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Unsteady reaction behaviors in reactive Co/Al multilayer foils

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ABSTRACT

Reaction dynamics in exothermic Co/Al multilayer foils are studied with high speed digital photography. Unsteady, spin-like reaction propagation is observed in which the net synthesis of a foil is accomplished through advancing transverse bands that propagate perpendicular to the net reaction direction. This unsteady behavior is connected to the final reacted foil surface morphology that exhibits periodic structures. The evolution of the reaction front shape and corresponding surface morphology are discussed with respect to Co/Al foil characteristics.

INTRODUCTION

Usually grown via thin film deposition techniques, reactive multilayer foils consist of repeated layers of two materials that react exothermically once they are encouraged to mix [1]. A local exothermic reaction produced by some stimulus generates heat, which in turn causes surrounding unreacted material to mix. If this process continues, a runaway reaction is produced which can propagate throughout an entire foil. Examples of exothermic material systems include Ni/Al, Co/Al, Ni/Ti, and Al/Pt. Reactive multilayer foils have been used for specialized joining applications [2, 3], and for synthesizing intermetallic compounds with precise control over final product stoichiometries and crystalline phases [4, 5].

In previous studies, reactions in exothermic reactive multilayer foils have been characterized in-situ with high speed macro-photography [6, 7] and with time-resolved x-ray diffraction [8]. These investigations illuminated important features of such reactions, including the influence of foil parameters such as heat of formation [6] and bilayer thickness on net reaction velocities [9], and the timescales of phase evolution during the reaction [8]. These previous works were however limited, with high speed photography studies having insufficient spatial and temporal resolution to capture local reaction dynamics, and with time-resolved x-ray studies being highly localized and preventing a global understanding of how a reaction front proceeds. In the present work, the dynamics of a propagating reaction front are investigated at the micrometer length scale with sub-5 microsecond time resolution in order to reveal how local phenomena contribute to final morphology and phase.

As motivation for this work, it was previously observed, that once reacted and cooled to room temperature, Co/Al reactive multilayer foils exhibit periodic surface morphologies that vary in wavelength and character with foil design [6]. Examples of periodic surface morphologies are presented in Figure 1 for two different Co/Al foils. For each foil, two or more morphologies are observed, however we will focus on the primary and secondary morphologies as indicated in Figure 1. In the present work the origin of these periodic morphologies is attributed to unsteady reaction phenomena observed directly for the first time in planar, reactive multilayer foils.

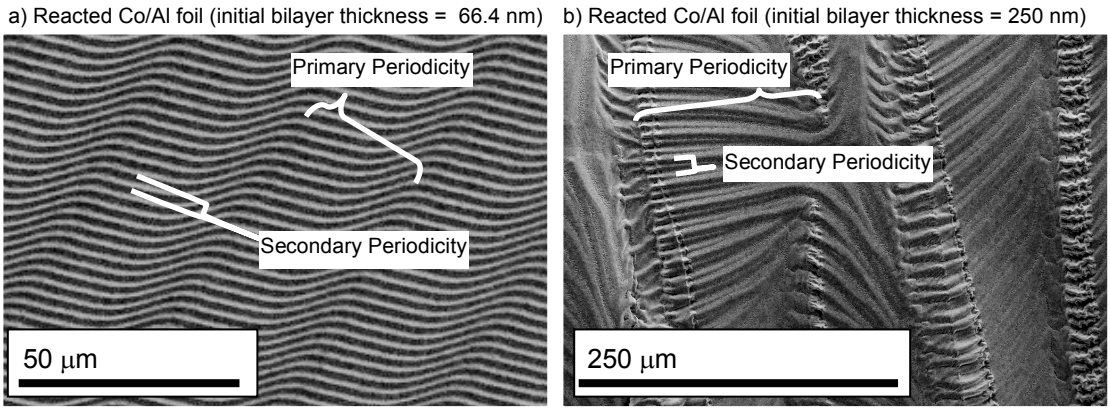

Figure 1. SEM images of Co/Al reactive multilayer foils after reaction in air. Both images are taken in plan view and show the reacted foil surfaces. a) Foil that initially had a 66.4 nm bilayer thickness, with primary and secondary periodic morphologies indicated. b) Foil that initially had a 250 nm bilayer thickness with primary and secondary periodic morphologies indicated.

EXPERIMENT

The Co/Al multilayer films were initially grown on Si(100) substrates with 400 nm thermal oxide via direct current (DC) magnetron sputtering. Films were grown with Co as the initial layer in order to facilitate removal from substrates. The base pressure of the growth chamber is 10^{-8} Torr, and sputtering is performed with a process gas of Ar at pressures of 10 mTorr. The physical features of a film are specified by two parameters: the total thickness of the film, and the bilayer thickness of the constituent layers. The total thickness of the Co/Al films is 7.437 μm for all films studied. The bilayer thickness is the sum of the thickness of an individual layer of each representative material in a film. For example, a particular bilayer thickness of Co/Al is 66.4 nm (Co = 26.4 nm, Al = 40.0 nm, thicknesses chosen for 1:1 stoichiometry), and 112 total bilayers are stacked in order to create a total film thickness of 7.437 μm.

