NBSIR 73-345

COMBUSTION OF METALS IN OXYGEN PHASE II: BULK BURNING EXPERIMENTS

Alan H. Tench
Hans M. Roder
Alan F. Clark

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

December 1973

Prepared for:
NASA-Marshall Space Flight Center
Astronautics Laboratory
Materials Division
Huntsville, Alabama 35812

NBSIR 73-345

COMBUSTION OF METALS IN OXYGEN PHASE II: BULK BURNING EXPERIMENTS

Alan H. Tench
Hans M. Roder
Alan F. Clark

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

December 1973

Prepared for:
NASA-Marshall Space Flight Center
Astronautics Laboratory
Materials Division
Huntsville, Alabama 35812

U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

This program was started to study combustion of the ordinary metals in oxygen, to provide information useful to designers of bulk oxygen handling equipment, particularly from the point of view of safety. We have studied the ignitability and combustability of carbon steels, stainless steels, aluminum alloys, titanium and copper metals, in oxygen atmospheres up to 60 psig. We encountered a violent reaction involving burning stainless steel and aluminum, a thermite reaction apparently, and have investigated this from a quantitative point of view. We have tried throughout to study the quantitative aspects of the combustion processes and related quenching effects. Ordinary steel and stainless steel burn quite readily at these low oxygen pressures, and the stainless steel-aluminum reaction produces intense heat with severe damage to neighboring structures. We are at the stage where further investigations could be carried out quite expeditiously and on a sound statistical basis.

Key Words: alloys; aluminum; combustion; ignition; oxygen; safety; stainless steel; steel; titanium.

1. INTRODUCTION

The burning of structural metals in oxygen is of interest to the industrial, medical, aerospace and defense fields. Sufficient understanding of the basics of metal combustion might have prevented such tragic oxygen accidents as those in the Apollo program and at the Brooklyn Memorial Hospital. To better understand the fundamentals of the heterogeneous metal combustion process, we are presently engaged in a research program "Combustion of Metals in Oxygen". This program is sponsored by NASA-Marshall Space Flight Center under Contract H92145A with Mr. John G. Austin as project monitor. The program was to be conducted in two phases. Research conducted under Phase I is reported in References [1], [2] and [3]. Phase II includes three parts:

1. Effects of bulk shape, mass and surface on combustion;
2. Ignition theory for minimum size and temperature for spot ignition;
3. Electron behavior in metal combustion.

The present report summarizes the progress on Part 1 of Phase II, which was the only part of Phase II initiated and funded. A sustained effort for this part of the program has been under way only since July 1973.

1.1 Goals

(i) Documentation of Bulk Burning Behavior. Firstly, we would seek simple information, describable in terms of direct visual observations. For instance, we found that 304L stainless steel, if brought to its melting point *and* allowed to spread out in a layer not more than 1/4 inch thick on a poorly conducting surface, would burn to completion *if* the oxygen pressure was over 50 psig. This was determined by simple observation, with no special apparatus.

e.g., remote high temperature thermometers. Thus, we sought to study effects of mass, shape, surface state, orientation, oxygen pressure, temperature, and flow of the metal on the combustion process.

(ii) Interpretation of results. This would proceed in two directions. First, we would try to set up a sound statistical basis for the above observations, in particular, since they were often of the Yes or No sort, e.g., did a complete burn take place, or did it not? Then, by least squares methods, we would try to get equations to fit the processes and to define suitable parameters. Second, we would use an analytical approach, to study the oxides produced on burning. Most metals have more than one oxide and apparently several may be in existence at any one time in the burning process. X-ray diffraction methods would be used in this connection. Phase I of this project has devoted considerably sophisticated efforts to a direct understanding of the metal combustion process by spectroscopic and other analytic methods, but we did not anticipate using these in Phase II.

(iii) Application of results to safety procedures. We would seek to study those factors which were rate-limiting to the combustion process and, in particular, exerted a pronounced quenching effect.

1.2 Experimental Procedures

(i) Large quantities (of the order of 100g) of metals would be used, of different sorts, with both gaseous oxygen and liquid oxygen as potential oxidizers. Low oxygen pressures (100 psig or less) were to be used, and ignition was to be promoted by supplying considerable quantities of heat to the metals.

(ii) Observations were to be largely visual, hence, of a simple sort, largely to determine the overall nature of the combustion that took place. Repeatability of the experiments was to be emphasized.

(iii) The dangerous nature of the experiments was realized, and they were to be carried out on a special safety site, already available at NBS, Boulder. Remote control and monitoring of the experiments was to be carried out.

The experiments conducted so far have been straightforward, and can be repeated readily, to allow for an adequate statistical interpretation. Efforts have been made all along to achieve speed and efficiency of operation, to allow a large number of experiments to be carried out. We are to the stage now where, with a few small modifications, we could run routinely several burns per day (8 or so) and could carry out quite searching investigations into various aspects of metal combustion, e.g., oxygen pressure dependence, quenching effects, effects of different geometries, and reactions between various metals (in particular, the stainless steel-aluminum reaction we encountered, which is a violent and dangerous sort of event) all with an adequate statistical basis and capable of a valid statistical interpretation.

The remainder of this report is in four sections, as follows:

(i) Description of apparatus,
(ii) Experimental procedures,
(iii) Description and assessment of results, and
(iv) Recommendations for future work.

2. DESCRIPTION OF THE APPARATUS

The apparatus consists of two parts, plus the recording equipment. (i) the combustion chamber, to contain the metal sample to be ignited in a controlled atmosphere. It is termed also the tank or the vessel.

(ii) the ignition apparatus, a radio frequency induction heater, to heat the metal sample to ignition temperature.

2.1 The Combustion Chamber

This is a stainless steel pressure vessel, shown in Figure 1. It is cylindrical, with capped ends, approximately 5 feet in diameter by 5 feet in height, and of approximately 1200 liters capacity. The walls are of 1/4 in thick 347 stainless steel plate, with welded seams. It was made here at NBS, Boulder, a number of years ago, to carry out hydrogen-oxygen explosion experiments. Standard ASME calculations show it to have a safe working pressure of 115 psig, and we anticipate using it to oxygen pressures of 100 psig. However, we were able to obtain sufficiently interesting results at 60 psig, and have not yet operated over that pressure.

Four observation ports are attached to the sides of the vessel. They are fitted with plexiglass windows, allowing a view of the center of the vessel. A larger single port is present at the top of the vessel, closed by a 1/2 in thick SS flange, and at first we operated through these five ports. This proved inconvenient, so that after the incident which necessitated major repairs, we had a large port (10 in x 18 in) welded into the side, giving good access to the interior. A bolt-on door was made to cover this port of 3/4 in 6061 aluminum with an 0-ring groove milled in it and secured by 5/16 in cap bolts (22 in number).

A sixth port was present, originally, at the bottom of the vessel. It received the 1 in diameter filling and evacuation line and incorporated a rupture disc safety valve. This port was destroyed in the incident mentioned and was then welded shut with only a 1 in drain plug in its place.

2.2 Valving and Gas Controls

The schematic is shown in Figure 2. Filling and evacuation are carried out through a 1 in diameter line entering at the top port. This

