

# COMBUSTION OF METALS IN CARBON DIOXIDE AND REDUCED-GRAVITY ENVIRONMENTS

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## INTRODUCTION

Ongoing exploration and future missions to Mars have given impetus to research on the use of natural resources of the planet. Since carbon dioxide ( $\text{CO}_2$ ) constitutes approximately 95% of the Mars atmosphere and since it reacts directly and vigorously with several metals, this investigation focuses on metal- $\text{CO}_2$  reactions as a possible combination for rocket-propellant production and energy generation. Magnesium (Mg) has been initially selected as the metal fuel owing to its low ignition temperature and high specific impulse and burning rate in  $\text{CO}_2$ .

Our studies in this field started with low gravity ( $g$ ) combustion tests of Mg in  $\text{O}_2$ ,  $\text{CO}_2$ , and CO [1]. Reduced gravity provided a clear picture of the burning phenomena by eliminating the intrusive buoyant flows in high-temperature metal reactions and by removing the destructive effect of gravity on the shape of molten metal samples. Suspended cylindrical metal samples of 2, 3, and 4-mm in diameter and length were radiatively ignited in low- $g$  to generate free-floating samples exhibiting a spherically symmetric flame with increasing metal-oxide accumulation in an outer shell. For the Mg- $\text{CO}_2$  combination, burning times twice as long as in normal- $g$  and five times longer than in Mg- $\text{O}_2$  flames were observed, revealing a diffusion-controlled reaction. The burning time is proportional to the square of the sample diameter. In tests conducted with pure CO, combustion was not possible without constant heating of the sample due to the formation of a thick carbon-containing coating around the Mg sample generated by surface reactions.

The following work presents two new studies that attempt to explain some of the low- $g$  experimental observations. First, a simplified one-dimensional, quasi-steady numerical model is developed to obtain temperature, species concentrations, and burning rates of the spherically symmetric diffusion flame around the Mg sample burning in  $\text{O}_2$  and  $\text{CO}_2$ . Second, a Planar Laser Induced Fluorescence (PLIF) technique is implemented to provide spatially resolved measurements of magnesium oxide (MgO) in the reaction zone of Mg samples burning in  $\text{O}_2$  and  $\text{CO}_2$ . These experiments reveal fundamental differences between the two combustion systems.

## NUMERICAL MODEL

A one-dimensional, quasi-steady numerical model of a spherically symmetric diffusion flame is developed to help in the interpretation of the low- $g$  results and to serve as a preliminary effort for further development of a more complete model of Mg combustion. The model uses CHEMKIN [2] and a transport package for kinetics and transport calculations. Due to the lack of kinetic and thermophysical data for the heterogeneous reactions of Mg and the absence of a complete condensation mechanisms of MgO, the present model does not take into account surface reactions, radiation heat transfer, or complete condensation processes. Only vaporization of Mg from the sample surface is considered and MgO condensation is treated with an Arrhenius-type rate expression for the production rate of the liquid, MgO(l), and solid, MgO(s), oxides. These condensed products are treated like gas-phase species with a low diffusivity by

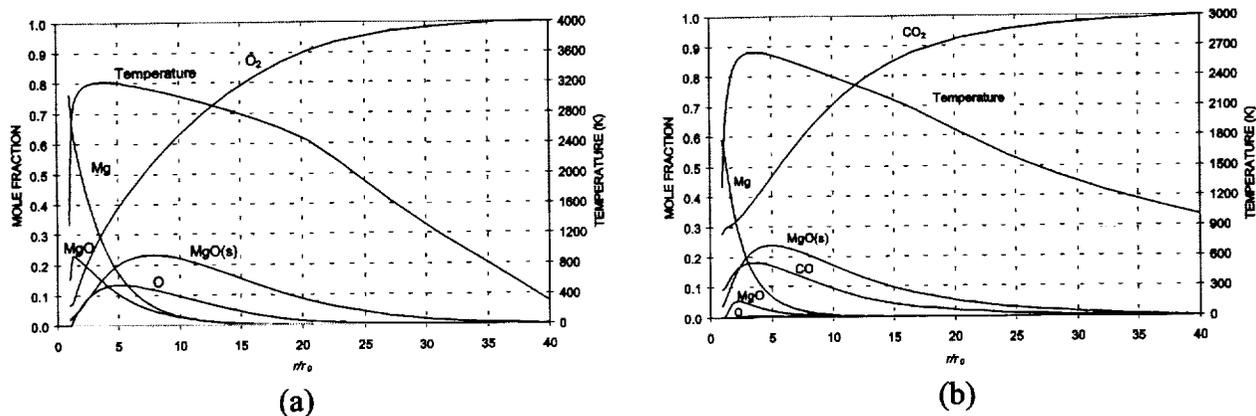
using a large value of the Lennard-Jones collision diameter in the transport property input. A collision diameter of 10 Å is chosen because is of the order of magnitude of the critical radius for condensation (3 Å) of MgO and small enough to avoid the treatment of a condensed phase. Equilibrium calculations are performed first to identify the most important species and to obtain the equilibrium temperature. The simulation is used to model the structure of Mg-O<sub>2</sub> and Mg-CO<sub>2</sub> flames. The Mg-CO<sub>2</sub> reaction mechanism contains the reactions of Mg with O, O<sub>2</sub>, CO<sub>2</sub>, and CO, and of CO and C with O<sub>2</sub> and O. Details of the model can be found in Ref. [1].