Following deposition, foils are carefully removed from their substrates, and cut into approximately 15 mm x 5 mm strips that are then suspended across the inner diameter of a washer (the experimental setup is shown in Figure 2). The foils are ignited with the spark from a

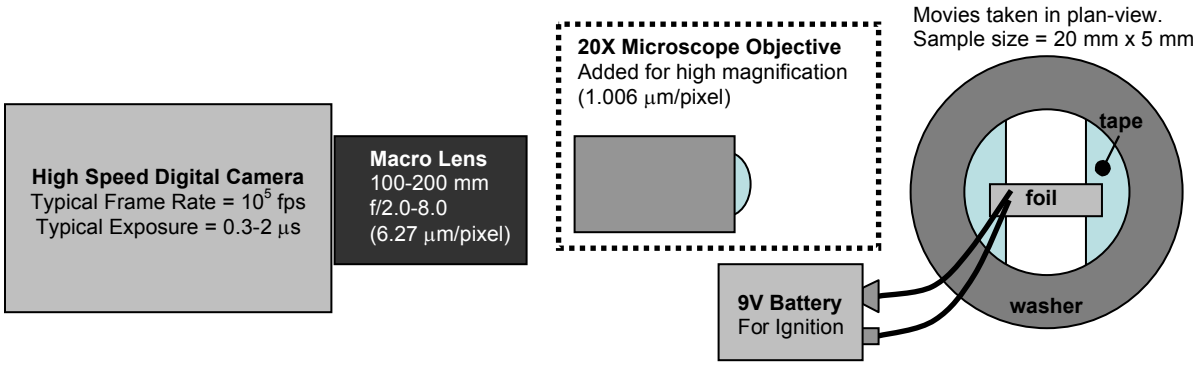

Figure 2. Experimental setup for high speed imaging of reactions in Co/Al multilayer foils.

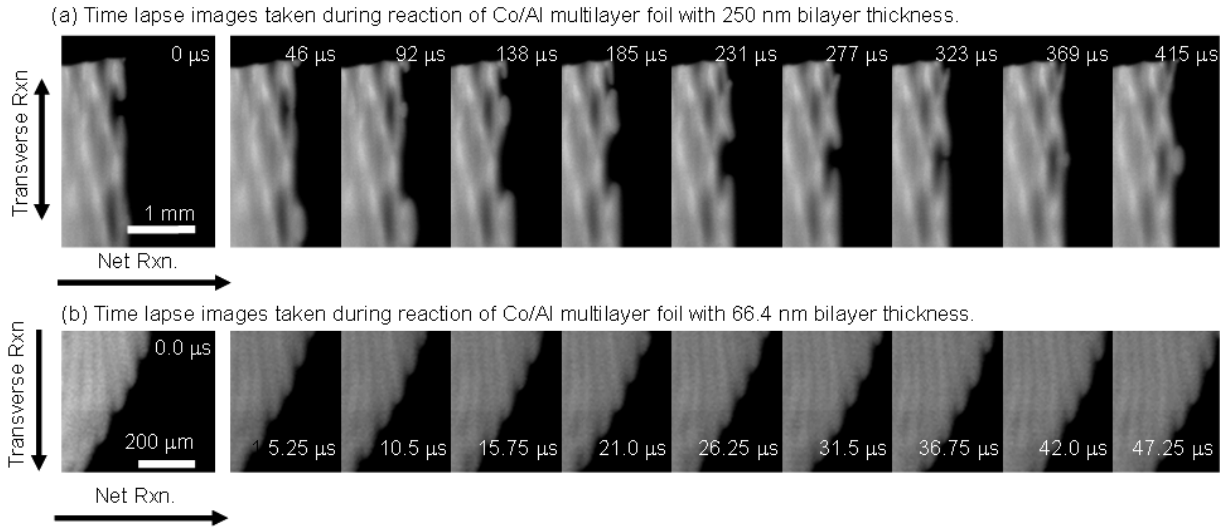

Figure 3. Reaction dynamics in Co/Al reactive multilayer foil with 7.5 µm total foil thickness and a) 250 nm bilayer thickness b) 66.4 nm bilayer thickness. Net reaction propagation from left to right in both sets of images. Scale bar in leftmost applies to all images; timestamp is relative to the first image in the sequence.

