Condensed-Phase Modifications in Magnesium Particle Combustion in Air

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Free-falling individual magnesium particles were produced and ignited using a pulsed micro-arc and burned in air. Particle combustion temperatures were monitored in real time using a three-color pyrometer. Black-body and MgO radiation histories were separated using interference filters and compared with each other. Particles were rapidly quenched at different combustion times and their elemental compositions were studied using energy and wavelength dispersive spectroscopy techniques. Particle combustion times and radiation histories were consistent with those reported previously. Measurements of the elemental compositions of quenched particles showed substantial amounts of dissolved oxygen, consistent with recent metal particle combustion studies using the same experimental technique. An estimate based on the rate constants reported in the literature for the magnesium vapor-phase burning, showed that the reaction rate is insufficiently fast to prevent oxygen gas diffusion through the vapor-phase stand-off flame to the particle surface. A combustion mechanism is discussed in which oxygen approaching the surface of a burning particle is dissolved in magnesium producing a new liquid-phase Mg-O solution. The heterogeneous reaction of oxygen dissolution begins simultaneously with the vapor-phase combustion and later on the heterogeneous reaction becomes the primary combustion mechanism. After the solution becomes saturated, an exothermic phase transformation, Mg-O_solution → Mg + MgO, occurs that contributes to the production of large amounts of oxide detected on the surfaces of partially burned particles and causes the observed oscillations and peaks in particle radiation. © 2000 by The Combustion Institute

INTRODUCTION

Magnesium combustion in air has been studied for a long time; early research proposed that the reaction occurs in a vapor phase [1], based on the low magnesium boiling point (of 1090°C). The observations of the extended stand-off combustion and condensation zones around burning magnesium particles supported this hypothesis. Oxide layers were, however, also consistently observed on the surface of partially burned magnesium particles. Accordingly, several experimental studies dealing with large particles and bulk samples indicated the significance of the surface Mg-O reactions during ignition and combustion of magnesium [2–5]. The irregular shape of the burning magnesium particles, unusual for metal droplets, was documented previously [6] and attributed to the formation of bulky solid oxide coatings. Formation of surface irregularities and thick (up to 40 μm) oxygen-containing layers with an Mg/O mass percent ratio of 80/20 (in addition to stoichiometric MgO layers with an Mg/O mass percent ratio of 60/40) was observed when 20-mm-diameter, 2.6-mm-thick magnesium discs were ignited in an air stream [2].

The radiation spectrum of burning magnesium ribbons was examined in detail in Refs. 7 and 8 and strong ultraviolet (UV) bands were observed that could not be produced by either Mg atoms or MgO molecules. Shevtsov et al. [5] observed continuous enlargement and, eventually, bursting of magnesium particles heated and oxidized in air and attributed this to the release of relatively small amount of hydrogen that had originally been contained in the metal. Because Brzustowski and Glassman [7] observed the UV
emission attributed to MgOH when there was no hydrogen or water present in the gaseous environment, the presence of hydrogen in magnesium was also proposed by Shevtsov et al. [5] as an explanation of those UV emission bands. In addition, the release of hydrogen gas with a small amount of unreacted magnesium vapor was proposed as a cause of the flashes observed at the end of magnesium combustion.

Another intriguing spectroscopic study of Mg particle combustion has been recently reported by Valov et al. [9]. The radiation times of Mg and MgO vapors were significantly shorter than the total particle radiation time. The interpretation proposed by Valov et al. was that the combustion ends when the radiation of the Mg and MgO vapors disappears and the continuing particle radiation is produced by the slowly cooling incandescent oxide shell. However, the radiation trace shown in their study indicated an increase in the particle radiation intensity after the radiation bands produced by Mg and MgO vapors disappeared. This radiation increase is not likely to be produced by an inert oxide shell that is being cooled down. Alternatively, exothermic surface and internal reactions could have sustained the high particle temperature and caused the observed extended black-body radiation.

Recent experimental research on combustion of various (other than magnesium) metal particles [10–15] indicated that heterogeneous reactions and internal phase changes play important roles in the combustion of many metals, including aluminum. In those experiments, free-falling uniform metal particles were formed and ignited in a pulsed micro-arc and burned in air and other oxygenated atmospheres, and their temperatures were monitored using an optical pyrometer. Partially burned metal particles were rapidly quenched, and their compositions and structures were analyzed. Because that approach proved effective with a number of metals, it appeared useful to conduct similar experiments for magnesium particles to investigate the relationship between possible surface and internal reactions and particle combustion behavior.

