IGNITION AND COMBUSTION OF BULK METALS UNDER ELEVATED, NORMAL AND REDUCED GRAVITY CONDITIONS*

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Introduction

Although experiments on combustion of metals can be traced back as early as 1782, it was not until violent reactions were observed between titanium (Ti) and oxygen (O_2) in the 1950's that a significant number of studies focused on the compatibility of metals with oxygen (ref. 1). Later, studies focused primarily on metal powders due in part for the use of metal additives in solid rocket propellants. More recently, attention has been given to the flammability properties of bulk, structural metals, due to the large number of accidents involving burning metal components in oxygen systems. In spite of all the investigations conducted on this field to date, there is still a lack of basic understanding of the processes controlling ignition and burning of bulk metals compared to the literature available for gaseous reactions. The difficulty of providing accurate models stems from the variety of complex variables affecting metal-oxygen reactions such as: metal type, phase changes, oxygen pressure and solubility in metals, mechanical and thermal properties of oxide layers, gravitational force, experimental apparatus and configuration, surface tension effects, and sample size to name a few.

This research effort is aimed at providing further insight into this multi-variable dependent phenomena by looking at the effects of gravity on the ignition and combustion behavior of metals. Since spacecraft are subjected to higher-than-1g gravity loads during launch and reentry and to zero-gravity environments while in orbit, the study of ignition and combustion of bulk metals at different gravitational potentials is of great practical concern. From the scientific standpoint, studies conducted under microgravity conditions provide simplified boundary conditions since buoyancy is removed, and make possible the identification of fundamental ignition mechanisms. The effect of microgravity on the combustion of bulk metals has been investigated by Steinberg, et al. (ref. 2) on a drop tower simulator. However, no detailed quantitative work has been done on ignition phenomena of bulk metals at lower or higher-than-normal gravitational fields or on the combustion characteristics of metals at elevated gravity. The primary objective of this investigation is the development of an experimental system capable of providing fundamental physical and chemical information on the ignition of bulk metals under different gravity levels. The metals used in the study, iron (Fe), titanium (Ti), zirconium (Zr), magnesium (Mg), zinc (Zn), and copper (Cu) were selected because of their importance as elements of structural metals and their simple chemical composition (pure metals instead of multi-component alloys to avoid complication in morphology and spectroscopic studies). These samples were also chosen to study the two different combustion modes experienced by metals: heterogeneous or surface oxidation, and homogeneous or gas-phase reaction. The experimental approach provides surface temperature profiles, spectroscopic measurements, surface morphology, x-ray spectrometry of metals specimens and their combustion products, and high-speed cinematography of the heating, ignition and combustion stages of the metal specimen. This paper summarizes the results obtained to date from experiments conducted under normal and high-gravity conditions.

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Experimental Apparatus

The experimental system is shown in Fig. 1. The radiation source consisted of a 1000 W xenon short-arc lamp with 250 W of effective broadband output radiation power. A feasibility study on the use of a continuous radiation short-arc lamp as an ignition source is presented in ref. 3. The light beam from the lamp is focused down by an aspheric lens to a 4 mm spot on the top surface of a metal sample providing a 1.75 MW/m^2 power density. The cylindrical metal specimen is 4 mm in diameter and 4 mm high and it is held in place by an alumina-silica holder. The 4.5 L stainless steel cylindrical chamber permits input radiation through the top quartz window. Optical access for the camera and spectrograph is provided through three fused-silica side windows. An oxygen environment (99.5% min. O_2) is used in all tests at an absolute pressure of 1 atm. The specimen surface temperature is measured with a Type B thermocouple located in the center of the sample at approximately 0.5 mm below the top surface. A 16-mm, high-speed motion picture camera provides a qualitative visual record of the combustion event and an estimate of flame propagation rates. Time-resolved spectral information on reacting species and products of combustion is obtained with a spectrograph/diode-array system. Surface morphology analysis is obtained with a Scanning Electron Microscope (SEM). Quantitative analysis of the chemical composition of quenched samples and combustion products is performed with an Electron Microprobe Analyzer (EMPA). The high-gravity experiments are conducted on a geotechnical centrifuge that is equipped with an onboard computer and signal conditioning system for remote operation. Further details of the various components of the apparatus and the experimental procedures are given in ref. 4.

