure oxygen systems. In addition to the data generation part of the program, the determination of fundamental ignition mechanisms are to be determined.

Experimental

Specimens of aluminum 6061, 302 stainless steel, and nickel alloy NØ6625, 5 mm in diameter by 5 mm in height, were ignited in commercially pure oxygen. Oxygen pressure varied from atmospheric to 5.171 MPa (750 psia) the maximum pressure at which reliable ignition could be obtained. Specimen ignition was carried out by heating the top surface with an 80 W cw CO_2 laser operating predominantly in the TEM_{oo} mode. The sample size utilized was the largest that would meet heating rate and maximum temperature requirements.

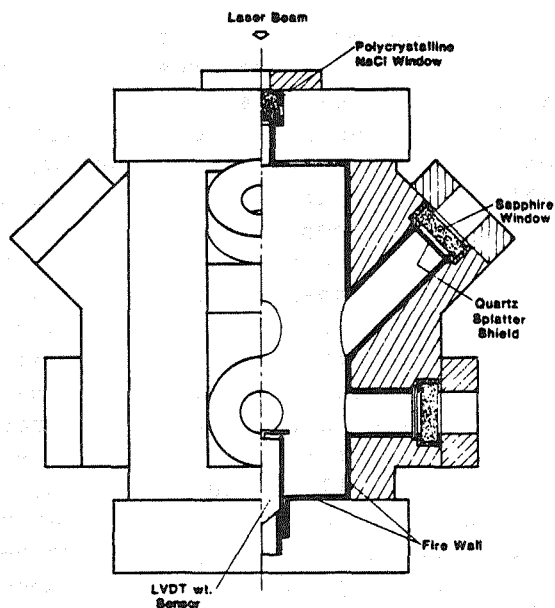The ignition studies were carried out in a high pressure combustion chamber, Figure 1, which was

Figure 1. High pressure combustion chamber.

designed to allow the manual mounting and adjustment of the specimen and to minimize pressure changes during the experiment. The free volume of the chamber is approximately 2.5 liters. The chamber has eight

general purpose ports; four were equally spaced at
45° to the chamber axis, and four equally spaced at
90° to the chamber axis. All port axes intersect at
a common point on the chamber axis. Each port has a
clear aperture of 6.5 cm^2.

Five measurements were made as follows:

1) mass,

2) brightness,

3) interior temperature,

4) mean top surface temperature, and

5) selected top surface spot temperature.

Mass data were obtained from a linear variable dif-
ferential transformer (LVDT) sensor which has a
100 g capacity. The mass sensor/data acquisition
unit was set up to give a mass resolution of 0.25 mg.
Brightness data, not quantitative measurements, were
obtained from a silicon photodiode. These data were
used to compare present results to past work; they
will probably be eliminated in future studies, since
the mean top surface temperature was a much better
indicator of surface events. The interior tempera-
ture was measured by inserting a W 6% Re vs. W 26% Re
or Pt vs. Pt 10% Rh thermocouple into a 0.64 mm diam-
eter hole drilled to within 0.25 to 0.40 mm of the
top surface. The thermocouple wire was insulated
with an aluminum-oxide-doped fiber-reinforced sili-
cate cement. Two-color ratio pyrometers were used to
measure the mean overall top surface temperature and
the selected top surface spot, 0.5 mm diameter, tem-
perature. The two-color ratio pyrometers were not
adversely affected by problems such as smoke or dirty
windows. In addition to the above measurements,
high-speed cinematography was used to obtain ignition
and combustion behavior. A framing rate of 250 fps
was used.

The test specimens were machined from commerci-
ally available material. Specimens of nonaluminum
based alloys were flame oxidized (blued) to reduce

reflectivity and improve absorptivity to the laser
beam.