Figure 1. The Combustion Chamber

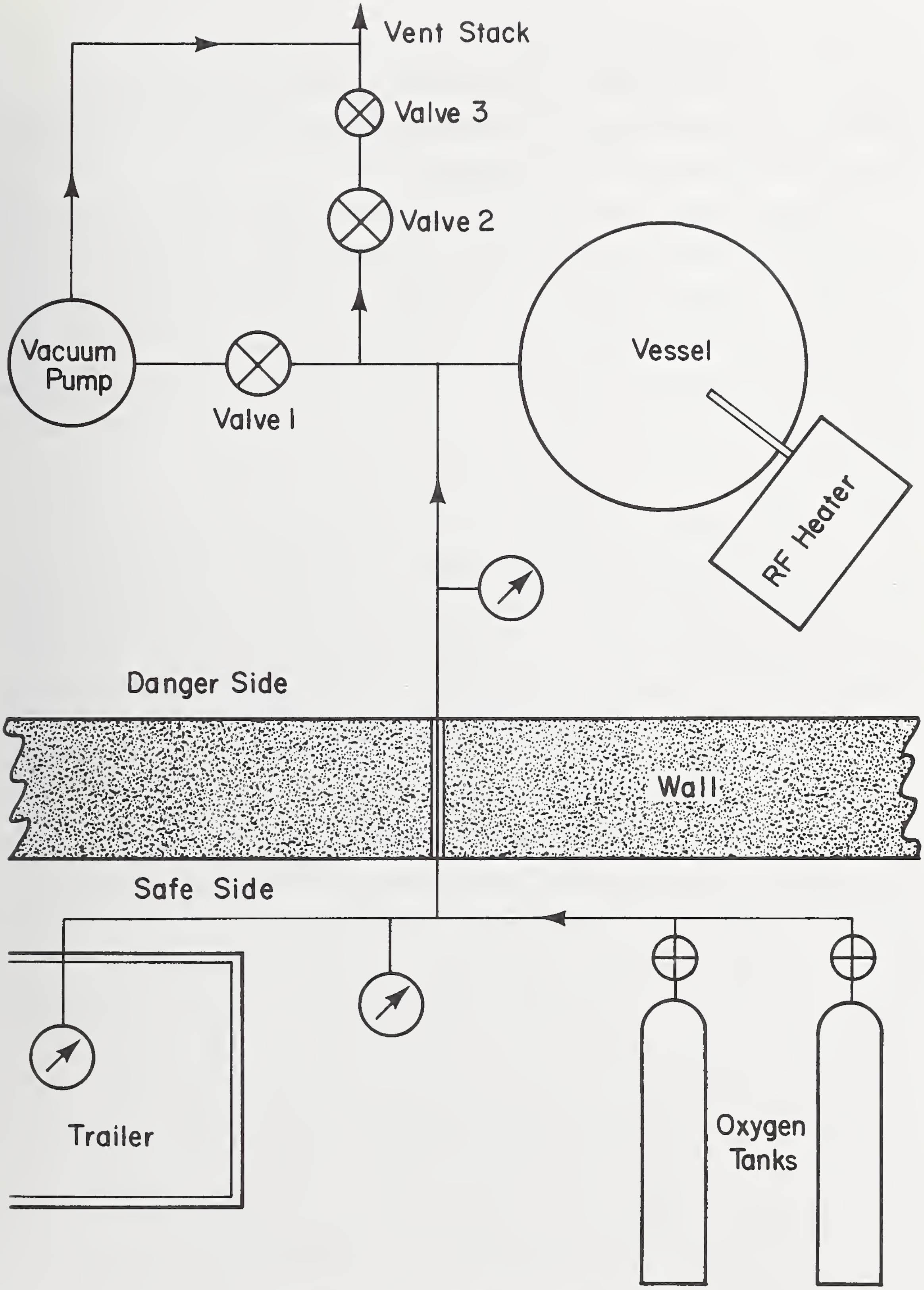

Figure 2. The Experimental Layout

line leads to (i) the vacuum pump to evacuate the vessel, (ii) to the oxygen or other gas bottles, and (iii) to the vent line to relieve the vessel pressure to atmospheric. Also, it supports the safety valve and provides access for the pressure gauges.

Three working valves are present. The vacuum valve is energized to open the line from the vacuum pump to the vessel; this valve is opened only when the vacuum pump is operating to evacuate the vessel. The vent valve is placed between the vessel and the atmosphere and is designed (a) to hold up to 100 psig of oxygen in the vessel and (b) to open under this pressure when its solenoid is energized. This vent will not hold a vacuum in the vessel against atmospheric pressure so that a hold valve is provided between the vent valve and the atmosphere which automatically closes when vessel pressure drops below atmospheric. This hold valve is not energized and opens automatically when the vent valve is open and the vessel pressure is above atmospheric. All three of these valve are either of all-metal or of PTFE-metal construction to comply with oxygen compatability requirements.

2.3 The Experimental Site

The vessel is installed behind a safety wall on a special site at NBS, Boulder, built to conduct potentially explosive experiments (especially where large quantities of liquid gases are used). The layout is shown in Figure 2. The wall is of 12 in thick reinforced concrete with sidewings to direct a potential blast towards a nearby uninhabited hillside. Small ports are present in the wall near ground level for control wires and pipelines to pass through to enable the experiments to be controlled and monitored from the safe side of the wall.

A trailer is present on the safe side and is used as headquarters and operating location when experiments are being actually run. Oxygen and nitrogen bottles are located on the safe side of the wall and a feedline runs through to the vessel. The vessel stands on a concrete pad and is covered by a porch-style roof but otherwise is open to the elements and is operated at outdoor temperature. The vacuum pump and the three working valves are on the unsafe side where they were placed originally, but eventually we would move these to the safe side (see Section 5. 3).

2. 4 The Ignition System

The metal samples require some means to ignite them; to date we have used exclusively a radio frequency induction heater. The requirements for ignition are that it be clean (non-contaminating), efficient (rapid heating) and consistent. We have contemplated using other means of ignition, e. g., chemical (thermite) or direct current heating and may eventually do so, but to date the RF heating has given good results and meets these three requirements. The heater is a commercial item already available at NBS, Boulder, operating at 690kc and capable of delivering up to 3000 watts of power. It is a simple, rugged device, water cooled and operating on 220 VAC and has worked well. The main difficulty encountered has been that it was designed for short range work, i. e., the sample to be heated is supposed to be only a few inches from the heater. Since we place the samples in the center of the vessel (approximately 5 feet in diameter), we had to design some sort of transmission line to conduct power from the RF generator to the sample a distance of 30 in or so. At first we tried parallel lines, but these (made of 1/4 in diameter copper tubing) proved inefficient and there was considerable power loss. Eventually we moved to a coaxial line made from two lengths of copper tubing (regular hard copper plumbing line), one piece inside the other but separated to provide insulation. At first the line was built for minimum impedance (the outside diameter of the inside tube was as close as possible to the inside diameter of the outside tube). However, later studies indicate that minimum impedance is not desirable for maximum power transmission and that the two diameters above should be in the ratio of 1.65 to 1 rather than 1 to 1. With this in view, we have designed and partly built a bigger transmission line which should be more efficient and moreover more trouble free, since the present line is subject to shorting out due to the closeness of the inner and outer tubes.

The sample to be heated is placed within the turns of a wound coil connected to the terminals of the RF generator. Water circulates through this coil for cooling purposes (otherwise the coil, too, becomes heated and will eventually melt). Coils are easily made from soft copper tubing, and we settled on 3/16 in diameter soft copper tubing as being generally suitable. With standard tubing connectors, these coils are readily mounted and demounted on the end of the transmission line.

For maximum coupling to the sample, the coil should be as closely invested to the sample as possible without actual physical contact (this latter results in short circuiting the turns of the coil with reduced coupling). It is an easy matter to wrap coils for each size and shape of sample using the sample itself as a mandrel if need be.

The amount of power generated by the heater is controlled by a rheostat, hand operated and originally mounted on the heater itself. This rheostat was demounted and reconnected to the heater by a transmission cord so that the power output could be controlled at some distance from the heater, in particular from the safe side of the blast wall. This allowed the heater to be set up and energized (but with zero output) at the unsafe side of the blast wall where it is located next to the vessel, and then powered up from the safe side of the wall to start the experiment.

The coaxial transmission line enters the vessel through a hole drilled in the plexiglass window of one of the observation ports, and the generator is placed alongside the vessel.

3. EXPERIMENTAL PROCEDURE

We have been much concerned with the safety aspects of this work, and Appendix A contains an account of the procedures approved by the Cryogenics Division Safety Committee and of the general requirements to be met in this respect. The incident described in Section 4 showed the strong advisability of taking all reasonable safety measures.

3.1 General

The sample to be ignited is placed within the coil either supported below on a platform or wrapped with two turns or so of asbestos paper and put into the coil to make a push fit held by friction but not in electrical contact with the coil. This latter procedure was used for all stainless steel samples where it worked well. These SS samples appear to heat uniformly and to melt almost all at once so that they drop in a mass from the coil in a consistent way. We were not anxious to use a potentially contaminating agent, such as the asbestos paper, but apparently it has little effect in the sort of experiments tried so far and has proven to be convenient and effective. Projected experiments include an investigation of the possible contaminating effects of this method.

Ordinary steel samples (1020 and 1075) proved harder to handle with respect to ignition using the RF heater. They tend to swell and buckle on heating, contacting the coil, resulting in short circuiting and a direct cooling, since the coils are made of water cooled copper tubing. We have not been able to attain the consistency of ignition with these ordinary steels that we have with the stainless steels, even though these ordinary steels burn much more readily when once ignited.

After placing the sample in the coil, the heater is switched on but not yet powered up. The vessel is sealed and the vacuum pump started to evacuate the vessel. No effort is made to attain a high vacuum, and usually we run the pump till the gauges show a reading around 25 in Hg below atmospheric. At our altitude (5400 feet above sea level), atmospheric pressure is about 26 in Hg. Our aim at this early stage of the project is merely to remove most of the ambient atmosphere so that subsequent filling gives a reasonably pure atmosphere of oxygen. On attaining a suitable vacuum, the pump is shut off and the RF heater is powered up momentarily to see that it is working properly as judged by the plate current reading on the power tube.

We move then to the safe side of the blast wall and open the gas valve(s) between the oxygen cylinders and the vessel. These valves are regular gas bottle reduction valves as used on welding kits and are used to fill the vessel to the desired pressure.

Heating power is then applied to the sample by operating the rheostat described in Section 1 on the safe side of the wall. The experiment is observed by means of TV cameras described in 3.2. When the sample is heated adequately, the RF power is turned down and the burn allowed to proceed spontaneously.

On completion of the experiment, the vent valve solenoid is energized to allow vessel pressure to fall to atmospheric. We then go around the wall, switch off the heater and open a port to allow the atmosphere into the vessel. The solid combustion products are recovered and the operation is complete.

3.2 Visual Monitoring

For safety reasons we retire to the safe side of the wall whenever there is substantial pressure of oxygen in the vessel (a. 20 psig) and an attempt is made to ignite a sample. Accordingly, to observe the processes, we use TV cameras aimed through the observation ports. One is connected directly to a commercial TV set on the safe side of the wall and is used for observations during the actual experiment. The other is used as a recording camera to record results on video tape and has been a great asset, since replays of the events are possible and it is inexpensive to operate.

Also, we use movie cameras (B&W and color) which, with their superior resolution, are of great aid in studying the burning processes.

