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RESEARCH MEMORANDUM

HIGH-TEMPERATURE OXIDATION AND IGNITION OF METALS

By Paul R. Hill, David Adamson, Douglas H. Foland,
and Walter E. Bressette

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Langley Field, Va.

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON
March 26, 1956

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HIGH-TEMPERATURE OXIDATION AND IGNITION OF METALS

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SUMMARY

A study of the high-temperature oxidation of several aircraft construction materials was undertaken to assess the possibility of ignition under high-temperature flight conditions. Tests have been made both in open and closed jets, and, in addition, the burning of metals has been observed under static conditions in a pressurized vessel containing either air, oxygen, or nitrogen. When heated in an atmosphere of oxygen or when heated and plunged into a supersonic airstream, titanium, iron, carbon steel, and common alloys such as 4130 were found to have spontaneous-ignition temperatures in the solid phase (below melting) and they melted rapidly while burning. Inconel, copper, 18-8 stainless steel, Monel, and aluminum could not be made to ignite spontaneously at temperatures up to melting with the equipment available. Magnesium ignited spontaneously in either type of test at temperatures just above the melting temperature.

A theory for the spontaneous ignition of metals, based on the first law of thermodynamics, is presented. Good correlation was obtained between calculated spontaneous-ignition temperatures and values measured in supersonic jet tests.

There appears at the present time to be no need for concern regarding the spontaneous ignition of Inconel, the stainless steels, copper, aluminum, or magnesium for ordinary supersonic airplane or missile applications where the material temperature is kept within ordinary structural limits or at least below melting. For hypersonic applications where the material is to be melted away to absorb the heat of convection, the results of the present tests do not apply sufficiently to allow a conclusion.

INTRODUCTION

In the engineering of missiles or other aircraft to fly at extremely high speeds it has been customary to choose materials that retain strength at design temperature. More recently, designers who have been concerned with aircraft under transient thermal conditions have planned to use the skin as a heat sink and, in some extreme cases, to use the heat of fusion, or melting, as a possible means of absorbing the aerodynamic heating.

However, since most materials of construction are combustible if heated sufficiently, the possible rapid oxidation at high temperatures makes it necessary to consider the problem from a chemical as well as from the thermodynamic viewpoint.

One of the main factors that tends to inhibit the oxidation of metals is the formation of an oxide film which separates the air from the base metal. The oxides of some metals are very effective inhibitors. Aluminum and chromium are perhaps the two best known examples of metals that form an effective protective oxide coating. On the other hand, molybdenum and tungsten are examples noted for their porous, powdery oxide that gives practically no protection.

Some experience with the combustion of metals has been obtained in connection with oxygen cutting torches in standard shop practice. Here, experience has shown that most nonstainless steels cut readily, whether plain carbon steels or common alloys. However, for chrome-bearing steels, the speed of cutting decreases, and the cutting temperature necessary increases as the chrome content is increased.

Also, there has been considerable research on the oxidation of metals, but most of it has consisted of measurement of corrosion rates or the rate of scaling of various metals in air or other mediums at high temperature over prolonged periods. In the present paper, however, oxidation is considered from the viewpoint of possible ignition and combustion due to the heat release from accelerated oxidation. It is proposed that if the oxidation occurs with sufficient rapidity, the heat of oxidation will overbalance the heat dissipated in various ways, and ignition and combustion will follow.

EQUIPMENT AND TESTS

It is difficult to design equipment to investigate high-temperature oxidation because oxidation destroys the equipment. Since, at this time, no adequate ground-test facilities are available to determine ignition temperatures and oxidation rates under very realistic conditions, various phases of the problem have been investigated in the facilities available by resorting to subterfuges to bring the material tested up to temperature. In one of these, metal rods attached to a radius-arm support were preheated in a coke furnace and then swung quickly into a supersonic blowdown jet having a stagnation temperature of 600° F.

The rod samples had hemispherical noses of 3/8-inch diameter which were instrumented with chromel-alumel thermocouples. When preheated to 2,400° F, rods of cold-rolled steel, 4130 steel, and Graphmo tool steel rose almost instantly to their melting temperatures of approximately 2,600° F and burned. Combustion appeared to take place over the entire nose and over the first inch of the cylinder, which usually necked down. From this point back, molten metal in a very fluid state streamed over the surface and terminated 4 to 5 inches back of the nose. Apparently this stream of metal evaporated and joined the conflagration. The entire rod was bathed in a luminous and ever-growing sheath of flame. Steels with substantial chrome content, such as 18-8 stainless steel, did not undergo spontaneous ignition, although these materials were heated close to their melting temperatures.

