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COMBUSTION OF METALS IN REDUCED-GRAVITY AND EXTRATERRESTRIAL ENVIRONMENTS

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INTRODUCTION

The combustion of metals is a field with important practical applications in rocket propellants, high-temperature flames, and material synthesis. Also, the safe operation of metal containers in high-pressure oxygen systems and with cryogenic fuels and oxidizers remains an important concern in industry. The increasing use of metallic components in spacecraft and space structures has also raised concerns about their flammability properties and fire supression mechanisms. In addition, recent efforts to embark on unmanned and manned planetary exploration, such as on Mars, have also renewed the interest in metal/carbon-dioxide combustion as an effective in situ resource utilization technology.

In spite of these practical applications, the understanding of the combustion properties of metals remains far behind that of the most commonly used fuels such as hydrocarbons. The lack of understanding is due to the many problems unique to metal-oxidizer reactions such as: low-temperature surface oxidation prior to ignition, heterogeneous reactions, very high combustion temperatures, product condensation, high emissivity of products, and multi-phase interactions. Very few analytical models (all neglecting the influence of gravity) have been developed to predict the burning characteristics and the flame structure details. Several experimental studies attempting to validate these models have used small metal particles to recreate gravity-free conditions. The high emissivity of the flames, rapid reaction, and intermittent explosions experienced by these particles have made the gathering of any useful information on burning rates and flame structure very difficult.

The use of a reduced gravity environment is needed to clarify some of the complex interactions among the phenomena described above. First, the elimination of the intrusive buoyant flows that plague all combustion phenomena is of paramount importance in metal reactions due to the much higher temperatures reached during combustion. Second, a low-gravity environment is absolutely essential to remove the destructive effect of gravity on the shape of a molten metal droplet in order to study a spherically symmetric condition with large bulk samples. The larger size of the spherical metal droplet and the longer burning times available in reduced gravity extend the spatial and temporal dimensions to permit careful probing of the flame structure and dynamics. Third, the influence of the radiative heat transfer from the solid oxides can be studied more carefully by generating a stagnant spherical shell of condensed products undisturbed by buoyancy. The relative influence of radiation heat transfer and of the diffusion of oxidizer on burning rates scan be discerned more easily by using an electric fields to selectively remove charged, radiating particles from the flame front allowing a more unimpeded flow of oxidizer. An electric field may also be applied to control the burning rate of metals in microgravity by generating ionic-wind induced convection of oxidizer. This control technique has also important practical ramifications in the control of solid propellant burning and pressure oscillation dampening. Fourth, the use of a reduced gravity environment is essential to simulate the behavior of metal reactions in planets with fractional values of earth gravity such as Mars and Venus.

The research described here is a continuation of a research program under NASA support and will focus on the *study of combustion of spherical bulk metal samples under various gravity levels, pressures, oxidizers, and external electric fields*. The results of our previous investigation have already uncovered the first clear evidence of the substantial effect of gravity on the propagation rate of heterogeneous metal combustion

and on the burning time of metals reacting in the gas phase. Use will be made of the same apparatus (previously flown several times on a reduced-gravity aircraft) modified to accommodate the study of unsupported, free-floating spherical samples and the effect of external electric fields. Planar laser induced fluorescence and rainbow schlieren systems will also be implemented to study the flame structure and temperature field. Reduced gravity will be obtained from the KC-135 aircraft to simulate low and partial gravity levels. In response to the Human Exploration and Development of Space (HEDS) Enterprise to search for appropriate in situ resource utilization techniques, we will study the burning characteristics of metal/carbon-dioxide reactions which has been identified as a promising energy source and propellant on the planet Mars. The experimental results will be compared with the results of the analytical models that have remained untested for many decades. In addition, we will develop a numerical model capable of reproducing the behavior of metal/oxidizer species by combining the full chemical kinetic mechanisms with the unique properties of these flames such as product condensation and heterogeneous reactions.