3.3 Liquid Oxygen Procedure

It is our intention to study the effects of liquid oxygen on metal burning processes. Accordingly, we need some means of introducing a quantity of liquid oxygen into the vessel. In view of the dangers of handling liquid oxygen, we decided to liquefy oxygen within the vessel itself by passing liquid nitrogen through a cooling coil in the vessel when the latter is filled to about 20 psig of gaseous oxygen. A simple set-up was made with an inlet and outlet on the top flange for vacuum insulated lines. Liquid nitrogen is pumped through these to and from a 3/8 in diameter copper cooling coil of seven turns placed in the vessel. This results in rapid condensation of oxygen on the coil at rates on the order of one liter of liquid per minute.

We made two tries to collect sufficient liquid oxygen to permit dropping a burning piece of stainless steel therein. However, difficulties arose in the retention of the liquid, since it evaporated as soon as it dropped into the collection vessels (poorly insulated), and we were not able to reproducibly carry out the intended procedure. A special collection vessel is to be built as described later. The aim is to see which of two processes predominates - the quenching effect of the cold liquid or its oxidizing effect.

The above illustrates the technical difficulties in this sort of work. We have to cater to extremes of temperature, considerable variations of pressure, an oxygen atmosphere with strong sources of ignition, and the need to view the process at all times.

4. DESCRIPTION AND ASSESSMENT OF RESULTS

A summary of the burning experiments conducted is given in table 1, a picture of the typical samples is given in figure 3, while the remains after a typical burn are shown in figure 4. In the short time we have had the apparatus operating, our procedures have been determined by feasibility mostly, in regard to the ease of ignition of various metals. Using the RF heater as described, we found soon that the stainless steel samples were much the easiest to ignite in a consistent way, strange as this may seem. Although ordinary steels seem to ignite and burn more readily than stainless steels, they are considerably harder to get to ignition temperature when using the RF heater, as indicated in 3. 1. The stainless steels retain their original shape up to melting point where they seem to melt all at once. They are held in the coil by friction and on melting drop out of the coil in one slug, usually. In addition, these stainless steels seem to couple better with the RF heater and to heat quicker than the ordinary steel.

In view of the above, we studied the stainless steels almost exclusively for a while in order to obtain some valid results with the equipment on hand and also in view of the importance of stainless steels (hereafter also abbreviated as SS) in oxygen-handling equipment. In

Table 1. Summary of the Bulk Burning Experiments

MATERIAL	SAMPLE PARAMETERS			TEST PARAMETERS			REACTION PARAMETERS		
	Configuration	Typical Dimensions	Weight	No. of Tests	Ignition Method	Oxygen Pressure minimum to sustain burn maximum used	Burn?	Reaction Severity	Quenching weight for 100g of burning SS
mild steel 1020, 1075	octagonal rod plate	3/4 x 1/4, 1/2, 1, 1-3/4, 2, 3-1/8"	3" ~185g	20 0	Induction coil	7 psig 60 psig	Yes (expect-yes)	mild	not established
stainless steel 304, 347, 316	round rod plate	1 x 1", 3 1/8 x 4-1/2 x 3-3/8	1 ~102g 235g · 100g SS	30 1	Induction coil burning SS	30 psig 50% 50 psig 90% 60 psig 100%	Yes Yes	mild vigorous	>235g
Al-alloy 6060, 5052	round rod plate	3/4 x 1", 3" 1/8, 3/16, 1/4, 1" x 4" x 4"	1 ~20g 1/4" plate ~183g + 100g SS^5	2 10	Induction coil burning SS	not established^1 60 psig	No - melts Yes	extremely severe	>183g, but <745g
Ti-alloy 5 Al-2. 5 Sn	round rod plate	1-1/8" x 1/2, 1 1/8" x 5" x 5"	1/2 ~38g^3 217g : 100g SS	2 1	Induction coil burning SS	30 psig^4 60 psig	Yes Yes	severe severe	>217g
Brass - Cu	round rod plate	1" x 1" 1/8 x 3-1/2" x 5-1/2	1 ~108g 350g · 100g SS	3 1	Induction coil burning SS		No - melts No - quench^5		<350g

[1] Used 60 psig to insure burning of SS ignition slug. Expect that lower pressures will suffice with different ignition method.
[2] In several very hot reactions (thermite^2) the RF coil melted ~85g of Cu. Remains show evidence of the copper having burned as well.
[3] For the 1" length, the applied power was insufficient to melt the specimen.
[4] Lower values not tried, expect 1 atm to be sufficient.
[5] No burn, see however 2.

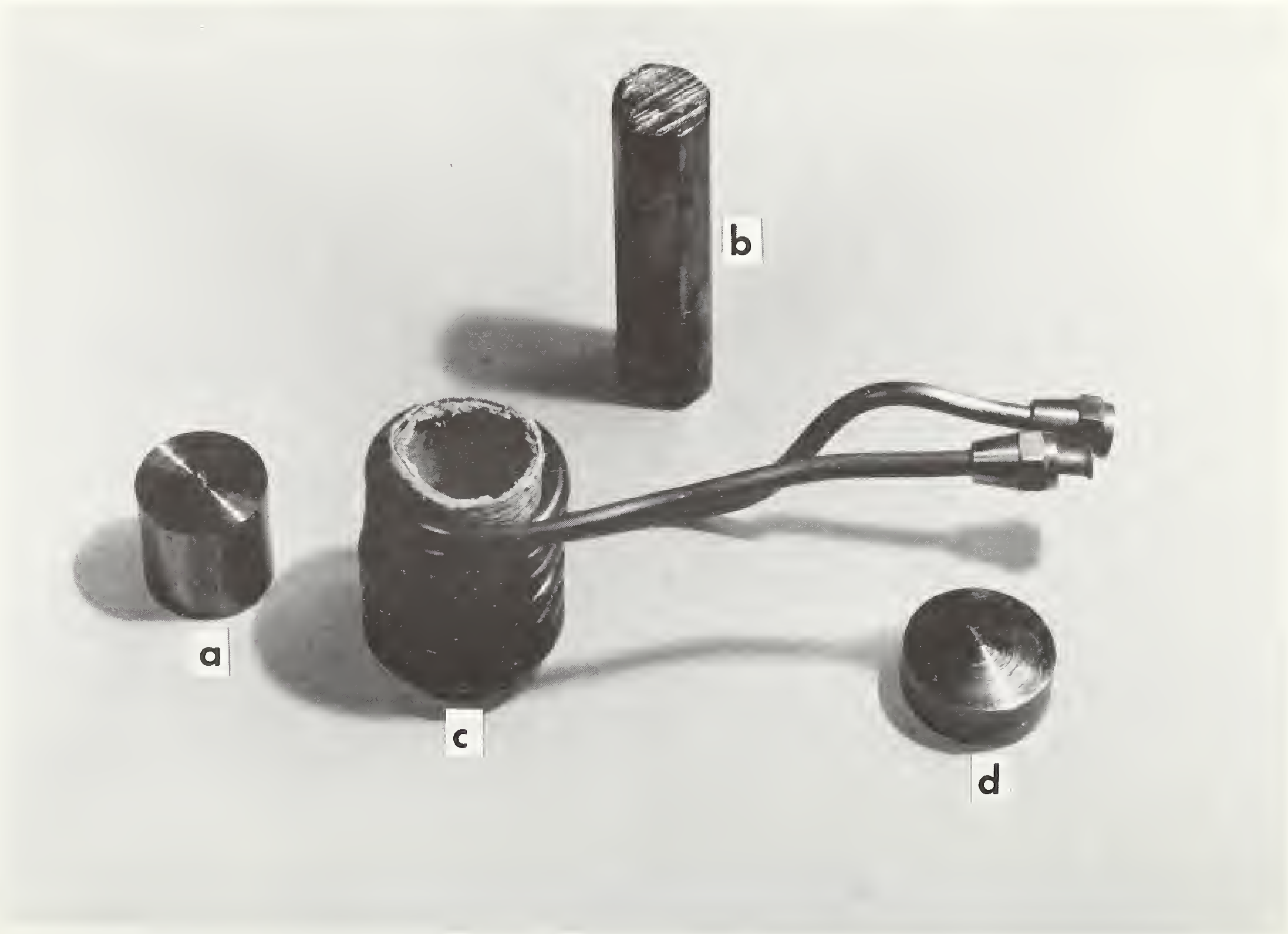

Figure 3. Typical Samples. a) Stainless Steel Slug 1 in, b) Octagonal Mild Steel 1075 3/4 in, c) Copper Coil with Stainless Steel and Asbestos, and d) Ti Rod 1-1/8 in.

