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Deposition and characterization of energetic thin films

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A B S T R A C T

A new approach for depositing thin energetic films is introduced using doctor blade casting. Magnesium (Mg) and manganese dioxide (MnO_2) is mixed with a solvent that includes a binder and is blade cast onto a foil substrate. This study investigated the effect of binder chemistry and concentration on combustion behavior. The Mg–MnO_2 system was studied in the following binder–solvent systems: Polyvinylidene Fluoride (PVDF) – Methyl Pyrrolidone (NMP); Viton® fluoroelastomer (Viton A) – acetone; and, paraffin–xylene. Films were cast onto substrates to approximately 100 μm thickness. Calorific output and flame velocity were measured for varying binder concentration. Calorific output increased with increasing binder concentration, to a maximum of 4.0 kJ/g, suggesting participation of the binder in the exothermic reaction. Flame velocity decreased with increasing binder concentration, with a maximum of 0.14 m/s. Binders are less conductive than metals and metal oxides thereby hindering the energy propagation with increasing binder content. Confined flame propagation tests were also conducted for the NMP/Mg–MnO_2–PVDF system, with a maximum recorded flame velocity of 3.5 m/s. High velocity imaging shows considerable differences in flame front, which may suggest a transition in propagation mechanism accounting for the observed increase in flame velocity.

1. Introduction

Thermites, consisting of a metal fuel and metal oxidizer, have been extensively researched for a large variety of formulations [1] and developed for use in welding and joining [2] as well as for thin film heat source applications [3]. Recent developments have included the study of nanopowder reactants in thermites [4], which are generally more reactive than their micron-scale counterparts. Many of the thermites studied have a high degree of gas generation. However, for some applications, high gas generation may not be desirable [5]. Dean et al. [6] discussed the role of particle advection in propagation of non-gas generating thermites. For loose powder, non-gas generating compositions, they showed flame velocities comparable to their gas generating counterparts and attributed these high velocities to condensed phase particles ejected from the reaction [6].

For practical use in many power generation applications, loose powder may not be suitable, and the thermite must be either pressed or mixed with a binder for a more contiguous solid. For this reason, powders can be combined with a binder that enables their application as films. Thermite film deposition methods vary greatly, and include electrophoretic deposition [7], sputter deposition [8], physical vapor deposition [9], and formation and population of 3D macroporous structures [10]. The deposition method is extremely important because it plays a large role in particle mixing, deposition thickness, and deposition density, all of which have been shown to affect combustion behavior and power generation performance [11,12].

A large number of binders have been used for depositions, including epoxy [13], nitrocellulose [14], paraffin and various fluoropolymers, such as Viton® fluoroelastomer (Viton) and Polyvinylidene Fluoride (PVDF). These binders participate in the reaction in different ways depending on their specific chemistry. For example, Bouma et al. reported that addition of Viton improved the mechanical properties of aluminum and molybdenum trioxide (Al–MoO_3), and increased impact ignition sensitivity by decreasing the porosity of the composite. Addition of small concentrations of Viton to aluminum and copper oxide was also shown to decrease the electrostatic discharge ignition sensitivity [15]. In other work, the hydrophobic fluoropolymer polytetrafluoroethylene (PTFE) was combined with aluminum to reduce wetting such that Al–PTFE pellets stayed intact and would still ignite after two months submerged underwater [16].

Binders are often fluoropolymer or hydrocarbon based. Some fluoropolymer binders such as Viton also participate as oxidizers in the reaction. Fluorine is highly electronegative and shown to be an aggressive oxidizer, particularly when combined with magnesium (Mg) fueled energetic materials [17]. Conversely, paraffin

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is a binder that has been used as a fuel in combination with a strong oxidizer, such as ammonium perchlorate [18]. Most of the studies involving binders focus on gas generating compositions and do not examine the role of the binder in heat of combustion or flame propagation. In studying thin thermite films for power generation applications, both heat of combustion and flame propagation velocity are critical parameters characterizing the performance of the film. For this reason, one objective of this study is to examine the influence of the binder on these combustion behaviors.

To prepare thin films, doctor blade casting is an inexpensive and easily utilized deposition method for colloid based materials and it has been found that that the degree of ordering obtained by doctor blade casting outperforms other deposition techniques such as ink-jet printing or drop casting [19]. Doctor blade casting has been utilized to cast dental ceramics [20] and Lithium ion batteries [21], but has not been applied for thermites or other energetic materials reported in the literature. Since many methods for thermite deposition are time consuming and costly, there is strong motivation to implement new deposition methods, such as doctor blade casting for thermite coatings. Therefore, another objective is to introduce doctor blade casting as a deposition method for thermite films.