**EXPERIMENTAL**

Magnesium particles were produced and ignited using a pulsed micro-arc method that was employed in our previous metal particle combustion experiments [10–15]. In this method, a pulsed micro-arc is initiated between a tool-cathode and a consumable metal wire, which serves as an anode. The tip of the metal wire is melted by the micro-arc pulse and a molten droplet is separated from the wire due to the pressure from the discharge. Each pulse results in the production of a single metal droplet. Hot metal droplets ignite immediately when they are formed in room air. Monodisperse metal droplets with predetermined diameters in the 100–500 \( \mu m \) range were produced using this technique using Cu, Fe, Al, Ni, Ti, Ta, Zr, Mo, and W wires. Because magnesium wires were hard to find, strips of magnesium ribbon were used in this work. A 99.8% pure, 0.15-mm-thick and 3.175-mm-wide magnesium ribbon (Johnson Matthew) was cut into 0.3–0.6-mm-wide strips that were mounted in the electrode holder and served as the consumable anode. Particles with diameters ranging from 250 \( \mu m \) to 400 \( \mu m \) were produced.

In the combustion experiments, particles burned in room temperature air. Particle radiation was monitored using a fiberoptic trifurcated bundle fed to three HC120-01 Hamamatsu photosensor modules, each equipped with an interference filter. The photosensors’ outputs were fed to a PC-based multichannel data acquisition system. This photosensor data acquisition unit served as a three-wavelength color pyrometer. In order to minimize contributions of the Mg and MgO bands in the measured radiation, the interference filters were chosen with the wavelengths of 436, 589, and 640 nm (10 nm half-bandwidth) that did not overlap with the Mg and MgO radiation bands [16]. The pyrometer was calibrated using a strip-lamp in the temperature range of 1600–2400°C. The same optical setup was also used to compare the radiation of a vapor-phase MgO band produced by a burning particle with the black-body radiation. Using the same fiberoptic bundle and three interference filters with very close wavelengths, 500, 510, and 532 nm, installed for these experiments, the
MgO band radiation (500 nm) could be separated from the black-body radiation (510 and 532 nm) recorded simultaneously.

Burning magnesium particles were quenched by their impingement onto aluminum foil for subsequent cross-sectioning and internal composition analysis. Samples of the quenched particles were embedded into epoxy, cross-sectioned, and polished to measure the internal particle composition. The cross-sections were etched using a water solution of oxalic acid dehydrate to avoid the effect of metal smearing during the polishing that was expected to be noticeable for such a soft metal as magnesium. Etching also revealed the sample microstructure better. Some particles were impinged onto silicon wafers for the subsequent scanning electron microscopy (SEM) analyses of their surface structure and composition. Surfaces of the quenched particles were studied using a Philips XL30 Field Emission Scanning Electron Microscope with an optimum image resolution of 2 nm. Internal compositions of both particle surfaces and cross-sections were surveyed using a PGT position tagged electron dispersive spectroscopy (EDS) system. More detailed composition measurements for the particle cross-sections employed a Cameca SX50 X-ray microanalyzer.

HYDROGEN IN MAGNESIUM USED

Since it has been proposed that noticeable amounts of hydrogen could be present in magnesium and play a role in its combustion [5], the gases that evolve at elevated temperatures from the magnesium used in these experiments were measured using gas chromatography. A sample of magnesium ribbon (0.2–0.3 g) was placed in a quartz tube. The tube was evacuated down to less than 0.1 mm of mercury, heated to 60–80°C for 2–3 min and flushed with argon; this procedure was repeated three times to remove any possible water from the surfaces. Then the tube was evacuated again and an oxygen–acetylene torch was positioned close to the quartz tube to heat the magnesium sample until it melted and to identify the amount and composition of the gas released. (A “blank” test was also conducted with an empty quartz tube similarly heated to a high temperature; it verified that the quartz tube alone did not release gases upon heating.) After melting was initially observed, heating continued for about a minute after which the torch was removed. In order to collect a gas sample, the tube was filled with argon to atmospheric pressure. Gas was analyzed using a Porapak N 12’ × 1/8” (80/100 mesh) stainless steel column installed in a 5830A Hewlett Packard Gas Chromatograph (GC). This column was chosen because it allowed the separation of hydrogen (reported by Shevtsov et al. [5] to emanate from the heated magnesium) from the argon diluent. The GC was initially calibrated using a Scott calibration gas mixture of 1% of hydrogen in nitrogen.

