Combustion of Mg and composite Mg·S powders in different oxidizers

Xinhang Liu, Mirko Schoenitz, Edward L. Dreizin*

New Jersey Institute of Technology, Newark, NJ 07102, USA

ARTICLE INFO

ABSTRACT

Micron-sized, spherical magnesium powders were ignited by a CO_2 laser beam and by injecting them in the products of air–C_2H_2 and air–H_2 flames. The same experiments were performed with composite Mg·S powders prepared by mechanical milling magnesium and elemental sulfur powders. The non-spherical Mg powder used to prepare composites was also explored in selected combustion tests. Flow conditions were varied in experiments performed in air with all materials. The combustion products were collected for particles burning in air; the products were studied using electron microscopy. Optical emission produced by burning particles was recorded using filtered photomultipliers. The emission pulses were processed to recover the particle burn times and their temperatures. Fine Mg particles burn in air very rapidly, with the burn times under 1 ms for particles finer than ca. 10 μm. The apparent trend describing burn time as a function of the particle size for such particles is $t\sim d^{0.5}$. The particles burn without generating a detectable standoff flame zone or producing smoke; combustion products are particles of MgO with dimensions comparable to those of the starting Mg powder particles. Both the particles burn times and their measured flame temperatures decrease slightly when particles are carried by faster air flows. The present experimental results is interpreted qualitatively assuming that the reaction occurs at or very near the boiling Mg surface and its rate is affected by both surface kinetics and the inward diffusion of oxygen. It is further proposed that the fine, solid MgO particles form either directly on surface of Mg droplet or in its immediate vicinity. Deposition of MgO crystals on liquid Mg causes little change in the particle burn rate. Combustion of Mg in air–C_2H_2 and air–H_2 flames occurs much slower than in air. Combustion of composite Mg·S particles follows a two-step process. In the first step, sulfur is evaporated. When the particles are heated by a CO_2 laser beam, rapid evaporation of sulfur leads to a sudden change in the particle velocity. Once sulfur is removed, the particles burn similarly to the pure Mg.

1. Introduction

Powders of metals and metallic composites or alloys are commonly used as high energy density fuel additives or primary fuels in pyrotechnics, explosives, and propellants [1–3]. This explains the sustained interest in metal combustion over many decades. Combustion of metal particles is also fascinating visually, producing bright luminous streaks with distinct spearpoints and/or micro-explosions [4–6]. Very early models of metal particle combustion were similar to that of a droplet of a hydrocarbon fuel, involving evaporation of the fuel from the particle surface and combustion occurring in the standoff flame and rate limited by gas phase diffusion processes [7]. For some metals, like boron, zirconium, titanium and others, this approach was found to be simply inappropriate as indicated by the Glassman criterion, comparing the boiling or saturation temperatures for the metals and their combustion products,

metal oxides [8]. For such metals, primary oxidation reactions were found to occur directly on the metal surface. For metals with relatively low boiling points, such as Mg, the hydrocarbon-like combustion model seemed more fitting. In his seminal papers [9,10], Law, analyzed an effect unique to combustion of such metals. The model proposed by Law accounted for the formation of condensed combustion products or smoke particles, which distinguishes fundamentally combustion of volatile metals from that of hydrocarbon droplets. The condensation of products was analyzed as well as their migration from the flame zone both towards and away from the burning particles. Such effects were found to be affecting the heat and mass transfer for the burning particles and thus the particle burn rates. The model served as the foundation of more detailed analyses, e.g., predicting the sizes of forming condensed MgO particles [11]. Later it was recognized that similar effects involving transport of combustion products from the flame might be responsible for the observed irregularities in metal particle combustion, causing micro-explosions [5,12].

Despite substantial progress in understanding metal combustion in recent years, catalyzed lately by development of nano-sized

---

and nanocomposite metal fuels [13–15], there were only a few studies focused on combustion of Mg powders, all dealing with coarse particles [16–19]. Primary applications of Mg as a fuel have been in pyrotechnic devices, although recently, there was interest in its combustion as a component of reactive materials designed for agent defeat applications [20,21]. In particular, the interest in Mg-based reactive materials has been motivated by development of composite Mg·S powders shown to release biocidal combustion products useful for agent defeat weapon systems [22]. Understanding the combustion mechanisms for such new Mg-based reactive materials and correlating these mechanisms with those of pure Mg powders are, therefore, of significant importance.

Under most circumstances, Mg is expected to primarily burn in the vapor phase, generating refractory condensed MgO particles. While the early studies by Law [9,10,23] have established a general approach to analyzing such combustion systems, the results and models are verified and relevant for particles coarser than ca. 50 µm, whereas most applications use finer powders. Combustion of fine powder particles and respective effects of varying flow conditions, involving, for example, turbulent flow, or effect of different oxidizing environments, e.g., air vs. steam vs. mixture of carbon dioxide and steam, remain largely unexplored. Detailed experimental data, necessary to justify further models are scarce. One of the main difficulties in quantifying the metal particle burn times experimentally is associated with broad size distributions of most metal powders, including Mg. Previously, it was common to assign the average measured burn time to the average particle size; however, this methodology could be misleading. Recently, an approach was proposed enabling one to quantify the particle burn times correlating particle size distributions with the statistical distribution of the measured burn times [20,24–26]. Results were published for combustion of fine Mg powders in laminar flames produced by hydrogen and oxygen [26] and by air and acetylene [20]. Here, this approach is further exploited to characterize combustion of particles of Mg and Mg·S composite powders in air at different flow conditions. In addition, the database for combustion of both materials in air–hydrogen and air–acetylene flames is extended.

