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Ignition and Combustion of Magnesium Particles in Carbon Dioxide

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Abstract. Metal-CO_2 propulsion is less known than in-situ resource utilization (ISRU) technologies. This concept, based on using Martian carbon dioxide as an oxidizer in jet or rocket engines, offers the advantage of no chemical processing for CO_2 and thus requires less power consumption than ISRU alternatives. In this paper, we study the burning behavior of the Mg in a CO_2 atmosphere to assess the feasibility of using Mg/CO_2 reactions as an in situ resource utilization technology for rocket propulsion and energy generation on other planets. From the experimental results, we can see that the critical ignition temperature increases with increasing the particle size and decreases with increasing the ambient pressure. In the CO_2 atmosphere, we found the complicated sequence of interaction modes including pulsating combustion in a wide range of ambient temperatures. The pulsation frequency is determined by the sample temperature at the phases of slow heterogeneous combustion between the flashes. The combustion mechanisms are discussed with consideration of processes in both a surface film and gas phase.

Introduction

In-Situ Resource Utilization (ISRU) is recognized as an enabling technology for exploration of Mars, which can significantly reduce the mass, cost, and risk of robotic and human missions [1-3]. The critical element in future missions is the large mass of propellant for a Mars ascent vehicle. Transportation of propellant from Earth to Mars requires tremendous increase in the initial mass of hardware in low Earth orbit as compared to prior no-return missions. Fortunately, the Martian atmosphere consisting of 95% CO_2 is the obvious and most promising in-situ resource. There are certain metals which can burn quite vigorously with CO_2 and release of energy. A chemical engine using metal-CO_2 propellants may be used for an ascent/descent vehicle in manned/unmanned sample-collection missions on Mars.

Owing to its high adiabatic flame temperature, oxidizer/fuel ratio, and heat per unit mass of fuel, as well as its low toxicity and ignition temperature, Mg has been identified as the most promising metal fuel with CO_2 as oxidizer [4,5]. The rocket using Mg/CO_2 propellant would make it possible to explore several sites on Mars during one mission without long-range rovers. To develop such an engine, we need the knowledge of Mg combustion in CO_2.

In recent years, Mg combustion in the atmosphere of CO_2 was studied by some researchers. Yuasa and Isoda studied ignition and combustion of large Mg discs in CO_2 and showed that Mg had easy ignitability and fast combustion rates in CO_2 [6]. They concluded that the combustion products consisted of MgO and CO. Shafirovich and Goldshlege conducted experiments with spherical particles up to 2.5 mm in diameter and found that the burning process was controlled by diffusion[7,8]. Legrand et al.[9] corroborated the experimental findings of Shafirovich and Goldshleger with particles in the 50μm to 2.5 mm range and established the $t_b = Kd_0^2$ relationship for the burning time.

In our studies, we introduced 1~35μm Mg samples, mounted on a thermocouple junction, into an electric furnace. The performed experiments haven a great body of new information on the combustion of Mg in carbon dioxide. On the whole, this process is characterized by important contributions of both gas phase and heterogeneous chemical reactions at the various phases. However, there is still a great deal to learn about the combustion mechanism. The purpose of the present experimental study was to investigate combustion of Mg particles in carbon dioxide over a wide range of ambient gas temperatures.

1, Experimental Apparatus and Techniques

The experimental setup (Fig.1) included a steel chamber (diameter 2[illegible] cm, height 20 cm), equipped with two glass windows and connected to a compressed CO_2 cylinder and an air outlet valve. An Mg sample (mass: 0.4 g, purity: 99.99%) mounted in the chamber was heated using an electric heating wire.

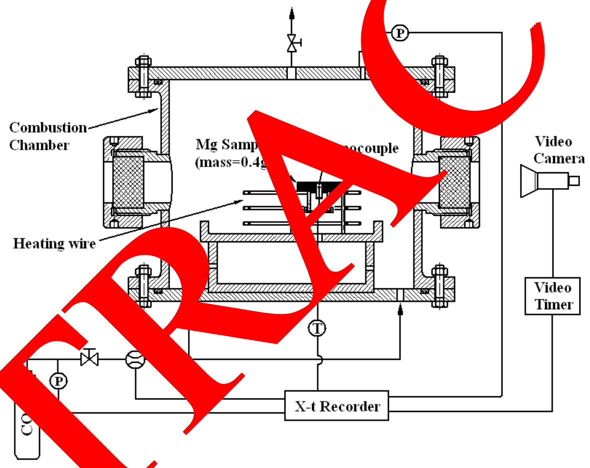

Fig.1 A schematic diagram of the experimental setup

The experiment was performed at the combustion chamber pressures P_a from 0.3 to 1.5MPa. Before each test run, the Mg sample in the chamber was heated in a CO_2 atmosphere at a predetermined pressure. In this study, the electric power of the heater was kept constant at 6000 W during ignition and combustion. The Mg sample temperature T_m in the chamber was measured using a K-type thermocouple with a 0.5 mm diameter. Condensed combustion products gathered after the experiment were analyzed by the SEM and EDS.

