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Mechanisms of oxide growth during the combustion of Al:Zr nanolaminate foils

Kyle R. Overdeep[a], Howie Joress[a,b], Lan Zhou[a], Ken J.T. Livi[a,c], Sara C. Barron[a], Michael D. Grapes[a], Katherine S. Shanks[a,d], Darren S. Dale[b], Mark W. Tate[d], Hugh T. Philipp[d], Sol M. Gruner[b,d,e], Todd C. Hufnagel[a], Timothy P. Weihs[a,*]

[a] *Department of Materials Science and Technology, Johns Hopkins University, Baltimore, MD 21218, United States*
[b] *Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14850, United States*
[c] *Integrated Imaging Center, Johns Hopkins University, Baltimore, MD 21218, United States*
[d] *Department of Physics, Cornell University, Ithaca, NY 14853, United States*
[e] *Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, NY 14853, United States*

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ABSTRACT

Reactive metal nanolaminates, most notably aluminum/zirconium composites, have been developed as fuels to aid combustion in explosive formulations. Thus far, however, their energy density is limited by incomplete oxidation. An *in situ* x-ray diffraction (XRD) study was performed on a 40 µm thick Al:Zr (atomic ratio 1:1) multilayer foil to track the growth of reaction products during ignition, combustion, and cooling (over approximately 5 s) to determine the mechanisms that prevent complete combustion from occurring. Simultaneous pyrometry provides the ability to relate the observed phase progression to the foil temperature throughout the reaction, and post-reaction cross-sectional electron microprobe and transmission electron microscopy (TEM) of the combusted foils identify the location, composition, and microstructure of each product phase.

We have used the combined results to develop an understanding of the growth mechanisms at play during the rapid reactions. The most significant finding is that the primary combustion product, orthorhombic ZrO_2, grows linearly throughout the first 1.3 s of the reaction, indicating interface-limited growth, but then switches to slower diffusion-controlled growth. The transition in growth rate coincides with the abrupt end of a temperature plateau that is associated with self-sustained combustion. A thick (≈8 µm) Al_2Zr layer is observed beneath the oxidized exterior in cross-sections of the reacted foil and is likely responsible for the reaction "turning off" before complete combustion is achieved. This underlying Al-rich intermetallic layer prevents the diffusion of aluminum away from the oxide interface, causing an increasing proportion of aluminum to oxidize. The resulting alumina creates a barrier to oxygen diffusion and is responsible for the incomplete combustion in air.

1. Introduction

Reactive nanolaminate foils consist of alternating layers of metals with negative heats of mixing. Each layer is typically 10-100 nm thick. With a small input of energy, the layers intermix to form intermetallic compounds in a self-propagating reaction [1–3]. Some combinations of materials, such as Al/Ni, Al/Pt, or Ti/B have particularly exothermic intermetallic formation reactions [4]. The intermetallic reaction in the Al/Zr[1] system is only modestly exothermic (0.4 kJ/g for Al:Zr in comparison to 1.3 kJ/g for Al:Ni [5]), but this combination of metals is of interest due to its ability to undergo extensive subsequent combustion by reacting with atmospheric oxygen and nitrogen [6,7]. Combustion of Al/Zr reactive materials contributes significantly more heat (16.4 kJ/g for 1:1 Al:Zr) than the intermetallic formation alone and increases the duration of the complete reaction from milliseconds to seconds in the case of foils of typical dimensions (approximately 40 µm thick, 1 cm wide, and 5 cm long). The energy density of Al/Zr reactive materials can also be higher than mixed fuel/oxidizer systems (e.g., thermites) because it combusts readily with gases from the environment and

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* Corresponding author.
E-mail address: weihs@jhu.edu (T.P. Weihs).

[1] To clarify notation, a slash (e.g., Al/Zr) indicates a general combination of Al and Zr. A colon (e.g., Al:Zr) specifies a stoichiometric ratio of Al to Zr (in this case 1:1). When no punctuation is used (e.g., AlZr) we are referring to the intermetallic compound with that chemical formula.

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therefore does not require an oxidizer to be included in the initial mass.

Previous work has demonstrated that while reacting in air, a 40 µm thick Al:Zr foil can sustain temperatures of approximately 1300 °C for nearly 2 s [6,7], which is a lower temperature and longer duration than would be expected from combusting particles. However, due to incomplete oxidation of these relatively large foils, less than 40% of the theoretical heat of combustion is released during its reaction even in a pure oxygen environment [7]. To improve the performance of these materials, it is necessary to understand the reaction mechanisms of the initial intermetallic formation and the subsequent oxide growth.

In this work, we performed time-resolved *in situ* x-ray diffraction experiments on ≈40 µm thick Al:Zr foils reacting in air to identify the progression of phases over time with a temporal resolution as short as 3 ms [8,9]. Pyrometry was performed simultaneously throughout the reaction. Combining these *in situ* results with post-reaction micrographs and chemical analysis of foil cross-sections, we propose a mechanism describing the combustion of these reactive foils. Most notably, zirconium oxidizes along the exterior of the foil via interface-controlled growth early in the reaction while aluminum diffuses towards the interior. The constant zirconia growth rate leads to a relatively constant combustion temperature. However, the selective oxidation of zirconium leads to a build-up of aluminum at the internal oxide-metal interface, which begins to oxidize as well, creating a mixed oxide barrier to oxygen diffusion. The barrier eventually causes a switch from interface-controlled growth to diffusion-controlled growth that decreases in rate over time. As the oxidation reaction slows and heat production decreases, the combustion temperature falls and the reaction terminates rapidly. The proposed combustion mechanism is supported by earlier computational [10] and experimental [11] work on thick Al:Zr foils, and is distinct from the mechanisms that control the far more rapid combustion of nano- or micro-scale metallic particles.

