



The influence of sample thickness on the combustion of Al:Zr and Al-8Mg:Zr nanolaminate foils

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ABSTRACT

Al:Zr and Al-8Mg:Zr nanocomposite foils do not combust completely in air because the penetration of oxygen and nitrogen into the foils can become limited as the product phases grow. The heat produced during the combustion of these foils could feasibly depend upon the volume fraction of the surface oxide layer that forms and therefore the initial foil thickness as well. To test this, Al:Zr and Al-8Mg:Zr foils of various thicknesses (9–61 μm) were fabricated by Physical Vapor Deposition and their heats of combustion were measured using bomb calorimetry in 1 atm of air. We found that combustion efficiency decreased significantly for Al:Zr foils as thickness increased, but Al-8Mg:Zr foils had a nearly constant combustion efficiency for the range of thicknesses studied. SEM-EDS measurements across the foil cross-sections showed that for Al:Zr foils, a distinct oxide layer formed on the external surfaces and there were low levels of oxygen and nitrogen toward their centers. For Al-8Mg:Zr foils though, there was minimal dependence between heat output and foil thickness, the surface oxide layer was more diffuse, and the oxygen and nitrogen contents were higher throughout the foil. We propose that the addition of magnesium improves heat generation by increasing the rates of oxygen and nitrogen diffusion and thus enabling the formation of solid solutions that are richer in oxygen and nitrogen throughout the bulk of the foils.

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1. Introduction

Metal fuel particles, especially aluminum, have been used as additives to aid in combustion for decades [1–3]. For maximum control over combustion properties, we can decouple the ignition temperature from particle size using reactive nanolaminate structures, allowing even large macroscopic foils to ignite at relatively low temperatures [4–7]. For a given composition, the ignition temperature can be set to the desired range by adjusting the reactant spacing, and the combustion properties can be tuned separately by adjusting the particle size. This is possible because the nanolaminate materials are composed of hundreds of layers of different metals stacked in a high-energy configuration. Each layer is only tens of nanometers thick, allowing for rapid interdiffusion between layers if a small input energy is applied. This intermixing between nanoscale layers initiates an exothermic intermetallic formation reaction that brings the materials to high temperatures in a burst of heat. Ignition is therefore independent of the size of the particle as a whole, and is determined instead by the internal bilayer structure.

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In previous studies, we identified a range of bilayer thicknesses that yield our target ignition temperatures (300–400 °C) for large foils [8,9] with chemical compositions (Al:Zr and Al-8Mg:Zr) that lead to significant combustion in air following initiation of the intermetallic formation reaction [10]. We have also previously shown that by including magnesium in the reactive nanolaminate structure, as with Al-8Mg:Zr foils, it is possible to improve combustion efficiency [10]. The results of this study, including pyrometry, bomb calorimetry, and elemental analysis of Al:Zr and Al-8Mg:Zr foils, indicated that more than half of the magnesium in Al-8Mg:Zr samples vaporizes during its reaction, creating vacancies throughout the foil. The magnesium remaining in the foil also creates oxygen vacancies in the ZrO_2 layer. The increase in vacancy concentration allows for improved diffusion of oxygen and nitrogen, and leads to higher net heat output than was measured for Al:Zr samples.

A related study [11] has shown that for Al:Zr foils, the ZrO_2 phase forms early in the reaction and grows steadily via interface controlled growth throughout the combustion stage. After approximately 2 seconds, the oxide layer is thick enough that growth becomes diffusion limited and combustion rapidly terminates. This mechanism has been supported by numerical simulations [12]. A corollary of having a limiting oxide thickness is that the gravimetric heat produced by these foils may depend on foil geometry. If a foil is thin, a large fraction of the metal may undergo oxidation

before it becomes diffusion limited. Conversely, if a foil is thick, the external oxide shell may constitute a smaller fraction of the total foil volume, leaving unreacted material at its center.

In the present study, we are investigating how the thickness of Al:Zr and Al-8Mg:Zr nanolaminate foils influences their combustion efficiency, temperature, and duration. The nanolaminate foils serve as uniform, model structures, and those studied here are nominally 52 mm long, 10 mm wide, and 9–60 μm thick. It is well-established that as a particle's diameter increases, the ignition temperature and burn duration also increase [13–17]. These effects are the result of the specific surface area (SSA) increasing. In a similar manner, changes in a foil's thickness lead to a significant change in its SSA because it is the smallest dimension by three orders of magnitude. Changes in length or width, however, have a negligible effect on a foil's SSA.

To perform this study, we fabricated Al:Zr and Al-8Mg:Zr foils of varying thicknesses and measured the heat generated by each using a specially-designed combustion bomb calorimeter [18]. We also measured the combustion temperature and duration for each foil. In order to explain the observed trends for combustion properties as a function of foil thickness, we also investigated the underlying mechanisms of combustion by measuring the oxygen and nitrogen content throughout the thickness of Al:Zr and Al-8Mg:Zr foils after combustion in air. Our goal is to identify the relationship between a foil's thickness and its combustion properties for both foil compositions, and we have developed a geometric model to help explore these relationships.