In order to accomplish the three main objectives of the study, the experimental configuration shown in Fig. 2 is used. In this arrangement the combustion of spherical specimens (4-6 mm in diameter) is studied under various pressures (0.005 atm-15 atm), oxidizers (O_2, CO_2, CO, N_2, and O_2/N_2, CO_2/CO, $CO_2/N_2/H_2O$ combinations), and at different gravity levels (0.01 g, 0.16 g, 0.38 g, and 1 g). The selection of the appropriate sample diameter is governed by the feasibility of achieving heating, ignition, and burning of the largest possible sample during the low-gravity time available on a typical parabola on the KC-135 aircraft – approximately 25 s for ±0.01 g and longer times for higher gravity levels. The samples are obtained from cylindrical rods machined down to an approximate spherical shape. Under low-gravity, the melting of the sample produces the final smooth spherical shape required. This approach lowers significantly the cost and time of manufacturing or machining a perfectly spherical specimen.
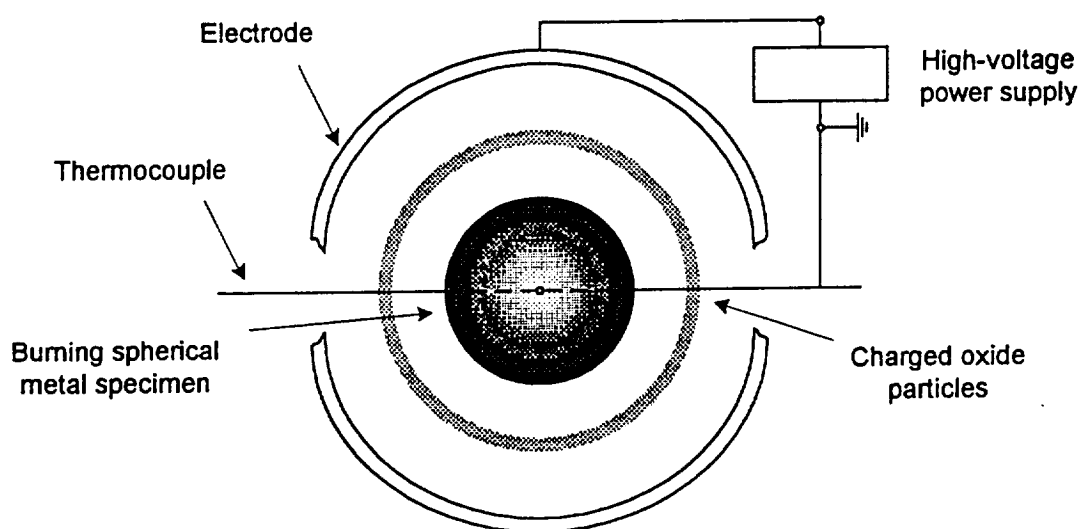

Figure 1. Experimental configuration to study the combustion of bulk spherical samples under various reduced-gravity levels, pressures, oxidizers, and external electric fields.

RESULTS AND DISCUSSION

The first set of experiments has been conducted with magnesium (Mg) samples burning in the low-gravity environment generated by an aircraft flying parabolic trajectories. Owing to its high adiabatic flame temperature, oxidizer/fuel ratio, and heat per unit mass of fuel, as well as its low toxicity and low ignition temperature, Mg has been identified as a promising metal fuel with CO_2 as oxidizer. The experimental effort is complemented by the development of a numerical model combining gas-phase chemical kinetics and transport mechanisms.

Magnesium specimens (99.95% purity) are burned in a pure CO_2 or pure CO environment (99.6% min.) at a 1-atm pressure. A high-speed, 16-mm movie camera provides surface and flame visualization; the images are also used for measurement of burning times. In addition to visible light imaging, time- and space-resolved spectral information on gas-phase reactants and products is obtained with an imaging spectrograph and diode array detector. The reduced-gravity experiments were conducted onboard the NASA KC-135 research aircraft in Houston, Texas. Up to 20 s of reduced reduced gravity (± 0.01 g) were available in a single parabolic maneuver.

The chemical-kinetic numerical modeling of the Mg-CO/CO_2 flames is performed using the CHEMKIN computer code. In the case of metal combustion experiments conducted in microgravity, a spherical flame is nearly achieved. Under these conditions, the burning can be modeled as a one-dimensional, spherically symmetric analogue to the CHEMKIN-based OPPDIF code that models the opposed flow of fuel and oxidizer in a diffusion flame configuration.