To accomplish these objectives, coatings consisting of magnesium (Mg) and manganese dioxide (MnO_2) were prepared with three different binder–solvent systems and coated onto a substrate using a drawdown blade. These coatings were examined to determine flame velocity and calorific output. Additionally, separate samples were prepared for flame velocity tests performed under confinement to investigate the role of confinement in reaction propagation for a low gas generating thermite. In application, these films are commonly used under sandwiched or confined conditions.

2. Experimental

2.1. Materials

Powders of magnesium (Mg) and manganese dioxide (MnO_2) were obtained from Alfa Aesar, both micron sized particles sieved to 325 mesh. A binder–solvent solution was mixed by adding solvent to a specific mass of binder until completely dissolved. Three different binder–solvent systems were investigated: (1) Polyvinylidene Fluoride (PVDF) – Methyl Pyrrolidone (NMP); (2) Viton A – acetone; and, (3) paraffin–xylene. The binder–solvent solution was added to a dry mixture of Mg and MnO_2 powders to achieve the desired weight percent of binder. The PVDF and Viton were added to the powdered mixture at mass percentages of 0.5%, 1.0% and 1.5%. Paraffin was not effective as a binder at concentrations below 3% by mass, and was therefore mixed with the dry powder at 3%, 5%, and 7% by mass. In order to compare the paraffin to a fluoropolymer, NMP/Mg–MnO_2–PVDF mixtures were prepared at these concentrations as well. This information is summarized in Table 1.

Additional solvent was added to the powder mixture to reach a total solids content (dry powder plus binder) of 40% by volume. Each solution was mixed in a centrifugal mixer (AR250, Thinky, Japan) at 1200 rpm for 4 min. The suspension was blade cast onto a 50 μm stainless steel substrate as well as uncoated glass slides using a 200 μm drawdown blade with an automated film applicator (Elcometer, 4340, Michigan). Blade casting, commonly referred to as doctor blading, is a process by which a slurry is cast as a film by drawing a blade across the slurry evenly. For this method, a thin slit cut into the blade ensures consistent deposition thickness. This process is illustrated in Fig. 1.

The only mixtures not cast onto 50 μm stainless steel were those prepared with paraffin. Paraffin mixtures cast onto 50 μm stainless steel would not propagate because the reaction was quenched by the excessive heat transfer to the steel. Instead, these mixtures were cast on a 25 μm stainless steel foil to facilitate combustion. The coatings were air dried in a fume hood, then transferred to a vacuum oven (Binder, VDL53.E2.1) for at least 6 h and dried at 60 °C. After all solvent had evaporated, the stainless steel substrate was cut into smaller samples and measured for coating thickness using a Starrett Electronic Indicator thickness gauge. Coatings on glass slides were removed from the substrate with a razor blade and recovered for calorimetry.

2.2. Flame velocities

Flame velocities were measured in two configurations. First, energetic coatings prepared on the foils as described above were cut to approximately 60 by 6 mm. These samples were fixed to a glass slide and placed in a combustion chamber so that flame propagation direction was perpendicular to the viewing direction.

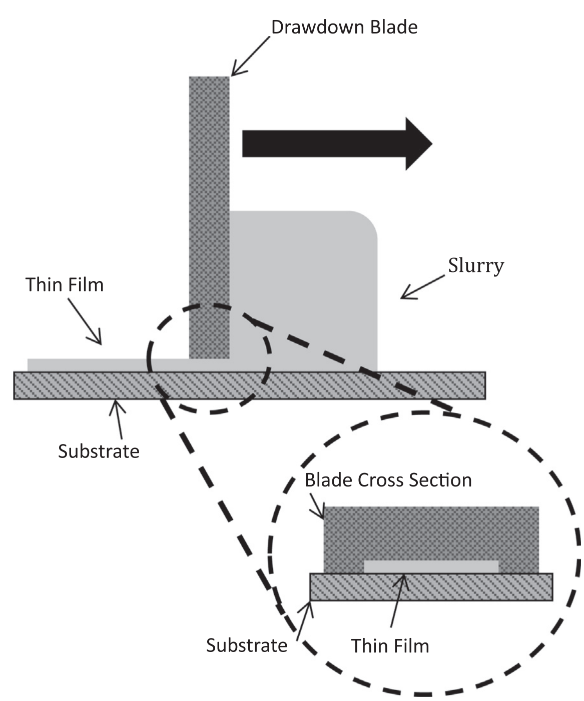

Fig. 1. Schematic of the doctor blade casting process. A thin slit in the drawdown blade is used cast a thin film onto the substrate.

Table 1
Mixture ratios for all solvent binder systems prepared with Mg–MnO_2.

Solvent	Binder	Percent solids in slurry	Mass percent binder in dry mixture					
			0.5	1.0	1.5	3.0	5.0	7.0
Acetone	Viton	40	X	X	X			
NMP	PVDF	40	X	X	X	X	X	X
Xylene	Paraffin	40				X	X	X