Because the magnesium cooled down during the refilling of the quartz tube with argon and during the sampling, the gas released from the magnesium at a high temperature could be reabsorbed. However, it was expected that the bulk of the gas released would quickly diffuse throughout the vessel under vacuum and then, after the vessel was filled with an atmospheric pressure argon, the diffusion rate back to magnesium would slow down significantly.

As expected, hydrogen was detected in the gas samples. Analyses of several gas samples collected one after another with intervals of about 2 minutes have shown that the hydrogen content declined indicating that reabsorption was actually occurring when the sample and quartz walls cooled. There also were additional peaks on the recorded GC traces indicating that other gas components were released from the metal; however, these were not identified. The maximum amount of hydrogen was measured as 0.28% of the gas mixture (after the tube was refilled with argon to 1 atm) in an experiment in which a 0.3 g magnesium sample melted. In order to estimate the full amount of hydrogen released from magnesium, the volume from which the gas was sampled (including the quartz tube, attached fitting, and a pressure gauge) was determined to be 56 ± 10 ml. Therefore, the entire amount of hydrogen released was about 0.177 ± 0.02 ml, or about (7 ± 0.8) × 10⁻⁶ mol of gas. Based on the comparison of the masses of magnesium and hydrogen, it was concluded that the hydrogen content in magnesium was only about (1.8 ± 0.2) × 10⁻⁵ mole %. However, the volume of this hydrogen when it is
gasified is close to the volume of the condensed magnesium. This assessment is consistent with that reported by Shevtsov et al. [5].

The presence of small amounts of hydrogen in magnesium is not unexpected because the electrolytic process that is currently in greatest use to manufacture magnesium employs a cell feed consisting of slightly hydrated magnesium chloride [17].

It is unusual that the gas is released upon heating the metal, when it is expected that the solubility of hydrogen in magnesium would increase at higher temperatures [18]. This solubility trend, however, is only valid for the interstitial solid solution of H in Mg, whereas hydrogen might also be present as a component of a different phase, e.g., Mg(OH)₂. It is known that a thin Mg(OH)₂ film always is present on magnesium surfaces [18] and it is also known that it starts to decompose at 350°C [17]. The products of the Mg(OH)₂ decomposition are MgO and H₂O below 420°C and MgO and H₂ above 440°C [18]. Thus, gaseous hydrogen can be released when magnesium is heated. This hydrogen release could cause deformation of and cracks in the metal particles increasing their surface/volume ratio that is very important during magnesium ignition, when the metal is being initially heated.

RESULTS

General Observations

Combustion times in air were in the range of 70–160 ms for the magnesium particles with diameters in the range of 250–400 μm. These combustion times correspond to the burning rate constant \( \beta = \frac{d^2}{\tau} \), where \( d \) is particle diameter and \( \tau \) is particle combustion time, in the range of \( 0.89 \cdot 10^{-2} – 1.0 \cdot 10^{-2} \text{ cm}^2/\text{s} \). This is in good agreement with the experimental \( \beta = 1.28 \cdot 10^{-2} \text{ cm}^2/\text{s} \) reported previously for magnesium particles burning in air and argon/oxygen mixtures with the oxygen mole fraction of 0.232 [6]. Also, particle streaks revealed spinning, jetting, and radiation jumps consistent with the previous observations.

Comparison of MgO and Black Body Radiation

Two typical examples of the simultaneously measured radiation traces recorded at the wavelengths of 500 nm (an MgO band) and 510 nm (black-body radiation) for two magnesium particles of different diameters are presented in Fig. 1. An additional black-body radiation trace was always measured using a 532-nm filter and it was always very consistent with the 510-nm trace. Therefore, in order to simplify the presentation, only two radiation traces are shown in Fig. 1 and discussed further. For a 400-μm-diameter particle, one can clearly see that during the first 90–100 ms of combustion the MgO radiation is significant and the radiation measured at the wavelength of 500 nm is greater than that measured at 510 nm. The two measured radiation traces become similar after 100 ms of combustion and stay similar for more than 70 ms until the radiation tapers off. This pattern is qualitatively consistent with that reported by Valov et al. [9]. Interestingly, oscillations origi-
nate in the radiation signals after the MgO vapor-phase band radiation becomes indistinguishable from the black-body radiation (time around 150 ms). For the smaller size (250-μm-diameter) particle, the comparison of the 500- and 510-nm radiation signals shows that the MgO band emission was significant during almost the entire combustion time and the 500- and 510-nm radiation signals became similar only during the last 10–15 ms of the 80-ms-long combustion event.