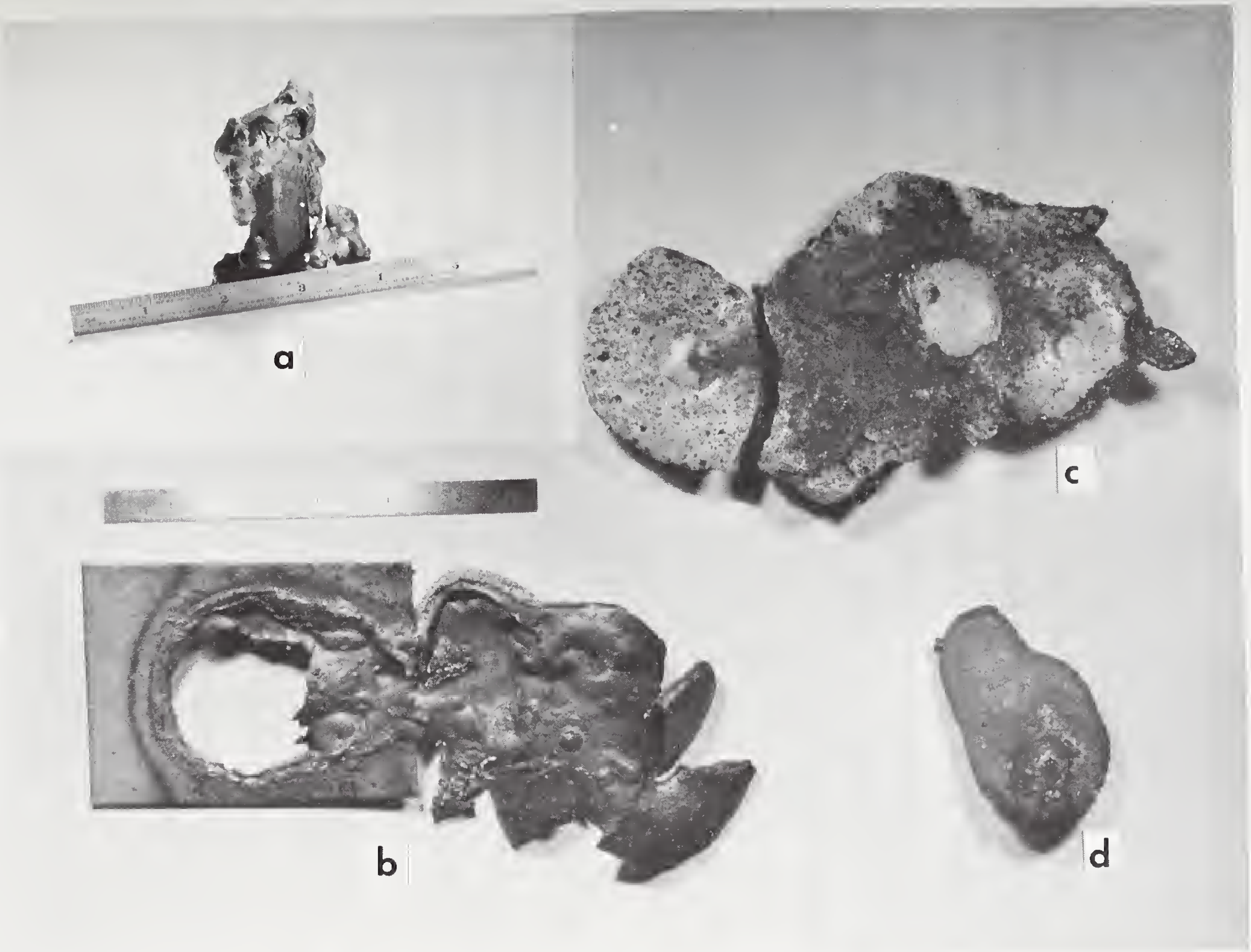

Figure 4. Typical Reminas After a Burn. a) "Candle" of Mild Steel, b) Stainless Steel Slug Dropped onto Stainless Plate, c) Stainless Steel Slug Dropped onto Aluminum Plate, Remains Include Copper Cooling Coil. d) Stainless Steel Slug Dropped onto Titanium Plate.

the course of this work, we encountered what is apparently a thermite reaction (see Appendix B), in which there is a violent reaction between SS and aluminum.

4.1 Stainless Steel Experiments

The material used was 1 in diameter 304L stainless steel rod cut into 1 in lengths to give a sample weight of 100-103 g. This is a true stainless steel, a low carbon steel (0.03% C) with nominally 19% Chromium and 10% Nickel. It is used primarily for its high corrosion resistance and not for any particular properties of strength or hardness as in the case of high carbon chromium steels, e.g., 336 or 338. It is one of the stainless steels commonly used in scientific apparatus, oxygen systems, and structural work.

These SS samples were wrapped in asbestos paper and pushed into a six or seven turn coil of 3/16 in diameter copper tubing so that the ends of the cylindrical sample were even with the ends of the coil. With the RF generator operating at full power (nominally 3000 watts) these samples would melt in about 100 seconds and then fall, ignited, out of the coil almost completely. At the end of the burn, there were usually a few grams of oxidized metal left adhering to the asbestos wrapping in the coil, so we assume that at least 95g of the original sample had melted out of the coil and had come into good contact with the oxygen present.

Since the experiments were viewed on the TV camera, we could get a fair idea of how fiercely the sample burned and for how long. More difficult to determine was the amount of burnt material produced and the amount of unburnt material left. Considerable smoke was produced on burning resulting in deposition of a film of powdered oxide over the interior of the vessel, and there seems to be no easy way to collect this for weighing or other analysis. The same problem was evident when spattering occurred. This is part of the general problem of containing burning metal. A highly refractory material is required which will not shatter on sudden contact with the molten mass and which will not provide a significant quenching effect. We settled for sand trays, but these were not ideal since sand was incorporated in the burning mass. Sandstone slabs were tried, but they cracked and let the burning metal fall through. We intend to look into high performance ceramics (of the rocket nose-cone type).

Thus, our initial experiments with SS 304L consisted of dropping burning slugs on to a sandbath, in various pressures of oxygen from 1/2 atmosphere to 60 psig. In no case did we seem to get ignition before melting. As far as could be determined by visual inspection of the process by TV monitor, sustained burning occurred only after the sample melted and fell from the coil. About 20 samples were treated in this way, and, although no statistical treatment has been attempted, we have reached the following tentative conclusions:

(i) Sustained burning will not occur generally below 50 psig of oxygen. Below this pressure, it was usual for the sample, on hitting the sandbath, to burn on its surface for a short while (seconds rather than minutes) and then extinguish. The remains contained a large contiguous mass of metal, apparently only remelted stainless steel. The lower surface, where it had rested on the sand tray, was usually quite bright and of metallic appearance. The upper surface was usually covered with a layer of dark oxide of variable thickness. The samples tended to remain in one piece and were weighed after trying to scrape off the adhering sand and adding the small amount of oxide adhering to the coil. Most samples showed small weight gain, e. g., they went from 102 g to 108 g (note that we lost oxide in the form of smoke, but we do not believe these losses to be large). Accordingly, we conclude that molten SS 304L will not burn readily below 50 psig of oxygen.

(ii) Above 50 psig of oxygen sustained burning will generally take place if the molten sample is allowed to spread out and form a fairly thin layer. When dropped on to the sand bath, the dense molten metal (density around 8 g/cc) tended to form a depression in the sand resulting in its containment in a mass of small surface area with a resultant suppression of burning. However, if it fell so that it spread out fairly evenly over about 15 square inches, then there was complete burning, apparently, to judge by the absence of particles of metal visible to the naked eye. The product was dark colored and quite brittle, being easily broken by hand. Masses of up to 190 g were obtained this way, although these contained an undetermined amount of sand believed to be small. Thus, above 50 psig of oxygen, complete oxidation of molten SS 304L will occur if adequate exposure to the oxygen is allowed.

Where the sample formed a depression in the sand and failed to spread out and burn to completion, we noted a consistent phenomenon during burning. One or more spark showers would occur during burning in the form of spattering from some location in the mass. These showers lasted for a minute or so. On examining the burnt sample afterwards, we found associated with the location of the shower, a piece of unburnt metal of a spheriodal shape embedded in the oxide layer. Apparently, it had been molten but had not burnt due to the formation of a thick layer of oxide (ca 1.0 cm) around it. These unburnt residues varied in weight from 2 g to 70 g. Their surface was smooth and bright, and they seemed to be unoxidized stainless steel.

Complete burning took about 3-4 minutes. Little change in oxygen pressure was seen as judged by inspection of the pressure gauges during burning, and there seemed to be no great rise in temperature within the vessel as judged by its surface temperature at the end of the experiment. Where spark showers occurred, they seemed to happen towards the end of the burn, and where more than one occurred, they usually were not simultaneous. Presumably, there was a build-up of the oxide layer followed by sudden rupturing.

4.2 Quenching Experiments

In view of the above conclusions that we could get consistent burning at 60 psig of oxygen where the 304L sample was allowed to spread out, we investigated the effects of allowing the sample to fall on to a metal plate to see whether this plate would conduct away heat at such a rate as to retard the burning, i. e., to quench the sample.

The first series of tests involved a plate of 6061 type aluminum. This alloy has nominal composition 1.0% Mg, 0.2% Cu, 0.2% Cr, and 0.6% Si. It is designed for general construction purposes where good corrosion resistance is needed and is much used in truck body construction. The plate had dimensions 4 in x 4 in x 1/4 in and weighed 183 g. It was placed on a sandbath about 1 in below the SS 304L sample (1 in x 1 in, weight approximately 103 gms, as before). The SS sample was ignited as previously by RF heating and fell out of the coil on to the plate. Oxygen pressure was maintained at 60 psig in all of these trials.

The first three runs were made all with the same plate and in each case there seemed to be substantial quenching, especially when the SS fell squarely on to the plate and did not flow on to the sand. In one case, the sample gained only 2 g in weight, in another 9 g, and in the third case 23 g where there had been considerable flow off the plate. The plate was little affected either in shape or weight, and the SS samples were pried off easily.

The above runs seemed a good indication that the shape and weight of aluminum involved would quench adequately the shape and weight of SS 304L involved at 60 psig of oxygen. In this sort of Yes <u>or</u> No test, a trial on three samples often is considered statistically valid. However, we decided to run a test on a total of 5 samples, i. e., two more after the above three. The fourth sample behaved in quite a different way to the first three.