A solid magnesium 20° total-angle cone was tested in a 1.5- by 4-inch nozzle at the Langley 11-inch hypersonic tunnel at a Mach number of 5.2 and an air stagnation temperature of 630° F. A graphite electric radiator with a radiating capacity of 100 kw/sq ft raised the magnesium temperature to 1,150° F. Structural disintegration of the cone occurred before an ignition temperature was reached.

An identical cone sample was placed in a $1\frac{1}{2}$-inch-diameter air jet issuing from an electrically heated stainless-steel pipe at a velocity of 300 ft/sec and a temperature of 1,600° F. Ignition of the cone followed a heating period during which about 1/4 inch of the nose melted off. The cone then burned steadily at the blunted nose until the entire cone was consumed.

In order to study some of the details of the mechanism of ignition under conditions of a controlled heat balance, wires of various materials about 1/16 inch in diameter and 2 inches long were heated by passing a high-amperage alternating current through the wire which, at the same time, was immersed in a static atmosphere of air, oxygen, or nitrogen. The wire was mounted normal to the axis of a 5-inch-diameter cylinder in which it was enclosed. The cylinder was able to withstand pressures up to 800 lb/sq in. and had a quartz window in one end to allow observation of ignition and burning. The wires were instrumented with chromel-alumel thermocouples 0.005 inch in diameter, capable of giving temperature measurements to 2,400° F.

DEFINITIONS

Before proceeding further with a discussion of oxidation and ignition, it seems in order to give some definitions and to examine the basic principles of spontaneous ignition. The symbols used herein are defined in the appendix. Consider a metallic surface oxidizing at high temperature. Figure 1 is a schematic representation of two quantities: The steeper curve represents the rate of heat released by oxidation,

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and the other curve represents the losses, which may be composed of convection, conduction, and radiation. The point where the rate of oxidation is equal to the losses is a critical point. If the slope of the oxidation-rate curve is greater than the slope of the losses curve, as in this figure, the temperature is in unstable equilibrium at this point. The temperature at this critical point will be referred to as the spontaneous-ignition temperature. If the temperature exceeds the spontaneous-ignition temperature it will continue to increase and, because of the exponential nature of the oxidation process with temperature, to increase rapidly. If the temperature is less than the critical value it will tend to decrease. Of course, the surface would never reach the spontaneous-ignition temperature if it were not heated by some forcing function, which is usually convection. In this case, convection reinforces oxidation and cannot be regarded as a loss. The spontaneous-ignition temperature is obviously a function of the particular environmental conditions as well as the material and, as is shown later, also depends on the history of temperature and environment. It may or may not exist below the melting temperature of the material.

RESULTS AND ANALYSIS

Figure 2 gives the results of heating a 1/16-inch-diameter wire in an atmosphere of air at 500 lb/sq in. abs. The wire, although nominally referred to as 1010 steel, is believed to contain somewhat less than 1 percent carbon. Figure 2(a) gives a time history of the wire temperature when heated with a 94-ampere current. For comparison, a time history of the temperature in an atmosphere of nitrogen at approximately the same pressure is shown. Although there is not much spread between the two curves, the difference in slopes is significant. To obtain figure 2(b) the wire is considered as a calorimeter. The slopes of the curves in figure 2(a) are plotted against temperature, but expressed as an apparent heating rate by using weight and specific heat as conversion factors. If the radiation and convection are assumed to be essentially the same in air and nitrogen at the same pressure and temperature, the difference in the apparent heating rate is due to oxidation. The difference, or oxidation rate, is plotted against temperature in figure 2(c) as the curve labeled 94 amp. The other curve, labeled 63 amp, is seen to have a considerably lower oxidation rate. The reason for this is shown in figure 2(d). The rate of oxidation, Btu/sec, is proportional to the rate of growth of oxide thickness. If the oxidation rate is converted to units of oxide thickness per second, if the oxide is assumed to be Fe_2O_3 with a heat of formation of 2,155 Btu/lb and a density of 327 lb/ft^3, and if the rate of thickness formation is integrated with time, the oxide thickness shown in figure 2(d) is obtained for the two heating rates. The wire with the slower heating rate has more time to

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oxidize and forms a greater thickness of oxide. The greater film thickness inhibits oxidation and gives the lower oxidation rate, as shown in figure 2(c).