**Black-Body Radiation and Temperature Measurements**

Two typical examples of traces of burning particle radiation measured through a 589-nm filter and respective color temperature curves (inferred using radiation signals at 589 and 640 nm) are presented in Fig. 2. The radiation and temperature traces during the first few milliseconds should be omitted because the data acquisition system was affected by the micro-arc used to produce and ignite the droplet. Examination of the radiation traces shown in Figs. 1 and 2 shows a trend similar to that observed for aluminum particle combustion: during the initial period the radiation signal is relatively smooth, but later sudden changes and oscillations originate in the measured signal. As can be concluded from comparison of the traces presented in Fig. 2, radiation oscillations were observed for some but not for all of the radiation traces recorded. A peak at the end of the radiation trace was always observed, even though its amplitude could differ significantly for different particles.

Figure 2 shows that the measured particle combustion temperature increases during the initial time period and then remains constant. The maximum measured combustion temperature is about 3100°C, which is very close to the magnesium adiabatic flame temperature in air, ca. 3200°C [19]. The observed temperature decrease preceding particle extinction occurs later during combustion, at which time, as could be concluded from the comparison of 500- and 510-nm radiation signals, the vapor-phase flame disappears. However, at the same time radiation traces exhibit pronounced sudden changes in luminosity, as seen from Fig. 2. The radiation jumps and oscillations observed toward the end of combustion do not cause significant changes in the color temperature traces.

Because the measured temperature significantly exceeds the magnesium boiling point, it cannot be interpreted as the particle surface temperature. An attempt has been made to resolve particle surface and flame temperatures by blocking the stand-off flame radiation when a particle moved across a slot array adjacent to the particle trajectory [12, 13]. However, even in this case, a high, 3100 ± 100°C temperature was measured, indicating that the stand-off flame radiation still prevailed in the measured signal. Note that the slot array could be used only during the initial combustion period, when the burning particle initial velocity resulting from its acceleration by the micro-arc was well-defined. Later during combustion, the particle velocity amplitude and direction changed randomly and it was not possible to find a position for the slot array so that particles would consistently move perpendicular to the slots. It is most reasonable to assume that the particle surface temperature was equal to the Mg boiling point, 1107°C, which is always much less than the temperature
measured optically and characterizing the stand-off flame zone.

Quench Times

The particles quenched on aluminum foil did not weld into the foil as did particles of aluminum, zirconium, and titanium that were similarly quenched in our previous experiments [10–15]. For both aluminum foil and silicon wafer substrates used in this research, the quench times determined from the particle radiation traces were in the range of 0.5–2 ms. However, in some experiments low-intensity particle radiation was observed for as long as 6–7 ms after the particle touched the substrate.

Quenched Particle Surface and Adjacent Smoke Clouds

Quenched particles were not spherically shaped, unlike the Al, Ti, and Zr particles studied previously. Particles that burned for more than 50 ms were covered by a thick white oxide shell that was very brittle and was destroyed when a quenched particle was removed from its original position on the substrate. It was, however, possible to observe that a large portion of metallic material was contained within the oxide shell for particles quenched after combustion times as long as 110 ms, i.e., after the MgO radiation became indistinguishable from the black-body radiation. We could not examine particles that burned longer than 110 ms because they would not adhere to the substrate, instead they appeared to bounce and continue to burn in air.

Smoke cloud shapes surrounding quenched particles were observed to be spherically symmetric even though the particles in the middle of the clouds were not spherical. An example of a particle quenched on a silicon wafer and surrounded by a smoke cloud is shown in Fig. 3. It can be seen that the smoke cloud diameter is about 1.9 mm while the thickness of the smoke ring is about 0.45 mm. The smoke ring consisted of clustered fibers of less than 100 nm diameter (Fig. 4a). In addition, large oxide particles were observed that were also covered with fine oxide fibers (Fig. 4b).