Tank Incident. (Fourth Sample) This trial was conducted in the same way as above at 60 psig of oxygen. The SS sample melted and dropped on the plate in the usual way. As seen on the TV monitor, there was a short pause with little burning activity. Suddenly, there was a resumption of burning and molten metal streamed off the supporting platform on to the bottom of the tank where it burned a hole (c. 15cm by 20cm), releasing the oxygen violently and incapacitating the vessel completely. Burning continued on the platform for some time after the pressure dropped. On going around to the tank, we saw that there had been considerable destruction in and around the bottom port with the fill and gauge lines in considerable disarray. The photographs (figures 5 and 6) give an indication of the damage.

Previous to this, we had one SS sample which had fallen directly on to the sand tray in 60 psig of oxygen but had run towards the side of the 1/32 in thick copper tray, melted a hole therein, burned a hole in the supporting aluminum platform (1/8 in thick plate) and had fallen on to the bottom of the vessel but with no untoward results (see figure 7). Quenching had been rapid, and we could easily pry the sample remains off the wall of the vessel. Apparently, in the case of the tank incident, there had been a thermite reaction (iron oxides reacting with aluminum metal to give iron plus aluminum oxides) which is known to be violent.

After repairing the tank, we were able to repeat this SS-Al type of reaction and record it on TV and color film. In one trial, a SS sample was dropped onto an aluminum plate 4 in x 4 in x 3/16 in thick, resulting in a vigorous reaction at 50 psig of oxygen. During this, tank pressure

Figure 5. Sample Tray, Tank Accident

Figure 6. Bottom Port View, Tank Accident

Figure 7. Copper Sand Tray SS Melt

rose to 55 psig, and the tank became quite warm to the touch. The copper RF heating coil was melted completely during this burn. Note that this coil is water cooled. There was evidence (red material present in the residue) of copper oxidation.

A second burn using an aluminum plate 5 in x 5 in x 1/8 in (weight 139 g) at 60 psig of oxygen again resulted in a vigorous reaction, recorded on color film.

Other burns, where the plates were bigger than the three above or where the oxygen pressure was reduced, showed good quenching.

At 30 psig of oxygen, a SS sample was completely quenched when dropped onto an aluminum plate 6 in x 6 in x 3/16 in. The plate showed only slight effects. At 60 psig of oxygen, an aluminum plate 6-1/8 in x 2-3/4 in x 1 in also gave complete quenching. In these cases, the SS sample showed little burning activity after it cleared the coil. On hitting the plate, it cooled and solidified rapidly with a thin layer of oxide on the upper surface and with the lower surface (in contact with the plate) quite bright and metallic appearing.

A similar result occurred when a <u>copper</u> plate was used. This plate was 3-1/2 in x 5-1/2 in x 1/8 in (weight 350 g), and quenching was thorough.

A 316 SS plate 4-1/2 in x 3-3/8 in x 1/8 in (weight 235 g) was partly burned when a SS 304L sample was dropped onto it at 60 psig of oxygen. The outer portions of the plate remain intact, but the center portion appeared to be completely oxidized. The molten part of the plate and the ignition slug flowed away from the rest of the plate before the entire plate could melt and burn. It appears that stainless steels need a great deal of heat supplied to them before they will burn vigorously at 60 psig of oxygen. It is a matter of great interest to determine what oxygen pressure will sustain burning of SS to which no heat otherwise has been supplied. For instance, if a SS plate at room temperature is suddenly ignited in one spot, what oxygen pressure is needed to sustain the burning of the plate to completion?

We conclude that the Fe-Al reaction is reproducible _if_ we have oxygen pressure of 60 psig or more _and if_ the aluminum plate is not over 3/16 in thick. A quantitative description of all of our Fe-Al experiments is given in figure 8.

A rough estimate shows that 100 g of SS cooled from melting point (c 1250°C) to 650°C (aluminum melting point) would yield 12,500 calories. To melt _200 g_ of aluminum, starting from room temperature, requires about 20,000 calories. It would be worthwhile to continue these Fe-Al reactions to investigate the mass dependence, i.e., is there a maximum mass of aluminum beyond which a fixed mass of burning SS will not cause ignition? The dependence on oxygen pressure would be of interest, too.

4.3 Combustion Studies on Aluminum, Ordinary Carbon Steels and Titanium

Aluminum. Cylindrical aluminum slugs were treated in the same way as the SS samples, being wrapped in asbestos paper and heated in the RF coil. They heated well, melting quickly and flowing out of the coil in one piece. However, even at 60 psig of oxygen, there was negligible oxidation, the molten mass merely solidifying to a normal appearing form of the metal. This result is not suprising since the ignition temperature for Al is considerably higher than its melting temperature, see table 2.

Ordinary Carbon Steels. As indicated previously, these steels appeared to ignite and burn readily but did not couple with the RF heater as well as the SS samples, and moreover were liable to swell and buckle so that the coils of the heater were shorted out, allowing the samples to

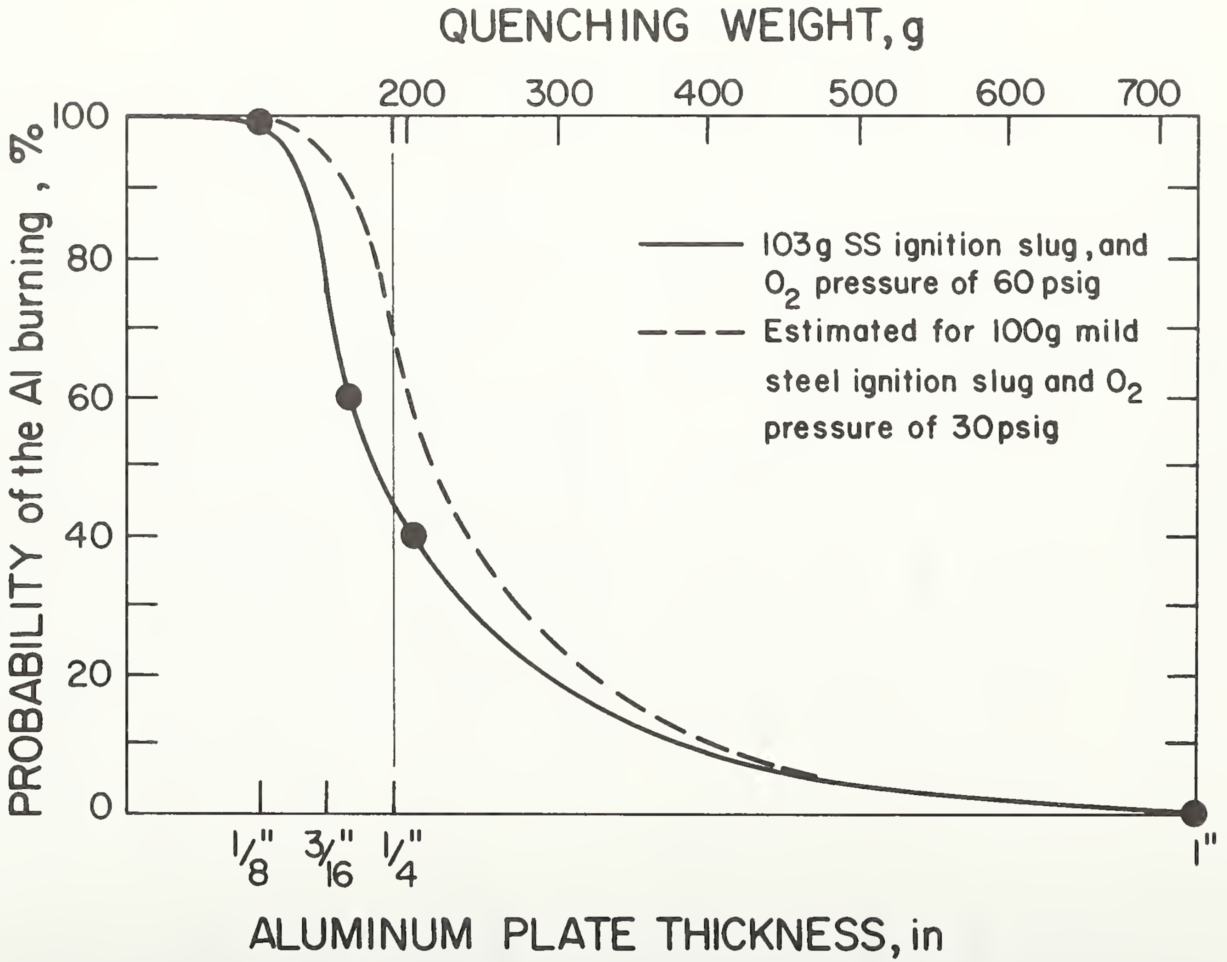

Figure 8. Quenching of the Fe-Al Reaction.

TABLE 2 - 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/cm K)	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]	
Non Metals									
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] This table taken from reference 4

[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.

quench. Some samples did burn, however, and one, a 3 in length of 7/8 in diameter 1075 rod, burned apparently to completion in less than 1/2 atmosphere of oxygen. This was recorded on black and white film (movie) and is impressive in the steady way in which combustion proceeds rather like a candle burning in air. To study combustion of these kinds of steels will require a different means of ignition unless we increase oxygen pressure to where the sample will sustain burning in the early stages of heating, thus obviating the need for further RF heating. We should bear in mind that the coils of the RF heater are water cooled so that any metal touching them will receive a severe quenching. We tried the asbestos paper procedure with these steels, but their swelling ruptured the paper leaving the metal in contact with the coils.

