COMBUSTION OF METALS IN REDUCED GRAVITY AND EXTRATERRESTRIAL ENVIRONMENTS

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The recent focus of this research project has been to model the combustion of isolated metal droplets and, in particular, to couple the existing theories and formulations of phenomena such as condensation, reaction kinetics, radiation, and surface reactions to formulate a more complete combustion model. A fully transient, one-dimensional (spherical symmetry) numerical model that uses detailed chemical kinetics, multi-component molecular transport mechanisms, condensation kinetics, and gas phase radiation heat transfer was developed. A coagulation model was used to simulate the particulate formation of MgO. The model was used to simulate the combustion of an Mg droplet in pure O_2 and CO_2. Methanol droplet combustion is considered as a test case for the solution method for both quasi-steady and fully transient simulations. Although some important processes unique to methanol combustion, such as water absorption at the surface, are not included in the model, the results are in sufficient agreement with the published data.

Since the major part of the heat released in combustion of Mg, and in combustion of metals in general, is due to the condensation of the metal oxide, it is very important to capture the condensation processes correctly. Using the modified nucleation theory, an Arrhenius type rate expression is derived to calculate the condensation rate of MgO. This expression can be easily included in the CHEMKIN reaction mechanism format. Although very little property data is available for MgO, the condensation rate expression derived using the existing data is able to capture the condensation of MgO. An appropriate choice of the reference temperature to calculate the rate coefficients allows the model to correctly predict the subsequent heat release and hence the flame temperature.

Quasi-Steady Model. Before simulating the transient phenomena, quasi-steady simulations are performed. The model correctly predicts the combustion parameters of methanol droplet combustion, used here as a test case. The flame temperature predicted by the quasi-steady simulator in both Mg/O_2 and Mg/CO_2 is very close to the vaporization-dissociation temperature and the melting point of MgO, respectively. However, the predicted high flame temperature in the Mg/O_2 case suggests the formation of MgO(l) in the flame and this formation is not captured in the present modeling effort due to the lack of the rate expression for the liquid-solid transition. The relatively small difference between the enthalpies of formation of MgO(l) and MgO(s) compared to the total heat released thus results in slight over-prediction of the flame temperature when only MgO(s) is included.

The predicted quasi-steady surface temperature, 1352 K for combustion in O_2 and 1317 K in CO_2, for a 1-mm diameter Mg droplet burning in both O_2 and CO_2 is close to the Mg boiling point at 1 atm (1366 K). Surface temperature being lower in the case of CO_2 is a direct result of the lower adiabatic flame temperature of the Mg/CO_2 system. The temperature profile near the surface shows a very sharp gradient due to the high enthalpy of vaporization of Mg. The

reaction of Mg with CO occurs very close to the surface and hence there is a step change in the temperature profile near the surface. The reaction with CO may very well be a surface reaction. For a given droplet diameter, the burning rate in O_2 is almost twice as fast as that in CO_2 for pressures above 1 atm. This ratio decreases with decreasing pressure.

The condensed phase oxide is treated as a gas-phase species with low diffusivity by arbitrarily assigning to it a high value of Lennard-Jones collision diameter in the transport property input data. The higher the value of the collision diameter, the higher is the accumulation of the oxide and greater is the hindrance to transport. The burning rate decreases with an increase in the collision diameter with a corresponding slight increase in the flame temperature, the flame standoff ratio, and the surface temperature for a given droplet diameter. The burning rate decreases with decreasing droplet diameter in both O_2 and CO_2 at a given ambient pressure. The extinction diameter is approximately equal to 30 micron in O_2 and 100 micron in CO_2 at 1 atm pressure. The burning rate in both O_2 and CO_2 increases with increasing ambient pressure. The increase in the flame temperature for a given diameter of Mg droplet is higher in O_2 than that in CO_2 for a given increase in pressure. The difference in the boiling point and the quasi-steady surface temperature of the Mg droplet of a given diameter decreases in O_2 and increases in CO_2 with increasing ambient pressure. The low-pressure extinction limit is found to be approximately equal to 0.05 atm for O_2 and 0.1 atm for CO_2.

Fully-Transient Model. Before beginning the transient simulations of Mg combustion, transient methanol droplet combustion was simulated with good agreement to published data. The ignition process is modeled as a spark ignition source near the droplet. The required initial temperature of Mg droplet to undergo burning is 1100 K in O_2 and 1200 K in CO_2 at 1 atm pressure. These values are close to the ignition temperatures published in the literature. The surface temperature approaches the temperature predicted by the quasi-steady simulations and is almost constant throughout the droplet interior. The predicted extinction diameter is 50 micron for a 1-mm diameter Mg droplet burning in O_2 and the total burning time is 1.24 s. Inclusion of gas phase radiation decreases the gasification rate and consequently predicts higher burning time. For large droplets, the radiation loss increases the extinction diameter.