The main objectives of the present experiments are to evaluate the burning of a spherical sample in a free-floating configuration in low gravity and to obtain a correlation of burning time with sample size. A spherical shape of the metal sample is achieved during low gravity after melting and while the specimen is suspended from the thermocouple wire. A smooth surface is not generated due to the oxide film coating formed during the heat-up phase. Nonetheless, a spherical flame forms around the sample after ignition (around 1100 K), which immediately melts the thermocouple wire in both sides permitting the unsupported burning of the metal. Steady-state burning is achieved with the visible flame edge at a radius twice the diameter of the original specimen. The burning sample remains at its central position, which is perturbed only by initial explosions and the g-jitter present in the airplane. The explosions are a result of the superheating of the metal vapor inside its protective oxide shell. This phenomenon is also observed in Mg-O_2 flames [1] and has been reported previously in Mg-CO_2 reactions [2]. Slow, steady burning follows the initial explosions with the increasing accumulation of solid products in an outer shell. The inner sample remains black with some solid white oxide forming in the surface.

Figure 2a shows the correlation of burning times with initial sample diameter for the low-g experiments along with the results from normal-g tests conducted by Legrand et al. [3] with particles in the 50 μm to 2.5 mm range. These results correlate well with the $t_b = Kd_o^2$ expression for the burning time, t_b, of Mg particles with initial diameter, d_0, although the burning times in low-g are twice as long as the ones obtained in normal-g. Previous experiments [1] with Mg in O_2 showed the same trend in burning times between

normal and low gravity. It appears that the slower combustion at low gravity is due to the reduced transport of oxidizer to the metal surface. This behavior is expected from a diffusion controlled reaction.

Several tests were conducted with Mg in pure CO with different sample sizes. The purpose of these experiments was to observe the possible role of the heterogeneous reaction $Mg+CO = MgO(s)+C(s)$ in the combustion of Mg with CO_2. Shafirovich and Goldshleger [4] first proposed a mechanism for the Mg/CO_2 reaction based on the gas-phase reaction, $Mg+CO_2 = MgO(s)+CO$ and the heterogeneous reaction $Mg+CO =MgO(s)+C(s)$ occurring on the sample surface. In all tests, a dim, slow flame developed around the sample after ignition. The condensed particles of MgO slowly moved outwards due to their initial momentum. The reaction continued while the external radiation from the lamp was present but immediately stopped after the lamp was turned off. The unburned sample retained its original shape prior to ignition with a thick black coating around it. This coating appears to be solid carbon C(s) that is formed during surface reactions. From the above results it is concluded that continuous reaction of Mg with pure CO is only possible as long as Mg vapor is continuously extruded through the increasingly thicker carbon coating. This situation may require a CO environment at a temperature above the ignition value.
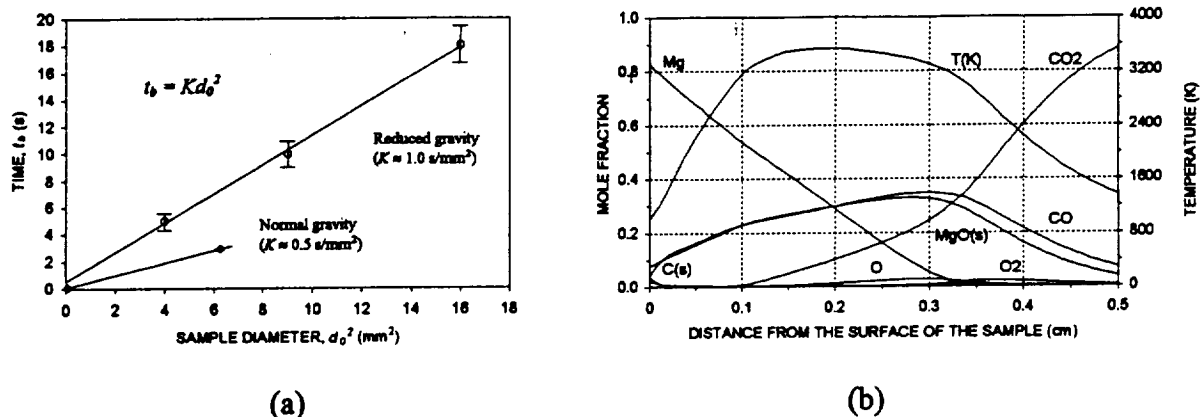

(a) (b)

Figure 2. (a) Burning time vs. initial sample diameter of Mg samples burning in CO_2 at 1 atm in reduced gravity (this investigation) and normal gravity (from [3]). (b) Temperature and concentration profiles from the OPPDIF model of the reaction zone near the surface of a Mg sample where Mg is vaporizing (left boundary) and burning in CO_2 that is diffusing from the surroundings (right boundary).