However, we have been able to appreciate that these steels are much easier to burn than the SS steels as may be expected if we regard corrosion as an oxidation process.

Titanium. Successful attempts were made to burn titanium metal. A 1-1/8 in diameter titanium rod was used; a 1 in length (weight 78 g) was wrapped in asbestos paper and treated in the same way as the SS 304L samples. Although this sample heated well, we were not able to ignite it or even to melt it under 30 psig of oxygen. A smaller piece (1-1/8 in diameter x 1/2 in length; weight 38 g) was treated in the same way at the same pressure with ignition and vigorous burning after only 30 seconds of RF power applied. Ignition seemed to take place in the coil with the flaming mass dropping out on to the sand bath and burning to form a considerable volume of oxide.

A titanium plate (Al 5%, Sn 2.5%; 5 in x 5 in x 1/8 in; weight 217 g) burned completely and vigorously when a SS sample was dropped onto it at 55 psig of oxygen. Pressure rose to 60 psig and considerable heat was produced. The SS and titanium both appeared to burn to completion with the titanium forming the characteristic layer of yellow titanium dioxide as in the laser burning studies of Phase I.

4.4 Liquid Oxygen Results

As indicated previously, we were able to liquefy oxygen in the vessel quite readily but did not have a suitable collection apparatus available to retain the liquid. An indication of a suitable set-up is given in Section 5.3, and we intend to drop burning SS samples into liquid oxygen at 60 psig of oxygen gas pressure to see whether quenching or enhanced burning occurs.

We did conduct two preliminary tests. In the first one, we used a 9 in diameter pyrex pie dish to collect the liquid oxygen. Burning of the SS sample must have been vigorous because spattering of molten, oxidized steel occurred all the way to the top interior part of the tank. The dish, of course, cracked; the iron oxide had melted through it all the way to the sand. In the second test, we used a polystyrene foam boat lined with Al-foil to contain the liquid oxygen. A 3 in copper disk about 1/8 in thick was placed to prevent the steel from penetrating the plastic foam on contact. The reaction again was vigorous. The copper disk was severely oxidized on its top surface. The foam boat burned up completely and, as expected, gave rise to a rather large pressure increase. The Al foil was partially burned and partially melted.

4.5 TV and Filmed Records

1) Black and White movie, of a 3 in length of 7/8 in diameter 1075 steel rod burning in 1/2 atmosphere of oxygen. Shows a steady process rather like a candle burning. Length is 5 minutes.

2) Composite video tape of 10 burns, length 25 minutes. Includes the thermite reactions.

3) Color movie of an SS-Al thermite reaction. Length 2 minutes.

4.6 Conclusions - Rules of Thumb

1) Iron and iron alloys will burn readily at low pressures of oxygen (60 psig or so).

2) Regular stainless steel burns easily and well.

3) Stainless steel serves to ignite other metals, notably aluminum and titanium. Note: SS and Al combinations in oxygen systems may increase the danger considerably. The SS-Al reaction is particularly vicious.

4) We have not been able to get copper, aluminum, or brass to burn by themselves at 60 psig of oxygen.

5) Oxide formation hinders combustion. If oxide is allowed to accumulate around the burning metal, it exerts a smothering effect.

6) Thresholds exist both for combustion and quenching, e.g., oxygen pressure or mass of quenching agent. This aspect needs a thorough statistical exploration.

7) To get good combustion at 60 psig or less of oxygen, iron and iron alloys must be melted.

5. RECOMMENDATIONS FOR FUTURE WORK

We recommend that the bulk burning experiments be continued, since we are at the stage now where, with small alterations to the apparatus, we could run several burns per day (8 or so) and could carry out searching investigations into various aspects of metal combustion.

5.1 Specific Experiments to be Conducted

1) Burning of SS 304L up to 100 psig of oxygen. Run standard tests with oxygen pressure over 60 psig. In particular, determine whether we can obviate the incomplete burning where the metal slug does not spread out to form a thin layer.

2) SS-Al thermite reaction. Do a good statistical study of varying thicknesses of Al plate on the reaction. Try different Al alloys, e.g., the Al alloys used in aircraft parts, the high Mg alloys, etc., to see how these enhance or depress the thermite reaction.

3) Thermite reaction with ordinary steels. If what we have seen with SS-Al is indeed the thermite reaction, then it should proceed more readily with ordinary steels, since they produce iron oxides more rapidly (by burning more readily). We could study this thermite reaction at much lower oxygen pressures and see what effect is to be had from variable oxygen pressure.

4) Burning of Al plates in various orientations. Determine whether orientation, e.g., whether flat or upright, affects rate of burning of Al plate.

5) Burning of various Al alloys. In particular, determine whether Mg content affects burning behavior.

6) Determination of combustion temperatures. Use spectrograph or other means.

7) Study weight changes more accurately. Use refractory crucible.

8) Study liquid oxygen effects on burning metals. Drop burning metal into liquid oxygen (see 5.3 for details).

9) Extinguishing agents. Study effects of water, carbon granules, etc.,

10) Oxygen gas jets. Study effects of jets of oxygen gas on burning metals.

11) High alloy stainless steels. These steels, e.g., 25/21L (25% Cr, 21% Ni), have high corrosion resistance and, accordingly, should not burn as readily as 304L.

5.2 More General Investigations

1) Develop a reliable means of ignition for ordinary steels, so that we can conduct the same sort of experiments with them as with SS. We would try AC current heating here.

2) Chemical analysis of combustion products. In particular, determine amount of unburned metal left. This is not a simple problem. In the case of titanium in the laser assisted burning experiments, we found by X-ray diffraction (study of powder patterns) that a variety of oxides are present. A residual pellet of material progresses from unburned metal in the center to fully oxidized titanium dioxide on the surface. Other studies (see reference 5) show that titanium oxides have variable stochiometry explainable in terms of variable occupance of lattice sites by the oxygen atoms, giving small but significant changes in lattice parameters. Similar behavior is to be expected in the other metal oxides and is a whole field of study in itself. However, our first needs are simpler, and the first is to determine the amount of unburned metal present in any residue. With stainless steels, there are at least three metals present (Fe, Cr, and Ni) so that some multiple leaching process may be necessary (dilute acids and alkalis, cyanide solutions). This will be worked up on some known mixture, e.g., powdered SS metal and various amounts of the metal oxides, to find a simple reliable process to show how much metal has been burned. X-ray studies can then be used to show which oxides are present in crystalline form.

3) Define valid statistical procedures so that our results are more quantative.

4) Addition of other gases, e.g., N_2, Cl_2 or F_2 to see what effect these have on combustion.

5) Investigate effects of sand and asbestos. Do these act as fluxing agents and so affect the rate of combustion of metals? Other construction materials, e.g., insulations, may be investigated also.

5.3 Modifications to the Apparatus

Since the vessel has a safe working pressure of only 115 psia, we feel that no major developments can be carried out to increase the pressure range. However, there are minor modifications to be carried out to get speed and efficiency and to allow series of experiments to be done to afford a sound statistical basis for our conclusions.

1) Reduction in vessel capacity.

A reduction in the vessel capacity by at least one half would be an advantage to conserve oxygen and to reduce filling time. At first we planned to fill the lower half of the vessel with sand, but this would add great weight and due to the porosity of the sand would not reduce the capacity as desired. Our plan now is to use surplus fire extinguisher tanks (c. 2 gallons capacity) and to pack the space around them with sand. Original capacity can readily be restored if need be.

2) Alteration of the valving arrangement.

Metal oxide dust is produced in these burns and has a tendency to clog the valves, freezing them shut. We intend to replace the present solenoid-operated valves with hand-operated valves on the safe side of the blast wall. These will be metal-PTFE valves to preserve oxygen compatibility.

3) Access to the vessel.

The door of the 10 in x 18 in port will be hinged in place and closed by six clip-operated dogs to reduce the time needed to open and close the vessel.

4) Coaxial transmission line.

As indicated in Section 2.4, we have started construction of an improved coaxial RF transmission line (to carry power from the RF heater to the sample within the vessel). This is expected both to increase efficiency (of power transmission) and reliability (freedom from arcing out) of the ignition process.

5) Liquid oxygen collection apparatus.

We have had no difficulty in liquefying oxygen within the vessel but must find a good means of retaining the liquid before dropping molten metal into it. This will be done by using a fairly narrow deep SS dewar to collect the liquid. The condensing coil will be placed towards the periphery of the vessel, and an insulated funnel and delivery tube will be used to conduct the liquid to the dewar, as shown in figure 9.

6) Observation ports.

The present observation ports are inadequate, since they are tunnels about 4 in long with a 4 in diameter opening at the inner end. This restricts the view of the interior of the vessel as can be seen in our TV and movie recordings, where often it is not possible to record the whole scene as needed. We will reset the ports with the windows flush with the vessel wall instead of several inches away as at present.

To record the liquid oxygen experiments, we will install an observation port in the top of the vessel to look directly down into the liquid oxygen collection dewar. Suitable openings for this port are present in the flange already.