2. Experimental methods

Foils were fabricated by simultaneous DC magnetron sputtering from two cathodes. Each cathode was directed at opposite sides of a water-cooled carousel rotating at the center of a vacuum chamber. One cathode contained an Al-1100 target (> 99.0% aluminum), the other a zirconium target (99.7% zirconium). Eight brass substrates were affixed to the carousel and received a layer of aluminum followed by a layer of zirconium as they rotated past each cathode. Additional details of the growth process can be found elsewhere [7]. The deposition rate was set such that a full revolution resulted in a nominally 1:1 atomic ratio bilayer of aluminum and zirconium ≈85 nm thick, and after several hundred rotations the total foil thickness was ≈40 µm. Following deposition, the material was peeled from the brass substrates to yield free-standing multilayer foils.

The *in situ* measurements were performed on Al:Zr foils (approximately 1 cm × 5 cm × 40 µm) in which reactions were initiated by uniform electrical heating described in detail in Ref. [12]. We used this method of ignition to minimize temperature variation across the field of view of the *in situ* probes. In this setup, schematically shown in Fig. 1, a foil is clamped between two sets of copper plates and a short, high-current pulse is sent through it. The magnitude and duration of the pulse were chosen to impart the minimum amount of resistive heating required to ignite the foil. This amounts to heating the foils to approximately 350 °C, at which point the pulse ends and the intermetallic formation reaction accelerates until completion and reaches its adiabatic temperature (near 1485 °C). A 10 ms pulse with a current density of 55 kA/cm^2 was used for this particular sample. *In situ* diffraction measurements were performed at the A2 beamline at the Cornell High Energy Synchrotron Source (CHESS). An undulator beam with an x-ray energy of 15 keV and a bandpass of 0.6% ΔE/E was used [13]. The flux was approximately 10^{12} photons/second with the beam size of 1×2 mm^2 (vertical x horizontal). The reaction is not necessarily completely homogenous, even with the “uniform” heating method of ignition, and so the diffraction measurements correspond to an average composition of the irradiated volume. Samples were mounted such that the bilayers were oriented normal to the beam and the long axis of the foil was horizontal. A hole in the baseplate allowed the incident x-ray beam to reach the detector. Transmission x-ray diffraction patterns were continuously recorded onto two area detectors. The first detector was a fast, small-area Mixed-Mode Pixel Array Detector (MMPAD) [14,15] that was used to track the initial intermetallic formation reaction which occurs over less than 30 ms. It recorded a frame every 2.86 ms but, due to its small input area, was only able to capture a small subset of reciprocal space covering scattering vectors $q = \frac{4\pi}{\lambda}\sin\theta$ (where λ is the radiation wavelength and θ is the angle at which the scattered beam is observed) with magnitudes varying from 24.7 nm^{-1} to 37.7 nm^{-1}. This range was insufficient to measure all the diffraction peaks of interest (peak positions are listed in Table 1). The second detector was a large-area (but much slower) amorphous silicon detector (DXR250RT, GE Inspection Technologies) that was used to track the evolution of multiple

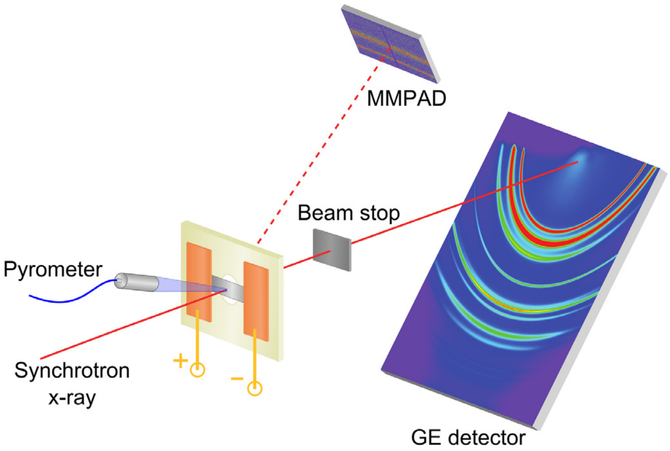

Fig. 1. The experimental setup for simultaneous *in situ* measurements of temperature and x-ray diffraction of a combusting Al:Zr foil. The reaction is initiated by resistively heating it with a 10 ms electrical pulse. Two x-ray detectors, the MMPAD and the GE detector, are used in tandem to cover the full range of q and time.

Table 1
Details of the characteristic diffraction peaks used to track each phase that was identified. The presented data was obtained from the Inorganic Crystal Structure Database (ICSD) [16] with the exception of the amorphous phase peak position, which is instead the experimentally observed position during the reaction at high temperature.

Phase	Crystal system	Room temperature peak position (nm^{-1})	Peak index
Al	Cubic	26.9	111
Zr	Hexagonal	25.6	101
Al_2Zr	Hexagonal	15.5	101
Al_3Zr_2	Orthorhombic	15.9	220
Al_3Zr_5	Hexagonal	17.7	200
Al_4Zr_5	Hexagonal	18.4	111
Al_2O_3	Monoclinic	42.2	113
ZrO_2	Orthorhombic	21.2	111
ZrO_2	Monoclinic	12.4	100
ZrN	Cubic	23.7	111
Amorphous	–	≈23.3	–