In many cases the particles bounced from the substrate leaving a cloud residue. When an optical microscope was used rather than the SEM, a spot of black smoke was apparent in the center of such a cloud in sharp contrast with the white color of the spherical ring. When pronounced oscillations were observed in the particle radiation signal, a long black smoke “tail”
was observed adjacent to the quenched particle surrounded by the spherical white smoke cloud. The compositions of the black and white portions of the smoke cloud were analyzed using an EDS detector and it was observed that in both cases the smoke consisted of stoichiometric MgO.

The surface of the particles was not smooth; instead, multiple humps could be seen. An SEM image of a particle quenched on a silicon wafer is shown in Fig. 5a. The particle surface at a higher magnification was observed to be covered by a porous layer (Fig. 5b). The layer consisted of stoichiometric MgO as was found from the EDS spectra.

**Quenched Particle Cross-Sections**

An example of a cross-section of a quenched magnesium particle is shown in Fig. 6. Large voids, similar to that observed in Fig. 6 were found in most of the cross-sectioned particles. Numerous small voids could also be seen in the cross-sections of the particles for which the quench time was long, i.e., radiation was observed to persist for a period of 5–7 ms after they touched the cold substrate. These small voids were not detected for the particles for which the quench times were shorter than 2.5 ms (Fig. 7).

The elemental compositions of the quenched particles were identified using a Cameca SX50 microprobe. A standard of MgO supplied by Cameca was used to calibrate the oxygen concentration measurement, and a cross-sectioned sample of the Mg ribbon used to produce particles for the combustion experiments served as a standard for the Mg concentration measurement.

The porous surface layer visible on the surface of quenched particles was also clearly seen in the particle cross-sections (see Fig. 6). Its thickness was found to vary within the 5–40 µm range. Interestingly, similar layers were observed to exist on the internal surfaces of the large voids detected in magnesium particle cross-sections. The elemental composition of the cross-sectioned porous layer was measured using the electron microprobe analyzer and it was identified that for both internal and external surfaces the layers consisted of stoichiometric MgO. This is in agreement with the EDS measurements that were available for only the external layers observed on the surface of the intact particles quenched on silicon wafers.

A background oxygen level below 3.5 atomic % was measured in the cross-sectioned magnesium ribbon used in this research. This oxygen level was, most likely, due to a thin (optically
transparent) oxide film that formed on the cross-sectioned metal surface at room temperature. The results of the oxygen content measurements conducted for a group of the cross-sectioned quenched particles are presented on a scatter plot, Fig. 8. Each data-point represents the result of a single composition analysis that corresponded to either a maximum (empty symbols) or minimum (filled symbols) oxygen content detected within each particle. Since the phases with different oxygen contents were observed inside the particles, the scatter between the oxygen concentrations shown represents the difference between different phases rather than the statistical error in the measurement.

It can be seen that the phases with the oxygen concentrations as high as 10 atomic % were identified in the particles burning longer than 30 ms. Maximum and minimum oxygen contents measured in the particles quenched after less than 20 ms of combustion are very similar; however, phases with significantly different oxygen contents were detected in particles quenched at longer combustion times. In these particles, the oxygen-rich phases coexisted with the essentially pure magnesium for which the measured oxygen content did not exceed the background level. The point-by-point wavelength dispersive spectroscopy measurements yielded the most accurate elemental composition analyses available in this research, but the measurements were very time-consuming and therefore only randomly selected points within the particles were analyzed. No conclusions can be made, based on these results, regarding the average oxygen content in the particles and/or oxygen distributions within the particles. However, the phases with different oxygen content could be visualized using the backscattered electron (BSE) images on which a phase rich with a light element, i.e., oxygen, appears darker than a purer metal phase. An example of a BSE image of a portion of a quenched particle cross-section showing good contrast between the oxygen-rich and oxygen-lean phases is shown in Fig. 9a. In addition to the point-by-point analysis confirming respective high and low oxygen contents within each area, an oxygen map was created for this same portion of the particle cross-section using an electron microprobe (Fig. 9b). The brightness of the oxygen map image is directly proportional to the local oxygen content. It can be seen that the oxygen map correlates well with the BSE image, so that
the oxygen-rich and oxygen lean areas can be clearly distinguished. Such BSE images and corresponding oxygen maps show that oxygen-rich and oxygen-lean phases are intermittently mixed within the particle and that the total amounts of dissolved oxygen are significant (on the order of several atomic %). Much more extensive measurements would be needed to quantify the rate of oxygen acquisition in the burning magnesium particles.