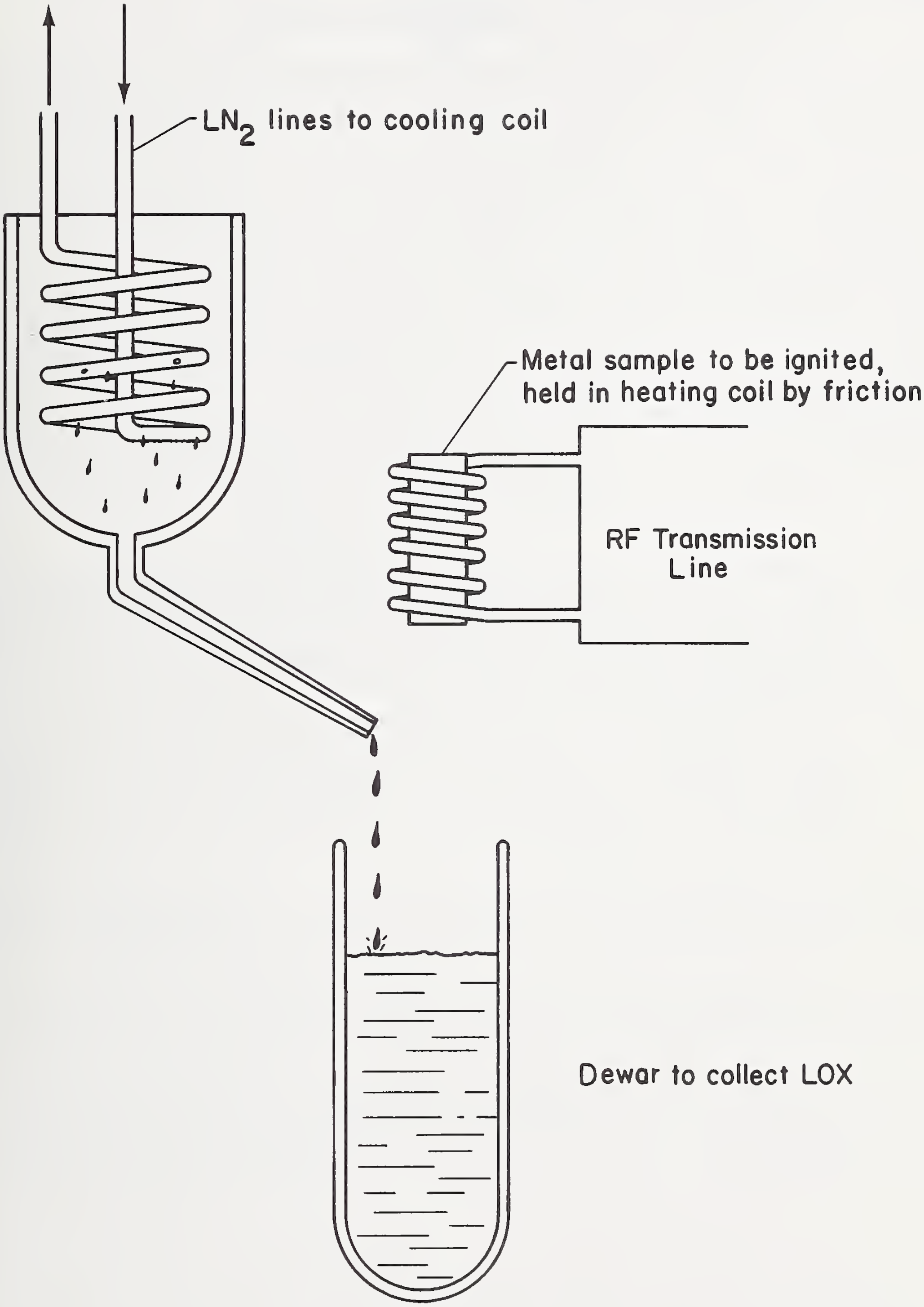

Figure 9. Liquid Oxygen Collection Apparatus

ACKNOWLEDGMENTS

We wish to express particular thanks to Mr. Larry L. Sparks and to Mr. John C. Moulder of this Division for their efforts on behalf of this project. Mr. Sparks was responsible for getting the project underway, in particular for developing the RF heating system and the oxygen liquefaction process, both of which were highly successful. Mr. Moulder was responsible for the success of the monitoring and recording systems, both TV and film, and his ready expertise in this and other regards is much appreciated. We are in debt to our project monitor Mr. John G. Austin for direction and valuable advice.

6. REFERENCES

[1] C. C. Runyan, J. C. Moulder, and A. F. Clark, Time-Resolved Spectra of Visible Radiation in Bulk Titanium Combustion, paper presented at 15th Annual Rocky Mountain Spectroscopy Conference, Denver (Aug. 1973).

[2] J. C. Moulder and A. F. Clark, Coherent Optical Filtering for Phase Contrast Photography in Combustion Research, paper presented at 15th Annual Rocky Mountain Spectroscopy Conference, Denver (Aug. 1973).

[3] C. C. Runyan, J. C. Moulder, and A. F. Clark, Time-Resolved Spectra of Bulk Titanium Combustion, to be published.

[4] A. F. Clark and J. G. Hust, A Review of the Compatibility of Structural Materials with Oxygen, to be published, AIAA Journal.

[5] S. Andersson, B. Collen, G. Krusse, U. Kuylensteirna, A. Magnéli, H. Pestmalis, and S. Asbrink, Acta Chem. Scand. 11, 1653 (1957).

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Boulder, Colorado 80302

Date : July 12, 1973

To : Alan H. Tench, 275.03

From : 275.06

Subject: Experimental Hazards Committee

Approval has been granted for the use of the metal combustion experimental apparatus with the following exceptions.

1. Establish a maximum working pressure of 100 psig on the experimental vessel.
2. Equip the vessel with a gas relief device which will prevent the pressure from exceeding 100 psig.
3. All personnel shall be behind the blast wall when the vessel is being pressurized with oxygen or when the oxygen in the vessel is being removed by means of a vacuum pump.

R. W. STOKES
Chairman, Experimental
Hazards Committee
Cryogenics Division
Institute for Basic Standards

cc: A. F. Schmidt, 275.00
J. E. Cruz, 275.06
J. M. Arvidson, 275.06
A. F. Clark, 275.03
G. C. Straty, 275.04

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Boulder, Colorado 80302

Date : July 10, 1973

To : Safety Committee, Cryogenics

From : Alan H. Tench, Metal Combustion Group

Subject: Request to conduct metal combustion experiments, using gaseous and liquid oxygen.

The proposed experiments are part of work being carried on in the Metal Combustion group, and are to be an extension of work already done therein.

There are two aims: (i) to study the burning of large quantities of metal (kilograms), and (ii) to study the effects of nitrogen on the combustion process. There is strong indication that nitrogen is necessary to cause spattering during combustion of certain metals, and this aspect is to be investigated in particular.

Accordingly, we need some container which will (i) provide a controlled atmosphere, e.g., pure oxygen, (ii) contain the combustion products for further analysis, and (iii) provide a measure of containment of potentially violent processes.

The proposed container for the experiments is now installed behind the North wing of the blast wall of the NBS Boulder facility where it is proposed to carry out the experiments. '

The container was furnished to us by R. O. Voth of Cryogenics and was used by him for hydrogen-oxygen explosion experiments. A diagram of his set-up is attached herewith. His calculations, based on ASME Handbook recommendations, show a safe working pressure of 115 psi (the safe pressure calculated on the basis of circumferential stress of the cylindrical portion). The side observation ports have 1/2" thick lucite windows which are calculated to have a safety factor of 2.9 at 100 psi, while the top cover plate plate of 1/2" thick stainless steel is calculated to have a safety factors of at least 3.0 at 100 psi.

The container has been tested to 60 psi (June 19, 1973), using nitrogen gas at ambient temperature. The test was to have been continued to 100 psi (in 10 psi steps), but a small plug in the teflon cap blew out due to being not tightened down properly. We intend to complete the test within the next few days.

Volume of container is calculated to be 1250 litres, and its weight about 1000 lbs.

Three (3) pressure gauges are connected to the container (one next to the container, one in the trailer, and one beside the gas tanks, on the safe side of the blast wall). A solenoid-operated pressure relief valve is in place in the vent line, and is operated manually from the trailer. Filling valves (between the gas tanks and the container) are also solenoid operated by a manual switch in the trailer. A vacuum pump is connected to the container to exhaust it prior to filling with the required gases. This pump has oxygen compatible oil, and the pressure relief valve is oxygen compatible also.

An ideal gas calculation on oxygen shows that if we burn one gram-molecular weight of Fe to FeO, and assume that the resultant heat is transferred at once to 40 moles of oxygen at a constant volume of 1000 litres initially at room temperature, then we can expect a temperature rise of 315° C with a corresponding pressure rise of approximately 15 psi. Accordingly, if we burn 50 gms or so of Fe in the container, initially filled with oxygen at atmospheric pressure and ambient temperature, we may expect no great increase in pressure but would have to consider temperature effects on the plexiglas, etc..

Plan of Operation

We intend to proceed cautiously (in view of the foregoing paragraph), and will start with gram quantities of metal at atmospheric pressure of oxygen or less. The metal will be ignited by RF (radio frequency) heating, which is introduced into the container by copper leads through the teflon cap in the top flange. These leads are already installed and tested, and we have heated a 10 gram sample of iron to a temperature considered sufficient to ignite it (1300° C) at 1 atmosphere of oxygen.

As a starting rule, we intend to retire to the safe side of the blast wall for any oxygen pressures above 15 psi over atmospheric. We intend not to exceed an oxygen pressure of 20 psi over atmospheric until the apparatus and procedures are thoroughly tested.

Degreasing of the container and all of its attached lines (including vent and gauge lines) has been carried out using a combination of washing (or flushing) with trichloroethane, hosing with detergent solution and spraying with Freon.