Although some molecular oxygen leaks through the reaction zone and reaches the droplet surface, its mole fraction at the surface is very small. The surface reaction rate being proportional to the square root of O_2 partial pressure at the surface is thus insignificant compared to the rate of evaporation and hence the combustion rate of Mg in vapor phase. The surface reactions are thus dominant only during the initial heating of the droplet. The surface oxide coating, however, may play an important role in the experimentally observed jetting and fragmentation.

The predicted extinction diameter is 60 micron for a 1-mm diameter Mg droplet burning in CO_2 and the total burning time is 2.52 s. As observed in the quasi-steady simulation, the Mg-CO reaction occurs very close to the surface and is responsible for the initial heat release. Along with a higher initial droplet temperature, the model predicts that a higher ignition temperature is required for combustion of Mg droplet in CO_2 than that in O_2. These both trends agree with the fact that combustion of Mg in CO_2 is a less energetic process than that in O_2.

The predicted burning rate constant is 1.14 s/mm^2 for the Mg/O_2 system and 2.52 s/mm^2 for the Mg/CO_2 system. The total burning time decreases with increasing pressure in both O_2 and

CO_2 for a given diameter Mg droplet, however, the decrease is quite small in CO_2. This is due to the smaller increase in the flame temperature (heat evolved) with increasing pressure in CO_2.

The predicted total burning times are almost twice as long as those observed in microgravity. However, the model is unable to simulate the jetting, fragmentation, and explosions observed in microgravity and thus the predicted burning times can be considered as the "quiet limit". Also important to note is that a strong ignition source is used in the experiments and the burning times are measured from the onset of a visible flame unlike the total burning time predicted by the model. However, the effect of this factor will certainly be less than that of the violent combustion observed in microgravity.

Simulation of an initially cooler droplet (surface temperature = 950 K) placed in a hotter O_2 environment (ambient temperature 1000 K) predicts the ignition temperature as 1090 K. The predicted burning time with the above initial conditions for a 1-mm diameter droplet at 1 atm pressure is 1.2 s.

The coagulation model predicts that MgO particles of about 0.03-micron and 0.2-micron diameter are present at the quasi-steady flame location in O_2 and CO_2 respectively. The higher particle diameter in CO_2 is a direct consequence of the lower flame temperature. Far away from the droplet surface (more than 100 times the droplet radius), particle size increases to about 3 microns. No quasi-steady solution is obtained when the thermophoretic velocity is included in the analysis. This result suggests that the particle accumulation observed in the experiments is a transient phenomenon and this may be responsible for the observed time-dependent explosions. From the present results it appears that the coupling of the coagulation model with the transient model is required to capture this process.

It should be noted that the combustion parameters obtained in both, quasi-steady and transient simulations of Mg particle combustion are affected by the approximations used in the condensation modeling and the reaction mechanism. The uncertainty in the reaction rate parameters is a major limitation of the results obtained here. Although the condensation rate expression and the kinetic mechanisms used in this work give the results in agreement with those observed (and expected), these rates are only approximate. The number of parameters is thus too large compared to the available experimental data. On the experimental part, data such as MgO properties, kinetics rate parameters, measured temperature and species profiles, and surface regression rate are required whereas future model development should focus on exact simulation of the experimental ignition conditions, and treatment for the oxide accumulation on the surface.

Rocket Motor Simulator. Future missions to Mars may use a rocket motor with Mg/CO_2 propellant for propulsion in the Martian environment. As an example of a practical application of the results of this study, a simulator was developed for the analysis of a future Mg/CO_2 rocket motor. This simulator can be used to predict the performance of the rocket motor and most importantly, when coupled with the coagulation module, it can predict the location of condensation and coagulation of the condensed phase MgO in the rocket nozzle. The simulation of MgO coagulation can help map the parameter space to explore the feasibility of an Mg/CO_2 rocket.

References

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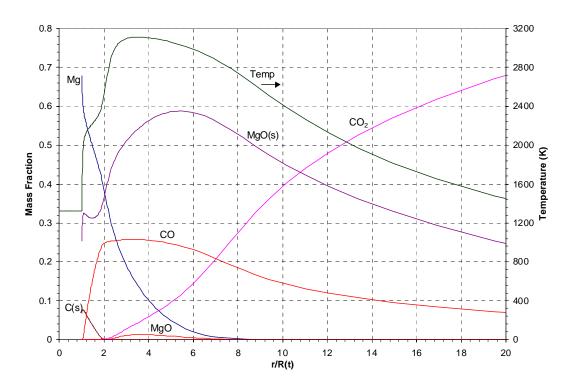
Figure 1. Species concentration and temperature profiles calculated during combustion of Mg in CO_2.