    To assemble the experiment, the insulated
thermocouple was inserted through the bottom of the
graphite block into the containment well and weakly
cemented in place. The containment well was then
lined with packed aluminum oxide powder to a thick-
ness of 2 mm on the bottom and 1 mm along the side.
The specimen was inserted firmly over the thermo-
couple and seated firmly on the aluminum oxide
powder, breaking the weak thermocouple/graphite block
cement bond. This allowed the thermocouple to float
and follow changes in position of the top surface of
the specimen. This assembly was placed on a contour-
ed section of foam firebrick and then seated on the
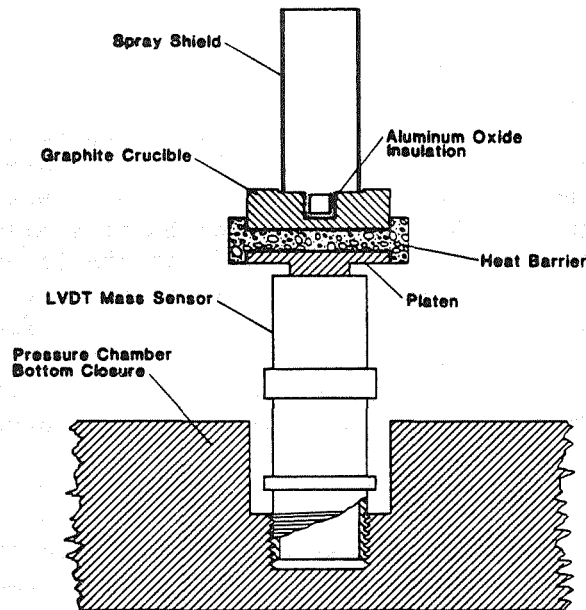platen of the LVDT, Figure 2. A cylindrical glass

Figure 2. Experimental set-up.

shield was placed over the containment well in order
to reduce the amount of molten/burning material

ejected from the combustion zone and also to reduce
the effects of convection on the LVDT mass sensor.

All sensor signals were digitized by 12 or 15
bit analog-to-digital converters. Data acquisition
times were either 10 or 20 ms per point for a total
experiment run time of 20 or 40 s.

Discussion and Results

The ignition and combustion results for three
metal alloys are reported. These alloys are repre-
sentative of large classes of alloys from which the
alloys were taken.

Definitions

Ignition Point

Ignition was considered to have occurred when an
accelerating or abrupt mean surface temperature in-
crease develops from the general heating rate trend.
The data point preceding this development was taken
as the ignition point. For vapor burning alloys this
point was usually well defined. For the liquid burn-
ing alloys, considerable care was taken to differen-
tiate temperature steps due to oxide scale from the
temperature step due to the oxidation of the alloy.
The ignition point for these materials usually must
be confirmed from mass and interior temperature data.

Ignition Temperature

Ignition temperatures are derived from the vari-
ous sensor signals at the ignition point. Smoothing
or extrapolating procedures may be used.

Aluminum 6061

Aluminum and aluminum-based alloys burn in the
vapor phase. Aluminum oxide is a protective oxide
and prevents the transfer of significant amounts of
oxygen to the molten metal surface. For pure

aluminum to ignite and burn, the covering aluminum oxide layer must be raised above the melting point or the vapor pressure of the molten metal must be sufficient to break the layer.

Two possible effects can be generated by alloying elements on the aluminum/aluminum oxide system. First, the protective oxide layer may be modified to become nonprotective, thereby lowering the ignition temperature. Second, there exists the possibility of energetic reactions between aluminum and alloying element oxides, effectively lowering the ignition temperature.

To test the possible effects of alloying elements, ignition tests using aluminum 6061 were carried out. This alloy has a nomial composition of 0.2% Cr, 0.27% Cu, 1.0% Mg, and 0.6% Si. Some or all of these alloying elements are present in various percentages in many other aluminum-based alloys. No iron is present; therefore the known iron oxide/ aluminum reaction will not confuse the results. Initially, tests were planned for oxygen pressures from atmospheric to 13.790 MPa (2000 psia). However, low surface absorptivity to the laser beam and higher convective cooling rates in the pressurized oxygen limited ignition to a maximum pressure of 2.413 MPa (350 psia).