**DISCUSSION**

**Particle Shape and Surface**

It was noted in these experiments that the shape of the particles became irregular very soon after their formation and large voids were detected in the particle interiors. As was discussed above, the hydrogen release is expected when magnesium is heated due to the decomposition of the Mg(OH)$_2$ film. This hydrogen gas release was directly observed to occur in the preliminary experiments in which magnesium was heated in vacuum. Therefore, it can be speculated that the hydrogen release was the cause of that initial particle shape irregularity.

The thick refractory MgO layer found on particle surfaces maintained, most likely, the irregular particle shapes. The presence of this layer with a heat conductivity much lower than that of metal could also explain why the particles did not weld into aluminum foil, unlike the Zr, Ti, and Al particles that have been welded into aluminum substrates in similar experiments [10–15]. Even though the heat conductivity of both magnesium and aluminum are high, the direct contact between the metals is prevented by the MgO layer with the low heat conductivity. Thus, the heat input into the aluminum foil from the magnesium particle becomes much less than it would be if metals contacted each other directly. This lower heat flow is insufficient to melt aluminum.

However, the origin of the bulk amounts of oxide on the particle surface is not obvious. Since the oxide was found on both external and internal (within voids) particle surfaces, it is unlikely that it was formed only by the deposition of oxide particles on the surface from the gas phase. Alternative routes would be a heterogeneous reaction on the particle surface and/or a phase separation occurring upon cooling of a liquid Mg-O solution, as discussed below.

**Oxygen Dissolution and Its Role in the Reaction Mechanism**

Direct evidence of dissolved oxygen being present within magnesium particles has been provided by the electron microprobe measure-
magnesium. Additional evidence of the presence of the dissolved gas within burning particles is the formation of multiple, small, spherical voids in the particles that were slowly quenched (cf. Fig. 7b). These voids could have been produced by a gas release when the gas solubility decreased during particle cooling. While the complete phase diagram for the Mg-O binary system is not available, it is known that the solubility limit of oxygen in solid magnesium is very low, well under 1 atomic % [18]. Based on the thermodynamic considerations, melting points, and continuity requirements, a phase diagram was proposed for this system by Massalaski et al. [18]. This phase diagram implies that a liquid Mg-O solution forms at temperatures exceeding the Mg melting point and the solubility limit for oxygen changes from about 0.1 to 50 atomic % as the temperature increases from 650°C (Mg melting point) to 2827°C (MgO melting point). Therefore, the oxygen-rich phase detected within quenched particles could have existed as a liquid solution in the burning particle and remained within the rapidly quenched particle as a metastable phase.

It is unlikely that the transport of the condensed MgO would have resulted in the formation of the Mg-O solution because solid MgO is known to be insoluble in Mg. This is consistent with the fact that a well-defined oxide film was present on surface of Mg particles. Alternatively, a phenomenon called “oxygen leakage” observed for counterflow diffusion flames with a variety of liquid and gaseous hydrocarbon fuels, e.g., [20, 21] and consisting of the oxygen gas penetration to the fuel-rich part of the flame could have occurred in these magnesium particle combustion experiments. The possibility that oxygen gas could diffuse through a flame to the surface of a burning magnesium droplet was explored by constructing a simplified numerical model that included both the reaction of magnesium vapor with the oxygen in air and the diffusion of oxygen through a spherically symmetric magnesium flow created by vaporization of the magnesium droplet.

The approach was to obtain the most conservative lower level estimate for the amount of oxygen near the surface. The predicted adiabatic flame temperature for magnesium in air (T = 3473 K or 3200°C) [19] that is only slightly higher than the experimentally determined flame temperature (3000–3100°C) was assigned to the flame zone instead of solving an energy equation to determine the temperature profile.

The basic steady-state species conservation equation was used to compare the chemical reaction rate with the rate of oxygen diffusion and convection:

$$\nabla \cdot (\rho \bar{U} Y_{O_2}) - \nabla \cdot (\rho D \nabla Y_{O_2}) = \dot{\omega}_{O_2} W_{O_2}$$

(1)

where \(\rho\) is the gas mass density, \(\bar{U}\) is the mass velocity vector, \(Y_{O_2}\) is the oxygen mass fraction, \(D\) is the oxygen diffusion coefficient estimated as \(D = D_0 (T/T_0)^{1.5}\) [22] where \(D_0 = 0.178 \text{ cm}^2/\text{s}\) [23] is diffusion coefficient at the temperature \(T_0 = 273 \text{ K}\), \(W_{O_2}\) is the molar weight of oxygen, and an Arrhenius type reaction rate formula was used for the oxygen reaction rate \(\dot{\omega}_{O_2}\):

$$\dot{\omega}_{O_2} = -k_0 \exp \left(-\frac{E}{RT}\right) Y_{O_2} Y_{Mg} \rho^2 \frac{W_{O_2} W_{Mg}}{W_{Mg}}$$