If the electric power was cut off at any time during the 63-ampere test, the temperature immediately fell off, showing that the losses were greater than the oxidation heat rate.

The leveling off, or negative slope, of the oxidation-rate curve above 2,200° F for the 94-ampere case is believed to be due to a nitrogen enrichment in the immediate vicinity of the wire, resulting from the high rate of oxygen usage and the small flow of air by natural convection. This belief is strengthened by the observed behavior of the temperature when the electric power was cut off at about 2,200° F. The temperature rose, showing that the losses were exceeded, but after rising a few hundred degrees the upswing stopped and the temperature fell back. This could hardly be due to anything other than exhaustion of the local supply of oxygen. With a replenishment of air the temperature started up again. This process was repeated as many as three times in a few seconds, after which the wire cooled off. It was therefore thought that wire tests in an atmosphere of oxygen would give more information pertinent to high-speed flight conditions in which oxygen supply is sufficient for spontaneous ignition.

Theoretically, the gas pressure does not affect the oxidation rate. A series of tests were made on steel wires in an atmosphere of oxygen to determine whether the pressure had a noticeable effect on the rate of oxidation. The pressure was varied from 1/2 atmosphere to 53 atmospheres. Any effect of pressure on oxidation rate was too small to be determined. A pressure of 33 atmospheres or 500 lb/sq in. abs was chosen for further work, and the results are shown in figure 3.

Figure 3(a) shows the rate of oxidation for three heating rates, and the curve labeled losses intersects the other curves at spontaneous-ignition temperatures. If the electric power was cut off at higher temperatures, the temperature rose rapidly, after which the wire burned until it was consumed. The integrated oxide thicknesses for the same heating rates are shown in figure 3(b).

Constant-temperature cross plots of figures 3(a) and 3(b) yield oxidation rate as a function of oxide thickness, as shown in figure 3(c). The points are experimental values obtained from the cross plots and were used to establish the coefficients of the engineering formula for oxidation rate,

$$Q_0 = \frac{134500}{\delta} e^{-\frac{42170}{T}} \qquad (1)$$

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which is represented by the solid lines in figure 3(c). The form of the dependence of oxidation rate on the temperature conforms to the Arrhenius law which adequately describes a large number of diverse chemical reactions. The denominator contains simply the oxide thickness δ. The dependence of the oxidation rate on the reciprocal of the oxide thickness is in conformity with the ion diffusion theory developed by Wagner. It agrees with the present data for fast rates of oxidation and also agrees with much of the oxidation data in the literature obtained on steels at lower oxidation rates. The form of equation (1) was obtained by making the observation that the diffusion function $\text{Constant}/\delta$ and the Arrhenius temperature function $Ae^{-B/T}$ are independent of each other, so that a combined equation can be obtained simply as the product of the two functions. This equation can be expressed as a rate of weight gain instead of rate of heat release, and integrated with respect to time at constant temperature. In that form it is known as the parabolic law of oxidation because the weight gain is proportional to the square root of the time (ref. 1). The parabolic law agrees with much of the constant-temperature test data in the literature for the oxidation of both ferrous and nonferrous metals which have nonporous or nonpowdery oxides, such as certain steels, chrome, copper, and aluminum. It follows that the form of the diffusion formula herein presented should apply for these metals over any range of conditions for which their oxidation characteristics have been shown to fit the parabolic law of oxidation. The constants must be adjusted for the particular metal according to test results.

However, the application of this formula has certain limitations. It obviously cannot apply at oxide thicknesses approaching zero. However, this formula apparently applies for a coating as thin as 0.0001 or 0.0002 inch. Strictly, the constants in the equation are adjusted for oxygen, but the equation may be used with air provided the surface is fully supplied with oxygen so that it remains saturated in spite of the rapid usage of oxygen. This point is illustrated in a subsequent paragraph. For aerodynamic ignition, saturation of the surface with oxygen seems to imply only that there must be a substantial mass flow of air or a substantial stagnation pressure. These conditions are usually present with high rates of heat transfer.

In order to determine whether the spontaneous-ignition temperature can be calculated for steel in a supersonic airstream, computations were made for the conditions of the round-nose rods tested in the preflight jet of the Langley Pilotless Aircraft Research Station at Wallops Island, Va. The test conditions are stated at the top of figure 4. The spontaneous-ignition temperature equation, which is a form of the first law of thermodynamics, is

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March 26, 1957

Page 7: In lines 11 and 13, the words "slight drop" should be changed to "slight rise."