The preignition oxidative behavior of the alloy was highly variable. Oxidation rates from undetectable to 15 mg $[O_2]$/s were observed. If detectable preignition oxidation occurred during a test, the event began at temperatures greater than 1800 K but did not necessarily continue throughout the experiment.

The ignition sequence was of two types—abrupt and accelerating. The abrupt ignition sequence took place within one data acquisition time period, 10 or 20 ms, and was concurrent with combustion. The accelerating ignition sequence usually lasted for 40 to 60 ms, but has lasted for as long as 140 ms; it

usually ended abruptly. This would imply that more than one mechanism is responsible for ignition and combustion or that one mechanism begins the process and a second is available to accelerate the event.

The specimen underwent a slow but constant change in geometry during heating. The original flat top surface became dome-like before ignition. In addition to the top surface change, the specimen sagged, becoming up to 1 mm shorter; the sagging slightly shifted the relative position of the top surface. Because of changes in the specimen geometry, the original 0.5 mm diameter central measurement point for the spot temperature measurement was randomly shifted from the original position. Using spot temperature data at low pressures plus data from special calibration tests, it was found that the maximum surface temperature was less than 2275 K. The calibration tests, which were conducted in air to prevent specimen combustion and failure of the tungsten-based thermocouple, also demonstrated that the mean surface temperature was an excellent indicator of the maximum interior temperature to within ± 20 K.

Using the previous definition of ignition point, the mean surface temperature at ignition was determined. Oxygen pressure varied from 0.069 MPa (10 psia) to 2.413 MPa (350 psia). These data are presented in Figure 3. Three of the data points, marked by a triangle, represent ignition that occurred on specimen cooling after failure to reach ignition temperature on heating. Insufficient laser power was the cause of the failures to reach ignition temperature. These data are considered unique and will be discussed separately. Five data points are marked by diamonds. These data are considered to deviate from the main body of data because the pyrometer field of view was set excessively high on the specimen. As the specimen sagged and the upper surface geometry changed, the only area within the field of view of the instrument would be the upper part of the dome, the highest temperature area of the surface.
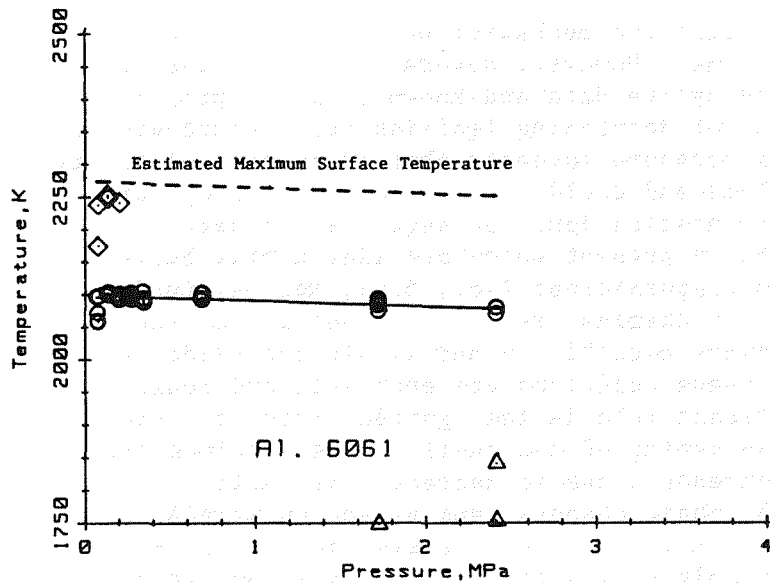
Figure 3. Mean surface temperature at ignition.

These data confirm the maximum spot temperature data, which peaked at 2266 K. Utilizing data from the low pressure experiment and the calibration test, an estimate of the temperature differential across the top oxide surface can be established. The most probable experiment-to-experiment value of the temperature differential would lie in the range 150 K to 200 K.