(2)

where the values for the preexponent \(k_0 = 5 \cdot 10^5 \text{ m}^3/(\text{mol} \cdot \text{s})\) and the activation energy \(E = 167 \text{ kJ/mol}\) are from Florko et al. [24] (similar activation energy has been proposed by Cassel and Liebman [25]). \(Y_{Mg}\) is the mass fraction of magnesium vapor, and \(W_{Mg}\) is the molar weight of magnesium. The effect of temperature variations was not accounted for in the transport terms because the temperature was taken everywhere to be the adiabatic flame temperature. This maximized the reaction rate and thus the oxygen consumption due to the reaction kinetics, which has the strongest temperature dependency of all the physical processes.

The mass fraction of magnesium \(Y_{Mg}\) was taken to be constant at the maximum possible value that can occur at atmospheric pressure and the flame temperature (i.e., the magnesium vapor pressure was equal to 1 atm) so that again, the reaction rate of oxygen and its rate of disappearance would be maximized. The more realistic case of magnesium consumption by reaction in the flame would decrease the reac-
tion rate and increase the computed levels of oxygen.

An average magnesium gas flow was determined from the droplet vaporization rate, \( m = 2.46 \times 10^{-4} \text{ g/s} \) obtained by dividing the mass of a 300 \( \mu \text{m} \) magnesium particle by the observed combustion time for this size particle. For the spherically symmetric flow, the one-dimensional equation for the mass fraction of oxygen within the flame zone surrounding a magnesium particle is:

\[
\frac{d^2Y_{O_2}}{dz^2} + \frac{m}{4\pi\rho Dr_0} \frac{dY_{O_2}}{dz} + \frac{\omega W_{O_2} r_0^2}{\rho Dz^4} = 0
\]

where \( z = r_0/r \) and \( r_0 \) is the radius of the entire flame zone surrounding the particle and estimated to be 1.05 mm (cf. Fig. 3). The transformation between \( r \) and \( z \) results in an independence of the radial coordinate for the coefficients of the first and second derivatives in Eq. 3 which represent the effect of mean gas flow and diffusion. The assumption of constant temperature means that all thermodynamic quantities in these coefficients are also constants. The only variability occurs due to the explicit appearance of \( z^{-4} \) in the last term representing the effects of reaction.

The region \( z \) is next divided into small intervals so that \( z^{-4} \) does not vary much in each interval. The following standard solution for constant coefficient differential equations is used in each interval:

\[
Y_{O_2} = A \cdot \exp(-\gamma_1 z) + B \cdot \exp(-\gamma_2 z)
\]

where \( A \) and \( B \) are constants and

\[
\gamma_{1,2} = \frac{m}{8\pi\rho Dr_0} \left( 1 \pm \sqrt{1 + \frac{64\pi^3 r_0^4 DYMg_k \exp(-E/RT)}{W_{Mg}m^2 z^4}} \right)
\]

within each interval.

However, the simplifying assumption that \( Y_{Mg} \) is constant (to maximize the reaction of \( O_2 \)) places an unrealistic constraint on the air side of the flame since \( Y_{Mg} \) must in fact vanish for large enough \( r \) (small \( z \)). While an accurate description of \( Y_{O_2} \) cannot be obtained because of these assumptions, the principle of seeking the lowest reasonable value for \( O_2 \) can be followed by assuming that \( Y_{O_2} \) drops off from its value at large \( r \) on the air side of the flame according to whichever of the two terms in Eq. 4 produces the most rapid decay. By using the plus sign in front of the square root term in Eq. 5, the solution will always underestimate the value of \( Y_{O_2} \).

Choosing intervals in \( z \) equal to 0.05, \( Y_{O_2} \) falls to nearly 83% of its initial value at the air side of the flame front in the first interval. The process is repeated in successive intervals of \( z \) with only the magnitude of \( Y_{O_2} \), and not its derivative, matched at the last computed point in the previous interval of \( z \). \( Y_{O_2} \) continues to fall, but somewhat less rapidly, until it is 0.008 (0.8%) of the original air value when the surface is reached. This is seen in Fig. 10 where the surface position and the position of the smoke ring visible in the quenched particle traces (cf. Fig. 3) are also shown.