Issued 11-12-57

NACA - Langley Field, Va.

$$Q_O \qquad = \qquad Q_{CONV} \qquad + \qquad Q_{RAD}$$

$$\frac{134500}{\delta} e^{-\frac{42170}{T}} = 1.32 \frac{k}{d} R^{.5} N_{PR}^{.4}\left(T_{AW} - T\right) + 0.000048\epsilon\left(\frac{T}{100}\right)^4 \qquad (2)$$

Conduction is omitted because the rods were quite uniformly heated. The first term represents oxidation and is taken from equation (1). The second term is Sibulkin's theory for the heat transfer on a hemispherical nose, which, in this case, had a diameter of 3/8 inch. The last term is the usual expression for radiation. The value of emissivity was taken as 0.88. The unknown quantity T, the surface temperature for equilibrium conditions, appears in each term. The solutions of this equation for oxide thicknesses of 0.0001 and 0.001 are plotted in figure 4. The theory shows a slight drop in spontaneous-ignition temperature with airspeed because the convection represents a loss. The measured spontaneous-ignition temperatures also show a slight drop with speed at the higher speed range. At 150 ft/sec, no ignition was obtained although the specimens were heated to near melting. Insufficient oxygen, together with nitrogen enrichment of the boundary layer, seems to be the most probable cause of the failure to ignite at low airspeed, although reduced erosion may possibly affect the result.

Some nonferrous materials such as Inconel and copper were tested to temperatures approaching melting in a supersonic blowdown jet with a stagnation temperature of 600° F, without obtaining ignition. The same results were obtained from the simple heated-wire tests in an atmosphere of oxygen. Figure 5 shows temperature-time histories for wires of several materials tested in oxygen at 500 lb/sq in. abs. Although the Inconel and copper were heated until they melted, no ignition was obtained. The rate of oxidation of these materials was too small to be measured by the techniques used. The break in the titanium curve is not associated with oxidation but is believed to result from the heat absorption by the alotropic transformation. When the electric power was cut off at 2,100° F the titanium spontaneously ignited and burned vigorously. Titanium was also found to burn vigorously in an atmosphere of pure nitrogen as well as in an atmosphere of air. The spontaneous ignition temperature in air at a pressure of 1 atmosphere was 2,900° F. Magnesium was observed to ignite when it melted, possibly because some of the protective oxide coating was floated off.

CONCLUSIONS

Tests of low-carbon steel and several other materials heated artificially in wind tunnels, in air jets, and under static conditions in atmospheres of air, oxygen, and nitrogen indicate the following:

1. When rapidly heated in an atmosphere of oxygen or when heated and plunged into a supersonic jet at Mach 1.4 or 2.0,

   (a) Iron or carbon steel and common alloys such as 4130 were found to have spontaneous ignition temperatures in the solid phase (below melting) and melted very rapidly while burning.

   (b) Inconel, copper, 18-8 stainless steel, Monel, and aluminum did not have a spontaneous ignition temperature in the solid phase, nor could they be made to ignite at, or close to, melting with the equipment available.

   (c) Titanium burned in atmospheres of air, oxygen, or nitrogen.

2. A good correlation of experimental and theoretical spontaneous-ignition temperatures was obtained for steel in supersonic airstreams. Comparable spontaneous-ignition temperatures were obtained by simulation in an atmosphere of oxygen.

3. The fact that the oxidation rate of some materials varies inversely with the oxide thickness suggests that, for some materials, catastrophic release of heat by oxidation may be prevented either by heating gradually or by prior oxidation.

4. There appears at the present time to be no need for concern regarding the ignition of Inconel, the stainless steels, copper, or magnesium for any ordinary supersonic airplane or missile applications where the material temperature is kept within ordinary structural limits or at least below melting. For hypersonic applications where the material is to be melted away to absorb the heat of convection, the results of the present tests do not apply sufficiently to allow a conclusion.

Langley Aeronautical Laboratory,
National Advisory Committee for Aeronautics,
Langley Field, Va., November 3, 1955.