The highest mean surface temperature at ignition occurred at 0.138 MPa (20 psia). A linear least squares curve fit of the data from 0.138 MPa to 2.413 MPa gave an ignition temperature dependency on oxygen pressure of -9.11626 K/MPa (-0.06285 K/psi). It is reasonable to assume that the peak surface temperature and peak interior temperature also followed this trend; this is shown in Figure 3. Observation of the specimen indicates that the ignition zone

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occurred in the central 50% of the top surface. This was the area of highest temperature.

The ignition mechanism has not been determined at this time. However, several possibilities are suggested by the data and known physical properties. The trend of decreasing ignition temperature with increasing pressure suggests that an oxygen solubility is involved and could also explain the abrupt and fast accelerating ignition sequence. Several oxides are probably present which are liquid well below the ignition temperatures; i.e., SiO_2, $MgSiO_3$, Cu_2O. A number of chemical reactions involving molten aluminum are possible on and within the oxide shell. Many of these reactions are energetic and could play a significant role in the ignition process. The steady weakening of the shell as the specimen temperature increases, due to decreased mechanical strength, phase changes, and expansion stress, is an additional complication. Several individual mechanisms probably play a role in the ignition process.

The ignition of several specimens on cooling, that had failed to reach ignition temperature on heating, was considered to be significant. The ignition was abrupt and considered to have occurred when the specimen surface either cracked or imploded from the negative differential volume change due to the larger expansivity of the liquid alloy. The energy produced by the oxidizing surface was thought to be trapped within the cracked or imploded area. Additional energy may have been added to the system by the chemical reaction of molten aluminum with various alloying element oxides. The total energy thus released was sufficient to raise the temperature of the surrounding oxide material past the ignition point, resulting in combustion. This would imply that molten aluminum alloys can be ignited at temperatures significantly below the normal ignition temperature.

302 Stainless Steel

The 300 series stainless steels have been extensively used in oxygen systems due to the many desirable properties shown by various alloys within this series. It has been considered desirable to determine the ignition and combustion characteristics of a number of alloys in this series because of their usefulness.

A large number of ignition tests have been made on seven alloys of the 300 series. The ignition and combustion characteristics have been similar for all seven alloys. The data for one alloy, 302, are presented here.

The 302 alloy has a nominal composition of 17-19% Cr, 8-10% Ni, 2% Mn, 1% Si, 0.15% C, 0.045% P, 0.030% S; the balance is Fe. The alloy has a melting range from 1672 to 1694 K. In the case of the stainless steels, the higher absorptivity of the oxidized specimen surface and the lower ignition temperatures allowed tests to be performed to oxygen pressures of 5.171 MPa (750 psia).

The preignition oxidative behavior of this alloy was uneventful. A black oxide surface would develop and gradually increase in thickness. Between 1500 and 1600 K, a detectable oxidation rate of up to 0.4 mg $[O_2]$/s developed. The surface oxide layer took on a granular appearance and became thermally insulating.

The ignition sequence began with the development of a small hot-spot within the central 50% of the top surface. The hot-spot increased irregularly in size until the specimen began to melt and self-sustained combustion developed. If the external heat source was removed during the ignition sequence, self-sustained combustion did not develop. A typical preignition-ignition sequence for a test at 1.724 MPa (250 psia) is shown in Figure 4.
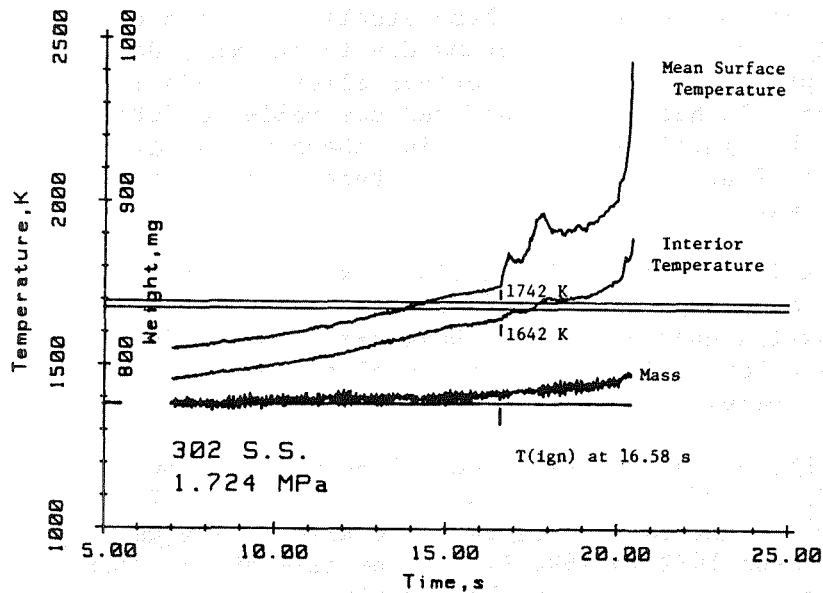
Figure 4. Typical waveforms about the ignition point
           for 302 stainless steel.