A simplified numerical model of the one-dimensional, spherically symmetric Mg/CO_2 flame was performed using the analogue opposed-flow diffusion flame configuration available from the OPPDIF code. The combustion process is modeled as a metal surface at the boiling point of Mg (1366 K) from which the metal is vaporizing. A counter flow of CO_2 is imposed to provide a stoichiometric mixture. The temperature in the CO_2 to ensure that the stoichiometric surface occurs within the defined computational domain of the model. The pressure throughout the reaction zone is 1 atm. The 12-step

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reaction mechanism and rate constants are determined from the literature. Since the rates for the Mg reactions with CO_2 and CO are not well known, sensitivity analysis was performed to obtain the best fit with experimental results. Figure 2b shows the results obtained from the OPPDIF code for temperature and species concentration. The temperature in the reaction zone remains relatively constant near the value of the vaporization-decomposition of MgO (3430 K). The temperature profile drops rapidly near the CO_2 boundary probably due to the dissociation of CO_2 at high temperatures and to the low exothermicity of the Mg-CO_2 and Mg-CO reactions. There is an indication that MgO(s) and C(s) form in the surface of the sample where Mg reacts with CO as observed in the experiments. There is also close agreement in the thickness of the reaction zone obtained numerically and the one observed experimentally. The observed location of the outer shell of MgO(s) coincides with the concentration peak of this element in Fig. 2b. Several OPPDIF runs were attempted with Mg reacting with different CO_2/CO ratios. No convergence was found for mixtures with more than 65% CO. In this way, the model predicts the absence of significant gas-phase reactions observed in the Mg-CO tests.

CONCLUSIONS

This investigation studies the burning behavior and flame structure of Mg in a CO_2 atmosphere to assess the feasibility of using metal-CO_2 reactions as an in situ resource utilization technology for rocket propulsion and energy generation on other planets. Suspended metal samples ignited in reduced gravity are used to generate free-floating, burning bulk metal samples exhibiting a spherical flame. Burning times twice as long as in normal gravity and five times longer than in Mg-O_2 flames are observed. The burning time is proportional to the square of the metal sample diameter. In tests conducted with pure CO, combustion is not possible without constant heating of the sample. It appears that surface reactions dominate in this case leaving behind a thick carbon coating around the molten Mg sample. It was found that free-floating metal samples burning in low gravity are very sensitive to g-jitter. The spherical shape of the flame tends to be distorted and the sample changes location in the direction of the gravity level experienced during the flight. Undoubtedly, this experiment could benefit greatly from the long-duration, high-quality microgravity environment provided by orbiting spacecraft.

The numerical modeling of the Mg-CO_2 flame structure using gas-phase chemical kinetics and transport mechanisms produced concentration profiles and a reaction zone thickness similar to the ones observed experimentally and a temperature profile close to the measured value. Currently, the model does not give a complete picture of the metal-oxidizer reaction since relevant physical and chemical mechanisms such as product condensation, radiation heat loss, and surface reactions are not included. There is also a lack of information on reaction rates of the most basic elementary reactions. Nevertheless, this initial modeling effort represents an encouraging first step towards the development of a realistic numerical simulation of metal combustion.

ACKNOWLEDGMENTS

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STUDENTS SUPPORTED

1. Abhijit Modak, Ph.D. Candidate

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PUBLICATIONS AND PRESENTATIONS

1. A. Abbud-Madrid, M.C. Branch, P. Omaly, "Combustion of Bulk Mg in CO_2 Under Reduced Gravity Conditions", AIAA Paper No. 99-0695, 37th AIAA Aerospace Sciences Meeting, Reno, Nevada, January 11-14, 1999.

2. A. Abbud-Madrid, P. Omaly, M.C. Branch, and J.W. Daily, "Combustion of Metals in Reduced Gravity and Extraterrestrial Environments", 5th International Microgravity Combustion Workshop, NASA Glenn Research Center, Cleveland, OH, May 18-20, 1999.

3. Christopher Dreyer, "Spectroscopy of MgO in an MgCl Seeded CH_4/Air Flame", presented at the Gordon Research Conference, Italy, June 21-25, 1999.