2, Experimental Results

The objective of the present experiments is to characterize the burning behavior of Mg in the different pressures of CO_2, as well as to obtain detailed information on the combustion of magnesium particles under different pressures. For this purpose, tests are conducted with spherical specimens with 1, 20, and 35μm diameter and at the pressure of 0.3, 0.6, 0.8, 1.0, 1.2, and 1.5MPa with pure CO_2. The following description of experimental results is based on the temperature measurements and film images used as diagnostic tools.

Well known picture of magnesium burning in CO_2 were observed in the experiments. The flame was very luminous and generated large quantities of white smoke. The brightness of spherical zone of white-blue colour with the center increased with ambient pressure increasing. In the different pressure, very slow reaction was observed at the lower ambient temperatures than the Mg melting point (923K), with the sample temperature being equal to the ambient temperature.

Fig.2 shows a typical example of the time variation of T_m from the start of a test run. The experiments show that Mg particles ignite in CO_2 if the sample temperature exceeds some critical value. Fig. 3 shows the critical ignition temperature of magnesium particles in the different pressures. From the experimental results, we can see that the critical ignition temperature increases with increasing the particle size and decreases with increasing the ambient pressure. Analysis of the obtained curves of the sample temperature variation shows that the oxidation law of Mg [illegible] the ambient temperatures is slightly lower than the Mg melting point.

Visual observations throughout the experiment give the following picture of the process. At first, the process beared a resemblance to the typical initial phase of heterogeneous metal oxydation with formation of adsorption centers, isolated areas of the film, and their subsequent coalescence. Ignition occurs at the top of the sample as a result of being heated. The ignition wave propagates across the sample, ultimately forming a spherical flame around it.

(a) 0.6MPa (b) 1.5MPa

Fig. 2 Pulsating combustion of 1µm Mg samples in CO_2 in the different pressure

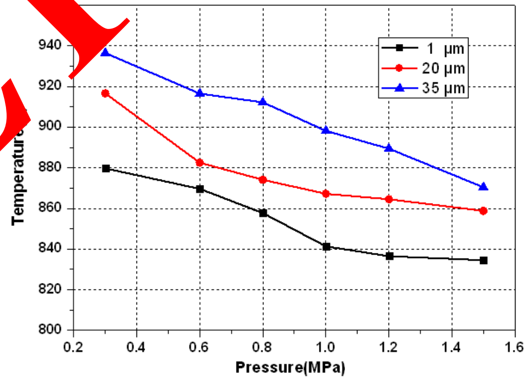

Fig. 3 Critical ignition temperature of magnesium particles in the different pressure

Combustion of Mg was pulsating in the CO_2 atmosphere, in the range of ambient temperature from 834 to 1100K. During a pulsation, a flash was observed. The pulsating combustion of Mg in CO_2 was studied in more detail with the reactor. It was found that the flash frequency and their total number significantly increase with a rise of the ambient temperature. Figure 2 present some typical curves of the sample temperature variation for the pulsating combustion mode. It is seen that there exists the sample overheating above the ambient temperature at the periods between the pulsations. We can say that the flashes occur on the background of slow heterogeneous combustion. It is the sample temperature at the heterogeneous combustion phases determines the flash frequency.

In the experiments, we observed the emergence of the light-colored spots with black points in the middle on the sample surface. The number of spots increases with time, and lastly a macro-crack arises on the surface film. A short time later, the sample surface is strongly deformed, thin-wall spherical bubbles appear on the surface. At the process end, the sample constitutes a conglomerate of gray spherical empty deposits. During the slow heterogeneous combustion, the sample is growing when the ambient temperature is slightly higher than the Mg melting point. The size increase becomes smaller and the average density of the condensed deposit increases with increasing the ambient temperature. Several explosions occur during the first seconds of combustion. Slow, steady burning follows afterwards with the increasing accumulation of solid products in an outer shell. The sample remains black with some solid white oxide forming in the surface. After a test, very fine particles of magnesium oxide are collected in web-like formations (figure 4).