Normal-Gravity Results

a) Qualitative Observations

High-speed movies of experiments conducted in normal gravity reveal the existence of three important and distinct phases:

i) The heating period, starting when the lamp radiation is applied until metal ignition, exposes the complexity of low-temperature oxidation mechanisms. The fast heating rate applied, 50-150 K/s, encourages metal expansion and rapid oxidation as evidenced by the appearance of spots, blisters, pores or cracks on the surface. Distinct types of oxidation are observed depending on the Pilling and Bedworth ratio of the metal, i.e., the volume of oxide formed/volume of base metal (ref. 5).

ii) The ignition phase is characterized by faster oxidation and a noticeable increase in energy release evidenced by the intense radiation emitted from the reaction zone.

iii) The combustion event varies in nature, speed and strength among the different metals tested. In the case of Fe, Ti, and Zr, a well-defined, self-sustained downward propagation (at 8, 30 and 25 mm/sec, respectively) is followed by a violent exothermic reaction including random outward expelling of small particles. For Mg and Zn the combustion phase evolved much faster with the generation of a fine oxide powder that formed a dust cloud which deposited uniformly on the walls and windows of the combustion chamber. Cu exhibited a smooth combustion phase characterized by a slow regression rate with a low-luminosity reaction zone (ref. 6).

b) Temperature Profiles

Temperature records also reveal uniquely the existence of the heating, ignition and combustion stages. Fig. 2 shows the temperature history of a typical Ti sample being heated at 1 atm under normal gravity. The figure also indicates the most relevant temperatures during the heating and ignition phases, as defined by Glassman, et al. (ref. 7). At the start of the heating period, there is a steep rise in surface temperature in the first second of heating caused by the sudden flux of radiant energy from the light source. After this initial jump, the temperature rise continues monotonically until a change in the slope around 1100 K. This change is caused by the latent heat associated with a crystal structure transformation from an hexagonal to a cubic lattice. A significant increase in the temperature rise follows this phase

transition due to the change in the oxidation mechanism from parabolic to linear. This point corresponds to the transition temperature, T_{trans}, or temperature where the oxide layer becomes a non-protective film and the oxidation rate becomes independent of time. After this point, the temperature continues to increase until a point of inflection is reached in the curve after which the temperature vs. time slope rapidly increases again. This point is identified as the critical temperature, T_{crit}, at which the heat generated by the metal oxidation first exceeds the heat lost through conduction, convection and radiation. Beyond the critical temperature, the metal specimen is driven into a thermal runaway region as a consequence of the exponential dependence of the reaction rate on temperature. After a time delay, the ignition temperature, T_{ign}, is reached. This corresponds to the appearance of a bright, luminous reaction zone. The acceleration of the reaction rate ultimately leads to the exothermic, self-sustained combustion event. At this stage, the temperature drastically increases to values in the range of 3500-4000 K. Similar behavior is observed for Zr and Fe. Temperature profiles for Mg, Zn and Cu vary significantly due to the existence of an intermediate plateau caused by the melting of the metal (ref. 4). Table 1 shows the transition, critical, ignition, and adiabatic flame temperatures at 1 atm of the different metals. All metals appear to be critical-temperature controlled with the exception of Zn, where a critical temperature is not observed. This behavior is typical of transition temperature controlled metals ($T_{trans} > T_{crit}$).

c) Spectroscopic measurements

Time-resolved measurements of gas-phase emission spectra have provided a clear, non-intrusive picture of the rapid evolution of reacting species and the formation of oxide products during the ignition and combustion phases of metals burning in a homogeneous flame front. In our experimental set-up the volume immediately above the top surface of the metal sample was focused by two condensing lenses onto a 25-micron wide aperture slit at the entrance of the spectrograph. Different gratings are used to capture broad and narrow spectral regions. Fig. 3 shows the emission spectra from the Mg-O_2 reaction at 1 atm under normal gravity conditions using a 2400 groove/mm grating to highlight the vibrational features of the green B-X system of MgO. The figure shows the time evolution of the gas-phase reaction in 33-ms intervals. The information provided by this figure becomes very important in order to estimate the location and relative abundance of the different species involved as well as the electronic and vibrational temperatures given by the intensity ratios of individual lines or bands. Comparison of time and space resolved spectra will be very useful on determining the effect of gravity-induced convection on the nature and character of ignition phenomena of bulk metals exhibiting gas-phase reactions.