Figure 1a shows the flame structure of a 2-mm diameter Mg droplet burning in pure O<sub>2</sub> at 1 atm pressure and 300K temperature. Mg vapor diffuses out from the particle surface towards the counterdiffusing O<sub>2</sub>. The surface temperature is only a few degrees below the boiling point of Mg (1366K). The temperature profile rises with a very steep gradient near the surface to a short plateau region where a maximum temperature of 3220K is reached. After the complete consumption of the Mg vapor, the slope of the temperature profile starts decreasing at a faster rate. The predicted maximum temperature of 3220K is slightly lower than the maximum equilibrium temperature of 3398K (vaporization-decomposition point of MgO). This difference in maximum temperature values may be attributed to the lack of an accurate liquid-to-solid condensation model, which may also be responsible for the absence of a large concentration of MgO(l) in the plateau region where the temperature exceeds the melting point of MgO (3105 K) and where the liquid oxide is the dominant species. As a result of the high flame temperature, a large amount of O is also present in the high temperature region. The significant concentration of O<sub>2</sub> at the surface indicates that heterogeneous reactions may play an important role.

The flame structure of a 2-mm diameter Mg droplet burning in a pure CO<sub>2</sub> atmosphere at 1 atm pressure is shown in Fig. 1b. In this case, the oxidizer ambient temperature is 1000 K since no convergence is obtained in the simulation for lower temperatures. This temperature is in agreement with experiments [1] where the Mg sample is ignited by heating the CO<sub>2</sub> gas around it. The maximum combustion temperature predicted by the simulation is 2645 K, which is lower than the equilibrium temperature of 3174 K. The cause of this discrepancy in maximum temperature values follows the same reasoning as in the Mg-O<sub>2</sub> case. The reaction zone observed in Fig. 1b is narrower than in the Mg-O<sub>2</sub> simulation, suggesting a slower molecular diffusion process in the case of CO<sub>2</sub> as the oxidizer. This result is in qualitative agreement with the low-g experiments where longer burning times are observed in Mg-CO<sub>2</sub> flames.

## PLANAR LASER INDUCED FLUORESCENCE EXPERIMENTS

A PLIF technique has been developed to provide spatially resolved measurements of magnesium oxide (MgO) in the reaction zone of bulk samples of Mg burning in O<sub>2</sub> and CO<sub>2</sub> atmospheres. Mg cylinders (4-mm-diam and length) are radiatively ignited in normal-g with a xenon-arc lamp. Samples are positioned at the center of an alumina block. No forced flow of oxidizer is imposed on the samples, but a strong natural convection plume develops as a result of heating and combustion. A Nd:YAG pumped dye laser is used as the excitation source. Detection is accomplished using a gated intensified CCD camera fitted with a set of bandpass, shortpass, and neutral-density filters. This excitation/detection scheme enables PLIF measurements in the presence of significant laser scattering from combustion-generated solid MgO particles. Magnesium-oxide PLIF is accomplished by excitation of the MgO B<sup>1</sup>Σ<sup>+</sup> - A<sup>1</sup>Π (0,0) transition, at approximately 601 nm, and observation of the resulting B<sup>1</sup>Σ<sup>+</sup> - X<sup>1</sup>Σ<sup>+</sup> fluorescence from 490 to 501 nm. Details of the experiment can be found in Ref. [3].



**Figure 1.** Numerical simulation of the flame structure of a 2-mm diameter Mg droplet burning in (a)  $O_2$  and (b)  $CO_2$  at 1 atm.

As indicated by the PLIF images of MgO, the combustion of Mg in 21%  $O_2$  (balance Ar) at 1 atm is shown to be a predominately gas-phase reaction with quasi-steady combustion. The reaction zone is approximately 7-8 mm in width and the reaction time is  $11.7 \pm 1.5$  seconds. Combustion exhibits a build-up period of approximately 1.5 seconds, followed by a quasi-steady period of approximately 5.2 seconds, and a burn-out period of 5.5 seconds with a rapid fall-off.