APPENDIX

SYMBOLS

N_{Pr}	Prandlt number
Q_0	rate of heat generated by oxidation, $Btu/sec\text{-}ft^2$
Q_L	rate of heat loss, $Btu/sec\text{-}ft^2$
Q_{CONV}	rate of convective heat loss, $Btu/sec\text{-}ft^2$
Q_{RAD}	rate of radiation loss, $Btu/sec\text{-}ft^2$
R	Reynolds number (based on nose diameter)
T	temperature, ^{o}F abs
T_{AW}	adiabatic wall temperature, ^{o}F abs
d	nose diameter of specimen, ft
k	conductivity of air, $Btu/(sec\text{-}ft^2)(^{o}F/ft)$
δ	oxide thickness, in.
ϵ	emissivity, $Btu/(sec\text{-}ft^2)(^{o}F)$

REFERENCE

1. Miley, H. A.: Fundamentals of Oxidation and Tarnish. The Corrosion Handbook, Herbert H. Uhlig, ed., John Wiley & Sons, Inc., 1948, pp. 11-20.

DEFINITIONS

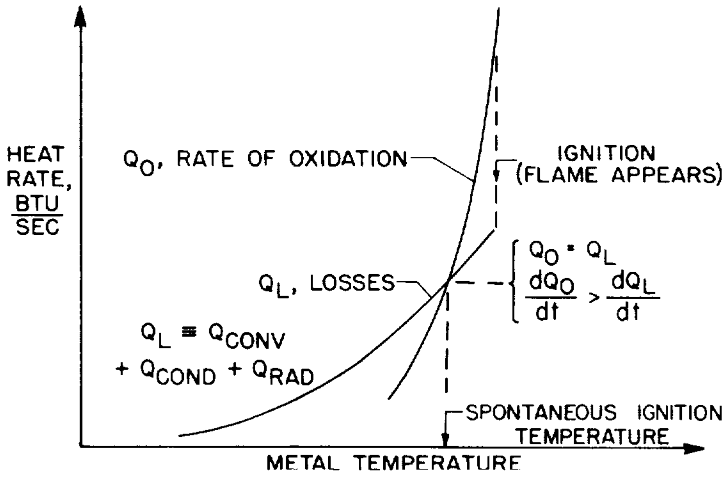

Figure 1

BOMB TEST TECHNIQUE

AIR; p=500 LB/SQ IN., ABS; 1010 STEEL

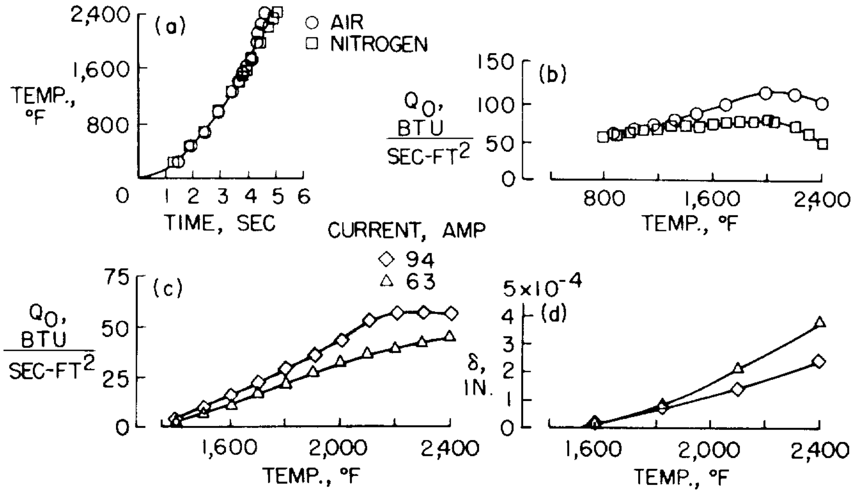

Figure 2

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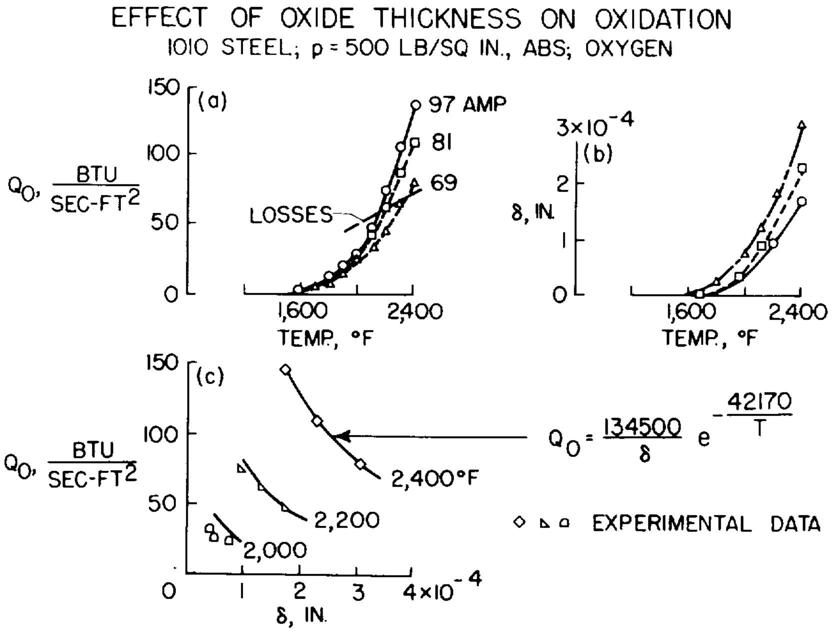

Figure 3

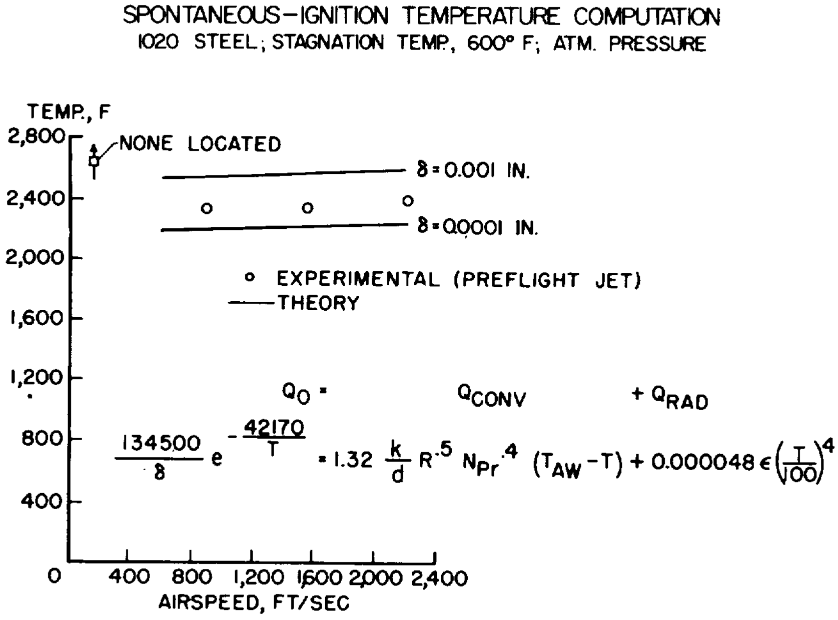

Figure 4

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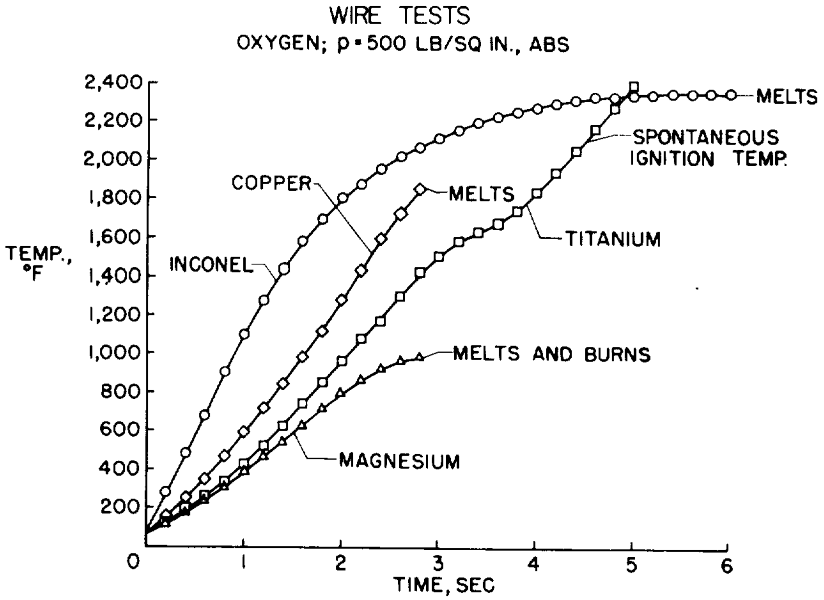

Figure 5

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