To supply liquid oxygen to the container, we intend to condense gaseous oxygen already in the container, by means of passing liquid nitrogen through a copper coil within the container, and collecting the condensed oxygen in a suitable vessel. This procedure has been designed by Mr. L. L. Sparks, and he succeeded in condensing nitrogen rapidly and amply so that there should be no trouble in getting liquid oxygen in the same way. Thus, we are spared the need to actually handle liquid oxygen and transfer it to the container, etc., with a great increase in safety and convenience. However we will not do any liquid-oxygen burning experiments until we have conducted a number of gaseous-oxygen burning experiments in view of the potential violence of the former. Further safety approval will be sought before liquid-oxygen experiments are carried out.

Operating Procedures

1. Ensure system clean. Install sample.
2. Open Valves 1 and 2. Close Valve 3.
3. Evacuate.
4. Close Valves 1 and 2. Open Valve 3.
5. Fill with oxygen (or other desired gas), to required pressure.
6. Turn on recording instruments. Ignite the sample.
7. Open valve 2 (to relieve pressure).
8. Close 2. Fill with nitrogen to 10 psi over atmospheric pressure.
9. Repeat Steps 7 and 8 if necessary (to flush system).
10. Open Valve 2.
11. Remove sample.

Page 4 - Omitted - for diagram of revised site layout see figure 2.

page 5.

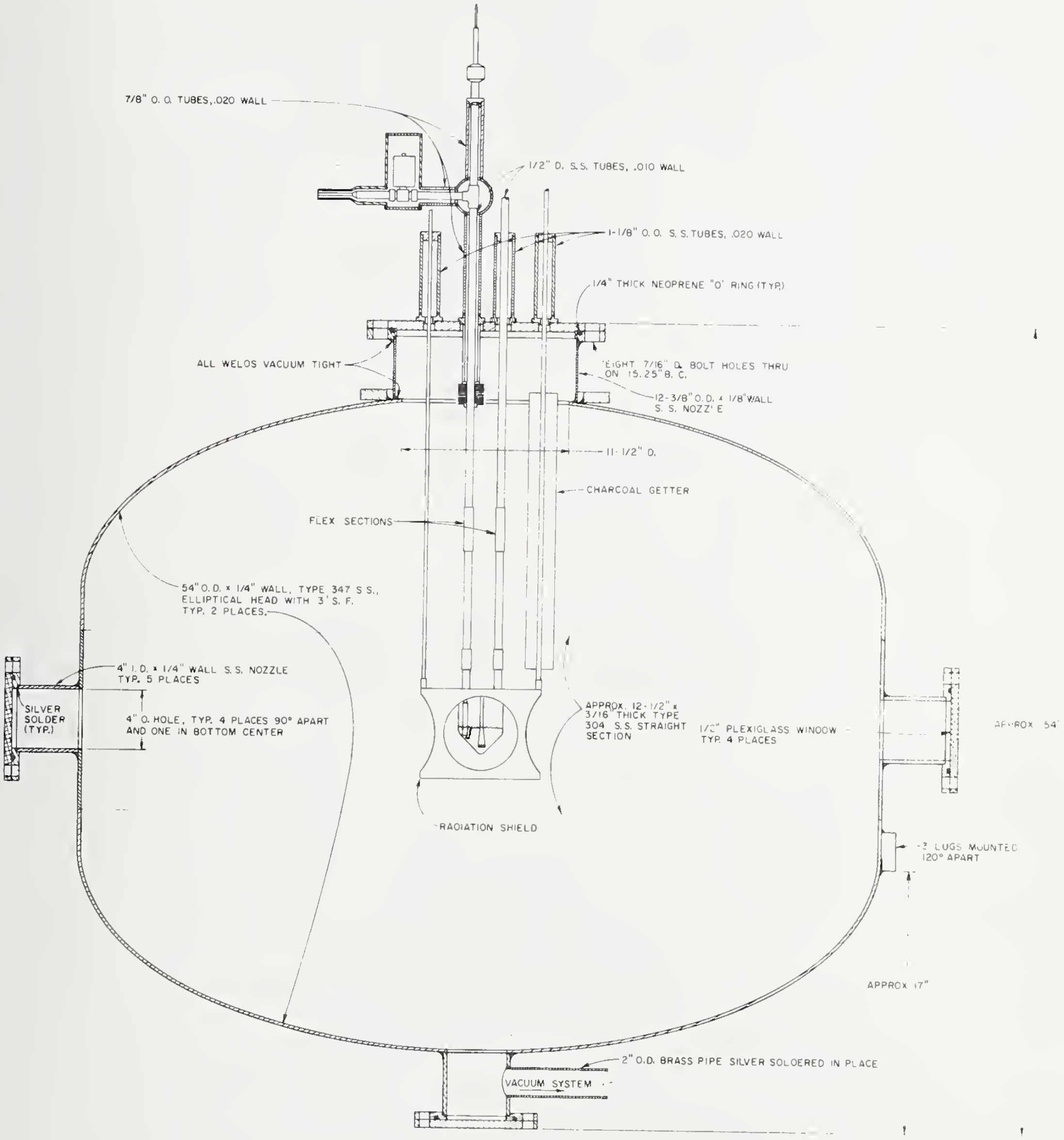

Figure 3.4.2 Assembly of Glass LH_2 Vessel and Large Metal Containment Vessel
(R. O. Voth Apparatus)

APPENDIX B

The Thermite Reaction

If finely divided aluminum is ignited, it burns with great brilliance to aluminum oxide. 7.47 kcals are liberated per g of aluminum. Because of its high affinity for oxygen, aluminum is used to liberate metals from oxides which are difficult to reduce and for the attainment of high temperatures, e.g., for the welding of iron. The mixture of aluminum filings and iron oxides, e.g., Fe_3O_4, used for this purpose is known as thermite. Temperatures up to 2400°C may be reached with it. The Goldschmidt process, the reduction of various metal oxides to the metals with aluminum, is used commercially to prepare chromium metal, especially where carbon free metals are required. The nobler metals, e.g.. copper, may give rise to an explosive reaction in this process.

Table 3 gives the heats of formation of the commonest oxide of various metals, and from this we calculate that 100 g of SS 304L will give 174 kcals on complete oxidation. The thermite reaction of the resultant oxides (Fe, Cr, Ni) is calculated to yield 148 kcals. The metals liberated in this thermite reaction may then be re-oxidized, yielding a further 174 kcals. Thus, a total of 496 kcals may be anticipated from the reaction of 100 g of SS 304L under the conditions described in our experiments. In the process, 43.4 g of aluminum are oxidized.

100 g of SS 304L on solidifying from its melting point and cooling down to 660°C (Mp of Al) yields 12.5 kcals. If we assume 10% oxidation, we obtain a total of 29.85 kcals yielded, and on this ground may postulate that a minimum of 30 kcals is available to be transferred to the aluminum plate. This amount is sufficient to start a thermite reaction, however, the actual amount of heat required for ignition of the Aluminum plate may be considerably smaller than 30 kcals because we cannot estimate the efficienty of the heat transfer.

Table 3. Heats of Formation of the commonest oxides of various elements, per gram atom of oxygen (16. 00 g of oxygen), in kcals.

Element	Oxide	ΔHf	Element	Oxide	ΔH_f
Ca	CaO	151. 9	Fe	Fe_3O_4	65. 5
Mg	MgO	143. 7	Ni	NiO	58. 4
Al	Al_2O_3	133. 0	H	H_2O (g)	57. 8
Na	Na_2O	99. 4	Co	CoO	57. 2
Cr	Cr_2O_3	93. 0	Pb	PbO	50. 8
Mn	MnO	92. 0	Cu	CuO	37. 1
Zn	ZnO	83. 2	Ag	Ag_2O	7. 31

FORM NBS-114A (1-71)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR - 73-345	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Combustion of Metals in Oxygen Phase II:
Bulk Burning Experiments

5. Publication Date
December 1973

6. Performing Organization Code

7. AUTHOR(S)
Alan H. Tench, Hans M. Roder and Alan F. Clark

8. Performing Organization

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS, Boulder Labs
DEPARTMENT OF COMMERCE
Boulder, Colorado 80302

10. Project/Task/Work Unit No.
2750439

11. Contract/Grant No.
H92145A

12. Sponsoring Organization Name and Address

NASA-Marshall Space Flight Center
Huntsville, Alabama 35812

13. Type of Report & Period Covered
Interim 4/72-9/72

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

This program was started to study combustion of the ordinary metals in oxygen, to provide information useful to designers of bulk oxygen handling equipment, particularly from the point of view of safety. We have studied the ignitability and combustability of carbon steels, stainless steels, aluminum alloys, titanium and copper metals, in oxygen atmospheres up to 60 psig. We encountered a violent reaction involving burning stainless steel and aluminum, a thermite reaction apparently, and have investigated this from a quantitative point of view. We have tried throughout to study the quantitative aspects of the combustion processes, and related quenching effects. Ordinary steel and stainless steel burn quite readily at these low oxygen pressures, and the stainless steel-aluminum reaction produces intense heat, with severe damage to neighboring structures. We are at the stage where further investigations could be carried out quite expeditiously and on a sound statistical basis.

17. KEY WORDS (Alphabetical order, separated by semicolons)
Alloys; aluminum; combustion; ignition; oxygen; safety; stainless steel; steel, titanium.

18. AVAILABILITY STATEMENT ☒ UNLIMITED. ☐ FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 38
	20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price

USCOMM-DC 66244-P71
USCOMM - ERL