d) Surface Morphology and Chemical Analysis

As illustrated by qualitative observations and by the temperature records, the character of the surface has a major effect on the ignition of metals. A more complete understanding of the ignition mechanism of metals requires monitoring the formation of the various oxide layers and their subsequent physical and chemical transformations. Fig. 4 is an example of the valuable information obtained from metallographic photographs to determine the nature and effect of oxidation processes on bulk titanium ignition. This figure is a SEM photograph showing a 390X magnification of the outer rim of the top surface of a titanium specimen quenched during the heating phase; the lamp was turned off when the specimen reached a temperature of 1550 K. The picture clearly shows the sequence of progressively higher oxides formed. The chemical composition of the main body (shown in the middle of the picture) is Ti+O, i.e. titanium metal with a 25% of oxygen in solution. This indicates that the metal nearly reached the limit of oxygen solubility before the quenching event. The thin (5 μm), intermediate layer has been identified as Ti_2O_3, a white oxide whose porosity and fragility is responsible for the parabolic-to-linear oxidation transition around 1230 K. After the onset of the time independent, linear oxidation process, a yellow-brown oxide layer rapidly starts covering the specimen. This thicker outer oxide coating (60 μm), rutile TiO_2, effectively protects the base metal from direct contact with the oxidizing medium, preventing an explosive reaction. It is this last layer that, after experiencing extreme mechanical stressing on the edges of the upper surface, suddenly breaks up exposing the base metal to the surrounding pure-oxygen

environment, leading finally to self-heating and ignition of the titanium specimen. Since buoyancy-induced free convection alters the advective transport of oxygen towards the metal surface , one can anticipate that the formation and influence of the various oxide layers might be different in other gravity environments.

Elevated-Gravity Results

High gravity experiments were conducted on the University of Colorado Geotechnical Centrifuge Facility. The experiment is subjected up to 130 rpm, an angular speed equivalent to an effective 20 g's acceleration. Fig. 5 shows the temperature histories of Ti samples subjected to different gravity levels.

A computational model of the experiment was developed to explore the effects of gravity and pressure on the heating phase of the metal sample under non-oxidizing conditions (ref. 8). The model includes the effects of conduction, convection and radiation heat transfer in the solid specimen and the surrounding gas. As predicted by this model, based exclusively on heat transfer mechanisms, the 3g's and 5g's temperature curves show a slower heating rate and a progressively longer delay for the ignition time. A higher buoyancy-induced convective flow increases the heat loss from the metal sample keeping the temperature lower than in the normal gravity case. However, this trend seems to reverse after the 5g's temperature curve, leading to faster ignition times for metal specimens subjected to higher gravity loads. This behavior may be explained by the existence of a competing effect between the convective heat loss and heat generation (by oxidation) mechanisms. At high gravity levels increased convection leads to an increase of oxygen transport to the metal surface resulting in higher oxidation rates. Higher heat generation may overcome the heat lost by convection promoting a faster temperature rise. This is specially true at temperatures above the transition temperature where the rate of oxidation of titanium changes from parabolic to linear. Moreover, after 5 g's the convective heat loss term increases only at a very slow rate, due to its $g^{1/4}$ dependence on gravity inside the Grashof number (Gr). With increased oxygen transport and a time-independent linear oxidation, the temperature rises at a faster rate. With an exponential dependence on temperature, the reaction soon becomes self-accelerating and ignition is reached. Fig. 5 clearly illustrates this effect on the 20 g's vs. the 1 g case, where the temperature curves quickly diverge after reaching the transition temperature. After ignition, the burning rates are significantly increased not only by the higher oxygen transport rates , but because the increased gravitational pull on the molten products as well. In the 20 g's case, the gravitational force is increased by twenty times, while the surface tension force exerted on the hot liquid products remains practically unchanged. The significantly larger Bond (Bo) number, i.e., gravitational force/surface tension force, generates massive dripping of molten products that ignite fresh metal ahead of the original reaction front.