     Interior temperatures at ignition are presented
in Figure 5. The solid lines represent the lower and
upper melting range of the alloy and the dashed line
represents the melting point of ferrous oxide or iron
deficient ferrous oxide. Analysis of the waveforms
of the interior temperature as well as the interior
temperature values at ignition strongly indicates
that ignition cannot begin until the ferrous oxide at
the alloy-oxide interface begins to melt. Thus the
ignition temperature of 302 stainless steel has a
lower bound of 1650 K. The interior temperature
waveform analysis also strongly indicates that at
oxygen pressures of 0.689 MPa (100 psia) and greater,
ignition will take place before the alloy-oxide in-
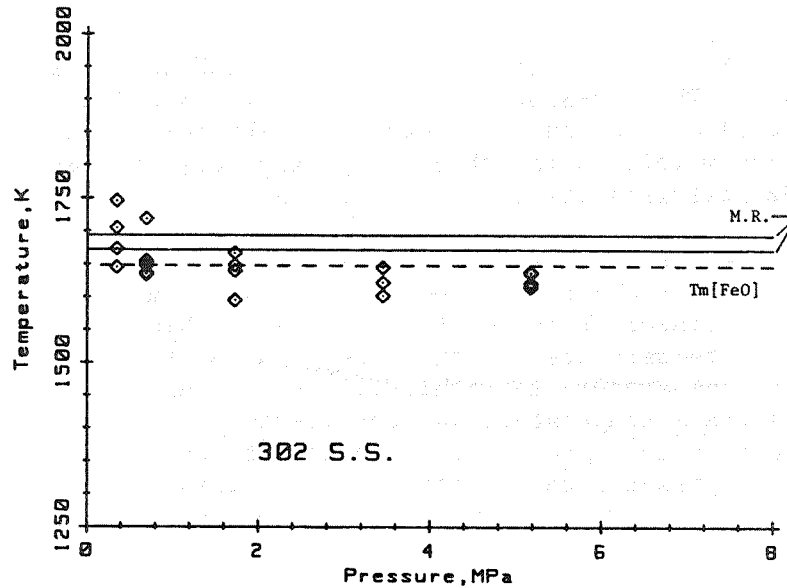terface temperature reaches the upper melting range
bound, 1694 K.

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Figure 5. Interior temperature at ignition.

Nickel Alloy NØ6625

Several nickel alloys are to be studied. However, the alloy NØ6625 is the only one for which data have been generated for oxygen pressures greater than 0.345 MPa (50 psia). Those data are presented here.

The NØ6625 alloy had a ladle analysis of 22.10% Cr, 8.77 Mo, 3.90% Cb+Ta, 2.44% Fe, 0.26% Ti, 0.17% Al, 0.04% C, 0.02% Si, 0.03 Mn, 0.005% P, 0.Q02% S and balance Ni. The alloy has a melting range of 1561 to 1622 K.