2. Materials

Three powders are investigated in this paper: two commercial magnesium powders and a custom-prepared composite of magnesium and sulfur. A spherical, 99.8% pure magnesium powder was obtained from Hart Metals. Its nominal particles sizes vary in the range of 1–11 µm. Scanning electron microscopy (SEM) images of this powder were shown in an earlier publication [20]. SEM images confirmed that the particles were spherical and their sizes varied within the range specified. The second, non-spherical, 99.8% pure, − 325 mesh magnesium powder used was by Alfa Aesar Stock #10233. Its SEM image was shown in Ref. [26]. The latter powder was used as a starting material to prepare composite Mg·S powders by mechanical milling and thus it was added as an extra reference material for selected experiments in the present study. A SPEX Certiprep 8000D shaker mill was used to prepare the composite Mg·S powder. The powder was prepared in hardened steel milling vials using + 100–170 mesh glass beads as milling media. Each vial was charged with 2.15 g of Mg and 2.85 g of sulfur, with a total powder mass of 5 g, comprising the stoichiometry of MgS. The milling media to powder mass ratio was 5. The milling time was 1 h. Images of this powder taken by a LEO 1530 SEM are shown in Fig. 1. A phase contrast enables one to readily distinguish between darker surfaces of Mg and lighter surfaces of S. Using glass beads resulted in effective coating magnesium particles with sulfur rather than in a fully-dense composite, for which both components would be mixed volumetrically. At the same time, using glass beads minimized the probability of initiating the reaction between Mg and

S mechanically, which was shown to occur readily when Mg and S were milled using steel balls [22]. The particle shapes are somewhat similar to those of the starting, − 325 mesh Mg powder, although some particles are flattened during the milling. Whereas the sulfur coating is discontinuous, it is well mixed with magnesium and no uncoated Mg particles or separate S fragments were detected.

Particle size distributions for all three powders are shown in Fig. 2. These size distributions were correlated, as discussed further, with the measured distributions of the particle burn times; the correlations yielded the effect of particle size on its burn time for each material. For both magnesium powders, the particle size distributions were reported previously [20,26]. These same size distributions recast in terms of particle numbers rather than volume fraction were used here and shown in Fig. 2 for these powders. For Mg·S composite, the powder was fed through the feeder, as in combustion experiments (see below), and collected on a double sided carbon tape placed above the feeder's nozzle. This way, the particle sizes analyzed were corrected for possible agglomeration and/or size classification of the powder by the feeder. SEM images of the collected powder particles were taken at different magnification and particle size distributions for each magnification were obtained using image processing. The different size distributions were combined, accounting for the difference in the number of particles within individual size bins per unit of the substrate area observed for each magnification. Details of such analysis were discussed elsewhere [25].

3. Experimental details

Combustion of all materials was experimentally characterized in three oxidizing environments: room temperature air, combustion products of an air–acetylene flame, and combustion products of air–hydrogen flame. In all experiments, the same, custom built powder screw-feeder was used descried in detail elsewhere [27]. The emission of the burning particles was recorded using two R3896-03 Hamamatsu photomultipliers (PMTs) equipped with 700 and 800 nm interference filters. The signals were saved and processed using a 16-bit PCI-6123 data acquisition board by National Instruments and Lab-view softwasre.

The combustion experiments are illustrated in Fig. 3. For experiments in air, see left panel of Fig. 3, particles exited the nozzle moving up and crossed the focused CO_2 laser beam directed horizontally. SEM stubs with double sided sticky carbon tape and with an aluminum foil (particle collection substrates in Fig. 3) were placed above the particle jet to collect combustion products. The products were examined using SEM. The air flowrate for feeding particles was initially set to 1.25 L/min. It was varied in subsequent experiments between 0.23 and 3.4 L/min. Variation in the air flowrate resulted in different velocities of the particles crossing the laser beam. These velocities were measured using images of particles moving in a modulated green laser sheet. The measurement results are shown in Fig. 4. It is observed that particles moved with velocities in the range of 0.2–2.5 m/s. The laser power was set to 87.5 W, which reliably ignited particles in all experiments. It was noted that at the laser power of ca. 50 W, Mg powders did not ignite. The beam was focused using a ZnSe lens to about 250 µm diameter. Thus, the maximum time for the particles to cross the laser beam varied from 0.2 to 1.25 ms, for the fastest and slowest moving flows, respectively. In a set of experiments, a cylindrical air knife was used to create a turbulent flow pattern just above the laser beam, where particles were expected to burn. Details of the experiments with the turbulent flow patterns were described earlier [24,28].

In different experiments, particles were axially injected into flames, as schematically shown in the right panel in Fig. 3. Two