Conclusions

An experimental system to study the ignition characteristics of bulk metals has been designed and tested under normal and high gravity conditions. Ignition and combustion tests were performed on Fe, Ti, Zr, Mg, Zn, and Cu specimens. Qualitative observations and temperature profiles have revealed the existence of the heating, ignition and combustion stages. These zones are characterized by well-defined surface structure changes, surface temperature behavior, luminosity and chemical activity. Time-resolved spectroscopic measurements reveal the dynamic evolution of the ignition event. Scanning electron microscope studies and x-ray spectroscopic analysis have given information on the oxide formation process. Preliminary results on the effect of higher-than-normal gravity levels on the ignition of Ti specimens have been obtained. The observed differences between the 1g and the high-g cases may be due to the existence of competing effects between heat transfer and oxidation mechanisms affected by buoyancy-induced free convection. Future work will focus on completing the elevated gravity tests and performing the microgravity experiments onboard the NASA-Lewis DC-9 Aircraft.

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Table 1. Important temperature values of all metals studied at 1 atm, normal gravity.

Metal	Transition Temp. (K)[a]	Critical Temp. (K)[a]	Ignition Temp. (K)[a]	Adiabatic Flame Temp. (K)[b]
Ti	1230	1620	1725	3993
Zr	1225	1555	1690	4278
Fe	1460	1475	1565	3400
Cu	1270	1355	1370	1400
Mg	720	950	975	3432
Zn	970	not observed	1170	2200

[a] From this investigation.

[b] From Steinberg, et al. (ref. 9), except for the estimated values of Cu and Zn.

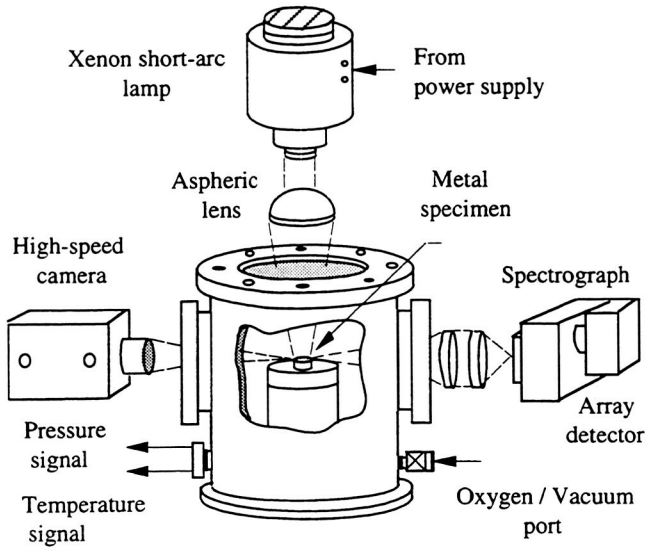

Figure 1. Experimental apparatus

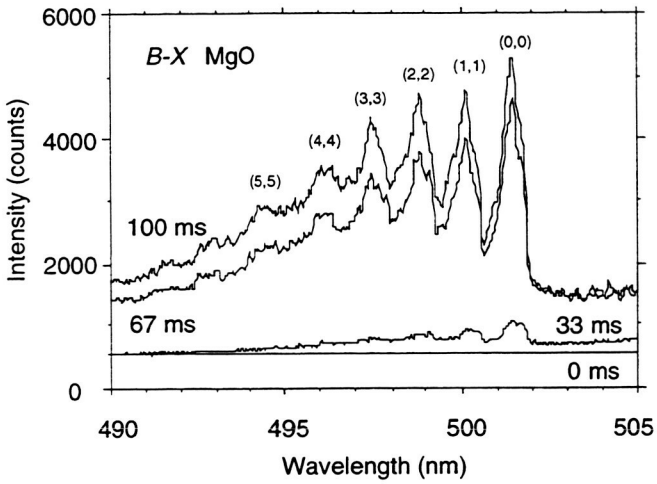

Figure 3. Time-resolved emission spectra from the ignition of a Mg specimen in O_2 at 1 atm.