Our observations indicate to a determining role of the product layer. The liquid metal is supplied to the evaporation surface by capillary forces. Thickening of the product layer during the process leads to increasing the effective surface of evaporation and reaction.

Let us discuss possible reasons for the pulsating combustion. As pointed out above, the flashes are separated by phases of slow heterogeneous combustion. The higher the sample temperature at these phases, the shorter the period between the flashes. This indicates that the flash is a result of the product layer development.

Fig. 4 Photograph of the condensed particles

One of the possible mechanisms for the flash initiation is a cracking of the surface film due to internal stresses. It is easily understood why at the equal ambient temperatures we observed the pulsating combustion in CO_2. As mentioned above, the flame temperature is close to 3000 K for Mg and CO_2. This correlates with the thermodynamic calculations.

Another mechanism is based on the balance of capillary forces on meniscus surfaces of liquid metal in pores of the surfaces film. It is thought that Mg ignition consists of several stages characterized by the position of the maximum in the chemical reaction rate. According to this concept, the reaction transits from the metal surface to the porous film, and then to gas phase, during the ignition process. We intimate that when the metal temperature is approaching to the boiling point, the vapor bubble arises inside the drop. Pressure in the bubble exceeds the ambient pressure by the value of capillary pressure. This leads to the fast flow of liquid in the pores and exclusion of the contained vapor. As a result, the flash occurs. The heat flux from the vapor-phase reaction zone is sufficient for the stable existence of the bubble and the steady vapor-phase burning.

The experiments and thermodynamic calculations of the adiabatic combustion temperatures and equilibrium product compositions for a Mg/CO_2 system at various reactant ratios allowed us to elucidate the mechanism and characteristic features of magnesium particle combustion in CO_2 and to propose an appropriate model for this process. Figure 5 shows schematic representation of Mg particle combustion in CO_2.

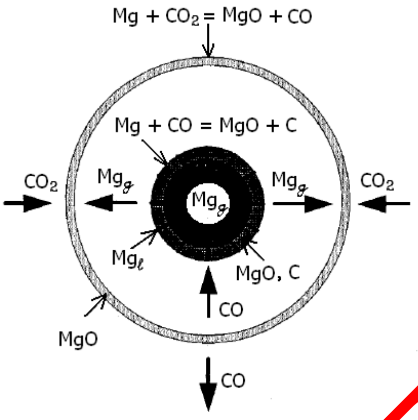

Fig. 5 Schematic representation of Mg particle combustion in CO_2

According to the proposed model, two spatially separated chemical reactions occur simultaneously in the course of Mg particle combustion in CO_2. The gas-phase reaction $Mg + CO_2 = MgO + CO$ (1) occurs at some distance from the surface of vaporized metal drop, while the reaction $Mg + CO = MgO + C$ (2) occurs near the surface, practically heterogeneously. The reactions are coupled by means of the CO mass transfer. Heat release in both the reactions play an important role in the process of metal drop evaporation.

In this light we portray the combustion process of a magnesium particle qualitatively as follows. Carbon dioxide diffusing toward a spherical Mg droplet reacts with Mg vapor diffusing away from the droplet, in accordance with Eq. (1). As the reaction (2) proceeds, carbon monoxide builds up at its front, and the concentration of carbon dioxide decreases.

The carbon monoxide produced in the gas-phase reaction (1) diffuses both toward the surface of the droplet and out to infinity. The part of it that moves toward the droplet enters into the heterogeneous reaction (2) with the magnesium. Magnesium oxide evolves in condensed form in this reaction. Carbon also remains on the surface of the droplet, as evinced by the black coloration of the condensed combustion products.

3, Conclusions

This investigation studies the burning behavior of Mg in a CO_2 atmosphere to assess the feasibility of using Mg/CO_2 reactions as an in situ resource utilization technology for rocket propulsion and energy generation on other planets. From the experimental results, we can see that the critical ignition temperature increases with increasing the particle size and decreases with increasing the ambient pressure.

A regime of slow heterogeneous combustion has been revealed. In this regime, the mass of the sample increases according to a law similar to the self-catalytic law at a temperature of the medium higher than the melting point of magnesium. The range of existence of the given regime in the scale of ambient temperatures separates the slow-oxidation and fast vapor-phase combustion regions. It has been shown that the macro-kinetic self-acceleration of the reaction in the regime of slow heterogeneous combustion can be connected with capillary spreading of magnesium over the pores of the growing oxide film and better vapor elasticity above the surface of the meniscuses of the liquid metal in the pores.

Acknowledgements

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