This estimate yielded a mass fraction of oxygen within the smoke cloud ring close to 18% of the ambient oxygen concentration. It would normally be anticipated that the chemical reaction zone is contained within the smoke ring, where the reaction products (condensed MgO) are found. However, even assuming that the reaction continues all the way to the particle surface, about 0.8% of the ambient oxygen concentration is found at the surface.

The fact that oxygen can survive on the magnesium side of the flame is due to the
relatively low reaction rate. Although the flame temperature and the heat of reaction are large, the reaction rate is controlled by the ratio of the activation energy to the local temperature in the simple Arrhenius type formula. The activation energy is so large that the resultant reaction rate is small in spite of the high temperature.

This estimate shows that oxygen can be transported to the particle surface in a single magnesium particle flame via diffusion through the stand-off vapor-phase flame zone surrounding the particle. Once at the particle surface, it can be acquired by the molten magnesium to form the MgO oxide and/or Mg-O liquid solution. The stoichiometric MgO phase could precipitate from the Mg-O solution once it is saturated. Indeed, based on the elemental composition measurements for partially burned and rapidly quenched particles, it is clear that oxygen has been dissolved inside burning liquid Mg particles and thus, when the particle temperature decreased (i.e., by the end of combustion), thermodynamically equilibrium Mg and MgO phases must have been formed. This reaction (transition from the Mg-O solution to the pure Mg and MgO) is expected to be exothermic and could have resulted in an increase of particle temperature and a radiation peak. In addition, this phase separation process is expected to generate inhomogeneity of both the particle interior and surface, and, thus, it could contribute significantly to the formation of large amounts of oxide found on the particle surfaces and promote asymmetric burning. Similar phase separation processes could have caused radiation jumps, oscillations, and particle micro-explosions that have been observed previously [6, 9] as well as in this research, but have not been explained. Further support for the hypothesis that such internal processes and phase changes are responsible for the experimentally observed features of magnesium particle combustion comes from the observation reported earlier [9] (and confirmed in these experiments) that by the end of the particle combustion no radiation from vapors of Mg and MgO could be detected, indicating that the vapor-phase reactions have not been actively occurring. Instead, heterogeneous reaction of oxygen dissolution and, later on, precipitation of the MgO phase could have caused continuing heat release, although not as great as that from the vapor-phase flame, but sufficient to maintain the particle high temperature which is inferred from the extended black-body radiation traces observed experimentally.

CONCLUSIONS

Earlier observations of the release of hydrogen gas from magnesium during its heating to the melting point have been experimentally confirmed. This hydrogen release is thought to affect particle shape and is expected to play a role in magnesium ignition.

Consistent with the previously published results, it has been observed that the intensity of the radiation bands of the Mg and MgO vapors is significant after particle ignition, but becomes indistinguishable from the black-body radiation at later combustion times (different for different particle sizes). It has also been observed that unburnt (or, partially oxidized) metal distinctly different from the MgO oxide was contained in the particles quenched after the MgO radiation decreased sharply, the black-body radiation exhibited oscillations and peaks.

Dissolved oxygen has been detected within partially burned and rapidly quenched magnesium particles. The elemental oxygen concentrations measured within the quenched particles significantly exceeded the very low solubility limit for oxygen in solid magnesium. Quenched particles were covered by a 5–50-μm-thick, porous oxide layer; similar oxide layers have been detected within the voids inside the quenched particles. An estimate based on the rate constants for magnesium vapor-phase combustion reported in the literature, showed that the reaction rate is insufficiently fast to prevent oxygen gas diffusion through the vapor-phase stand-off flame to the particle surface.

It is thus proposed that the oxygen diffuses to the surface of burning particles and is dissolved in liquid magnesium. A new phase, liquid Mg-O\textsubscript{solution} is thus being formed inside burning magnesium particles. This heterogeneous reaction of oxygen dissolution begins simultaneously
with the vapor-phase combustion but later on, after the vapor-phase flame ceases, becomes the primary reaction mechanism. After the solution becomes saturated, an exothermic phase separation, Mg-O\text{solution} \rightarrow Mg + MgO, occurs that contributes to the production of large amounts of oxide detected on surfaces of partially burned particles and causes the observed oscillations and peaks in particle radiation.

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REFERENCES


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