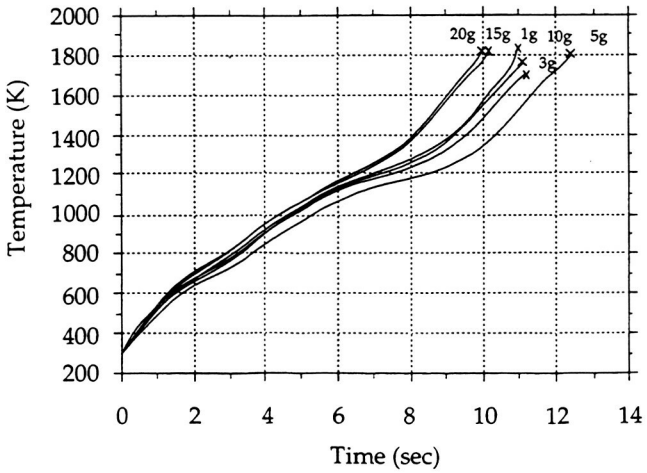

Figure 5. Temperature vs. time behavior of bulk titanium samples subjected to different gravity loads.

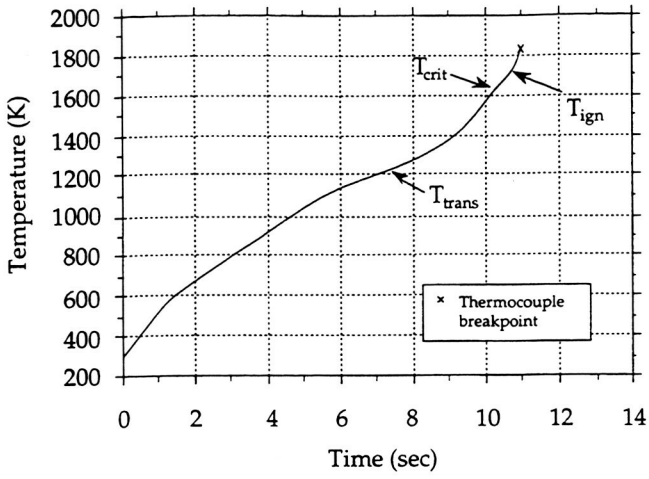

Figure 2. Temperature profile and important temperature values (transition, critical and ignition) of bulk titanium at 1 atm and normal gravity.

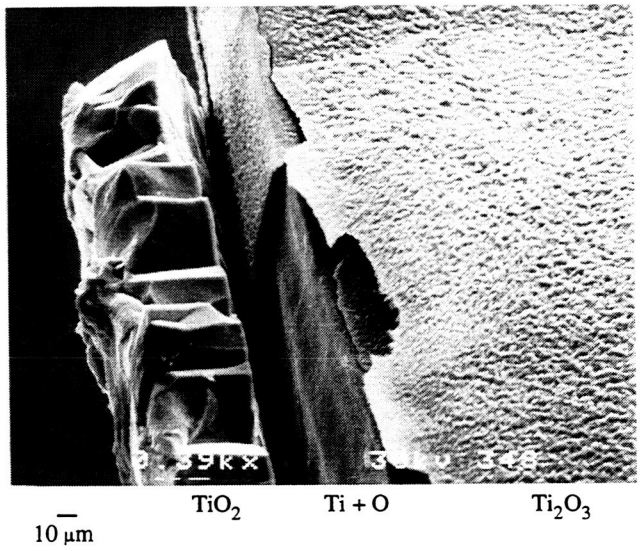

Figure 4. SEM photograph (390X) taken from the outer rim of the top surface of a cylindrical Ti specimen quenched at 1550 K during the heating phase in O_2 at 1 atm under normal gravity.