Combustion of Mg samples in pure  $CO_2$  and in 80%  $CO_2$  (balance Ar) at 1 atm reveals a more protective surface layer as compared to  $O_2$ . This layer is seen to inhibit reaction at low partial pressures of  $CO_2$ , while the gas-phase reaction is intermittent at high partial pressures. The reaction proceeds in an unsteady, pulsating manner, as opposed to the quasi-steady combustion in  $O_2$ . Reaction times of approximately 5 seconds are shorter than in  $O_2$ , but unburnt Mg remains on the base. A representative PLIF image from a reaction burst of Mg burning in 80%  $CO_2$  is shown in Fig. 2a while Fig. 2b shows a surface plot of the PLIF signal vs. time and position along the vertical centerline of the sample melt. The surface of the melt is located at approximately 2.8 mm in Fig. 2b. As in combustion with  $O_2$ , the large discontinuous signal seen at  $t=0$  is due to scattered lamp light. Lamp shut-off occurs at  $t=1$  second. Several rapid pulsations are evident that appear for only one frame. The pulse durations are shorter than the 10-Hz laser rate. No continuous gas phase reaction is observed. Analysis of the melt following reaction shows a core of unreacted Mg surrounded by a black carbon-containing layer with white MgO deposits on top. It appears that this layer inhibits the transport of Mg into the gas phase, while periodic fracturing of the surface releases Mg vapor that rapidly reacts with surrounding  $CO_2$ . Gradual build-up of the carbon layer eventually extinguishes the reaction.

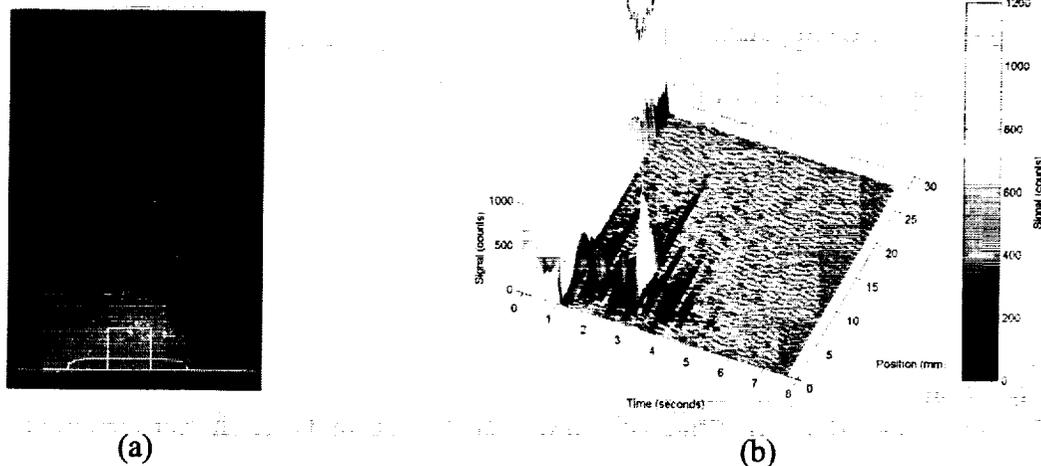
Analysis of the MgO PLIF signal strength reveals that the MgO mole fraction during combustion in 21%  $O_2$  is slightly below the equilibrium value. In the case of Mg burning in 80%  $CO_2$ , the MgO mole fraction is significantly below the equilibrium value. This discrepancy is not surprising considering the presence of heterogeneous reactions, incomplete reaction, and unsteady combustion.

## CONCLUSIONS

A numerical model and PLIF measurements are conducted to support the low-g combustion experiments of Mg- $CO_2$  to assess the feasibility of using metal- $CO_2$  reactions as an in situ resource utilization technology on Mars. The flame structure predicted by the one-dimensional, spherically symmetric, quasi-steady model shows a maximum temperature close to the

vaporization-decomposition point of the metal oxide, as well as the coexistence of the gaseous and condensed phases of the oxide product. It also confirms the experimental results of a diffusion-controlled reaction and a slower burning rate of Mg in CO<sub>2</sub> as compared to O<sub>2</sub>. The discrepancies between the numerical simulation and the experimental observations may be attributed to the absence of accurate condensation, radiation, and surface-reaction models.

The PLIF experiments provide confirmation of the pulsating nature of Mg-CO<sub>2</sub> combustion observed in the low-g tests and also prove the feasibility of using the PLIF technique to determine the spatial variation of particles and some species concentrations. Although this study indicates that Mg energetically reacts directly with CO<sub>2</sub> in the gas phase, further work is necessary to establish the ignition and steady-state combustion methods required for a successful operation of a Mg-CO<sub>2</sub> rocket on Mars.



**Figure 2.** PLIF signal of MgO during combustion of Mg in 80% CO<sub>2</sub>, 20% Ar. (a) PLIF image during a gas-phase reaction burst showing outlines of the original cylindrical sample and the disk-shaped melt just before lamp shut-off; (b) time and vertical distribution of the PLIF signal.

#### ACKNOWLEDGMENTS

This work is supported by NASA under Grant NAG3-2220. The authors gratefully acknowledge the technical supervision of Robert Friedman from NASA Glenn Research Center.

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