The preignition oxidative behavior of this alloy was uneventful. A thin black oxide layer would form until the alloy surface began to melt. At this point, if the heating rate was too slow, a thick solid oxide layer would form and could prevent

ignition. If the heating rate was adequate, ignition would occur shortly after the upper surface began to melt.

The ignition sequence began with the development of a small hot-spot within the central 50% of the top surface. The hot-spot would rapidly expand and un-supported combustion would develop. The temperature and mass waveforms for this alloy were very similar to 302 stainless steel.

Interior temperatures were available for igni-tion taking place below 1700 K. For those ignitions for which interior temperatures are available, the interior temperature was the same value as the mean surface temperature to within $\pm$15 K. Therefore the mean surface temperature was considered to be a good estimate of the interior temperature at ignition. Figure 6 presents the ignition temperatures. The
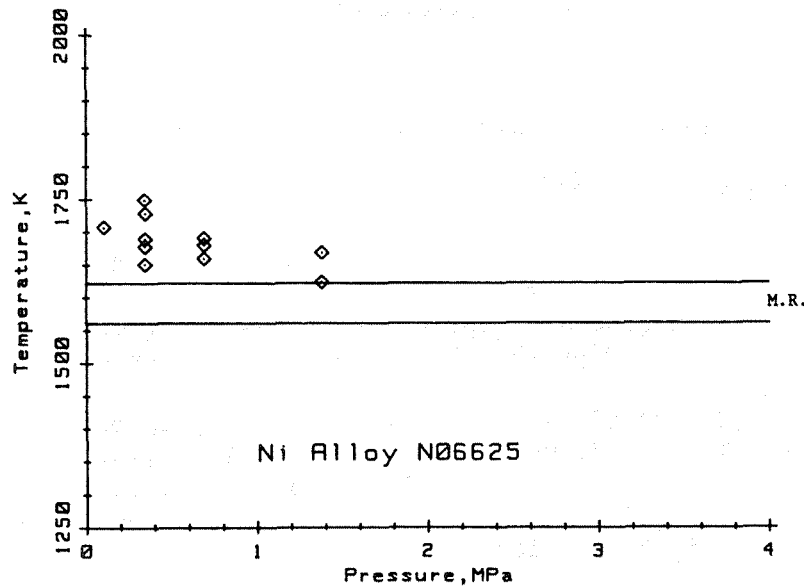

Figure 6. Mean surface temperature at ignition.

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limited data do not warrant any conclusions on the dependence of ignition temperatures with oxygen pressure.

Conclusions

The conclusions given below are based upon a bulk specimen, i.e., low surface to volume ratio, undergoing nonuniform heating. The upper surface of the specimen, where ignition occurs, was freely radiating. Experiments carried out on high surface to volume materials, i.e., powders or small particles, or under uniform heating conditions may give different ignition data and thus change or modify the conclusions.

Aluminum 6061

1. For a heated undisturbed surface:

    a. the ignition temperature was less than the melting point of aluminum oxide.

    b. the ignition temperature decreased with increasing oxygen pressure.

    c. the preignition and ignition sequence data indicated that several mechanisms were in the ignition sequence.

2. For a previously heated undisturbed oxidized surface, ignition could occur during cooling.

3. Conclusion 2 would imply that either a heated or a previously heated cooling disturbed surface could ignite at temperatures significantly below the undisturbed ignition temperature.

302 Stainless Steel

1. For a heated undisturbed surface, ignition occurred at temperatures equal to the melting point of ferrous oxide, 1650 K, or higher; but below the liquidus temperature.

2. For oxygen pressures up to 5.171 MPa (750 psia), unsupported combustion was not concurrent with ignition.

3. For a heated undisturbed surface, the ignition temperature range was independent of oxygen pressure beyond 0.345 MPa (50 psia) and up to 5.171 MPa (750 Psia), the present data limit.

Nickel Alloy NØ6625

1. For a heated undisturbed surface, ignition occurred within or beyond the alloy liquidus temperature.

2. For a heated undisturbed surface, unsupported combustion was not concurrent with ignition.

Acknowledgments