2. Experimental methods

2.1. Fabrication: sputter deposition

Nanolaminate foils were sputter deposited with two different compositions: Al:Zr and Al-8Mg:Zr. The Al:Zr foils were approximately 50 at.% Al and 50 at.% Zr. The Al-8Mg:Zr foils were 46 at.% Al, 4 at.% Mg, and 50 at.% Zr, as an Al-Mg sputter target that was 92 at.% Al and 8 at.% magnesium was used in place of the Al target. The Al and Al-8Mg targets were 99.99% pure, and the Zr target was 99.7% pure; all were purchased from Plasmaterials, Inc. in Livermore, CA. Foil fabrication has been explained in depth previously [10], but in brief, each metal (Zr and either Al or Al-8Mg) was simultaneously magnetron sputtered onto brass substrates affixed to a rotating, water-cooled carousel. Foil length and width were dictated by a pattern of tape on the substrates that determined the boundaries between strips of foil, and foil thickness was adjusted by varying the deposition time. The total sputtering rate was approximately 1 $\mu\text{m}/\text{hr}$. The foil widths and lengths were fixed at 10 mm and 52 mm, respectively, while foil thickness was varied from 9 to 60 μm . Bilayer spacing was held constant at approximately 80 nm for all foils [19]. All foils were removed from their substrates for testing.

2.2. Heat of combustion: bomb calorimetry

The heat generated by a combination of intermetallic formation reactions and combustion reactions was measured in a specially designed bomb calorimeter described elsewhere [18]. It was designed to minimize heat sinking of the reacting foils, maximize surface area available for oxidation, and ignite foils with a low-energy spark. The calorimeter is extremely sensitive, with an energy equivalent of $279 \pm 6 \text{ J/K}$, allowing for measurements on the order of just tens of Joules. We were not interested in measuring the enthalpy of complete combustion, typically performed in 30 atm of oxygen, but rather the combustion efficiency in a limiting environment more representative of real-world performance in air. Therefore, heats of combustion were measured by reacting

foils in 1 atm of air, in which partial combustion occurs based on the kinetics associated with the foil's composition and geometry, allowing us to assess what combination of properties may lead to improved performance.

Variations in foil thickness and hence foil mass caused the quantity of oxygen required for complete combustion to vary significantly, creating a bias in the bomb calorimetry experiments. There was excess oxygen within the chamber for smaller mass foils, but there was an oxygen shortage for larger mass foils. We will refer to this as the "oxygen requirement bias", and we developed a rigorous correction method to subtract the effects of this bias and isolate only the influence of the foil geometry. This was accomplished by characterizing the oxygen requirement bias using foils where thickness (and therefore SSA) was held constant, but mass was varied by adjusting the foil width. **Figure S1** shows this data for Al:Zr (a) and Al-8Mg:Zr (b) foils, and verifications that the corrections were valid are provided in **Figure S2** and **Figure S3**. It was hypothetically possible to avoid the oxygen requirement bias altogether by adjusting the pressure of air or the partial pressure of oxygen for each foil. These were not feasible approaches, however, as we could not control these parameters sufficiently to account for small changes in foil mass.

2.3. Post-reaction analysis: SEM/EDS, and 3D laser profilometry

After reacting in the bomb, foils were mounted in epoxy discs, cross-sectioned, and polished. Each sample was then viewed in a Scanning Electron Microscope (SEM) using Energy-Dispersive X-Ray Spectroscopy (EDS) in order to correlate heat measured in the calorimeter with oxygen and nitrogen penetration into the foil. Foils that produced more heat per gram were expected to have greater oxygen content, and viewing the post-reaction oxide/metal foil structure revealed how the geometry of any given foil may have influenced its combustion properties.

A Jeol 6700 SEM with an EDAX EDS detector was used for imaging in backscatter mode to provide contrast between the different phases. EDS line scans showed composition as a function of distance through the thickness of the foil and were averaged to give a comparative estimate for total oxidation and nitridation of the sample. This is only a semi-quantitative analysis because oxygen and nitrogen are light elements and standardless calibration software was used. We therefore have limited confidence in the accuracy of the absolute values, but the errors are expected to be consistent from sample to sample. Thus, the chemical data is best utilized for qualitative comparisons to indicate which foils contain greater amounts of oxygen or nitrogen, and where these gaseous reactants are located within the sample.

The surfaces of Al:Zr and Al-8Mg:Zr foils reacted in air were also investigated using 3D laser profilometry, specifically with a Keyence VK-X100 series confocal laser microscope. Values for roughness and surface area per projected area (SA/A) were calculated and averaged from three different regions from a foil of each composition. Both foils had an original thickness of approximately 37 μm .

2.4. Burn temperature and duration: pyrometry and high speed videography

A two-color pyrometer, built in-house, was used to measure the temperature of the reacting foils. The pyrometer functions as follows: An optic is focused onto a 1 mm diameter circle at the center of each foil and light is channeled from the focusing optic into the pyrometer with a 600 μm fiber optic cable (Ocean Optics, Inc.). The signal is split into two equal beams using a bifurcation of the

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