9 V battery. A Phantom v12 high-speed digital camera from Vision Research is used to collect high-speed movies of reactions, with typical frame rates ranging from 60,000-120000 fps, and image exposure times of 0.3 – 2 µs. Multiple lenses are used to obtain the desired spatial resolution, including a 100 mm Macro Lens f/2.0 from Zeiss, a 200 mm Macro-Telephoto Lens f/2.8 from Nikkor, and a 20X microscope objective coupled to the Macro lens was used to provide optimum spatial resolution of 1.006 µm per pixel. All movies of reactions were taken in plan-view, with the sample in air at ambient conditions. No external lighting is necessary as the exothermic reaction of the Co/Al foils produces heat that results in the emission of light.

RESULTS/DISCUSSION

Still images captured from high-speed movies of exothermic Co/Al foils with 66.4 nm and 250 nm bilayer thicknesses undergoing reaction are presented in Figure 3. These images demonstrate that the net left to right propagation of the reactions is accomplished through

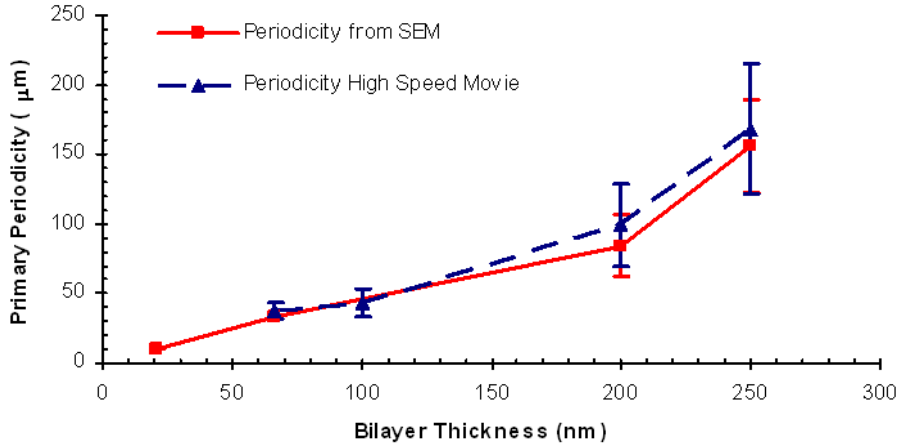

Figure 4. Primary periodicity measured from reacted foils (following cool-down) in SEM and in-situ (during reaction) from high-speed photography.

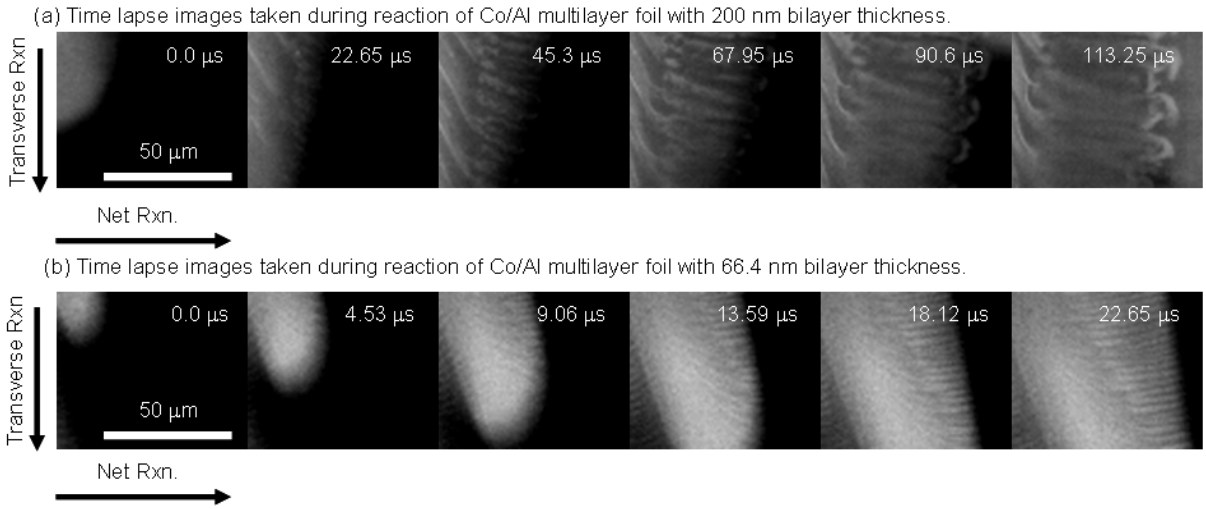

Figure 5. Reaction dynamics in Co/Al reactive multilayer foil with 7.5 μm total foil thickness and a) 200 nm bilayer thickness b) 66.4 nm bilayer thickness. Images show that the secondary periodicity forms during the passage of a transverse reaction band.

transverse traveling reaction bands. This is a general phenomenon, observed for Co/Al foils with bilayer thicknesses of 20.9 nm and 200 nm as well (not shown for brevity). Measurements of the width of transverse reaction bands made from high-speed movies, and the width of the primary periodic morphology (see Figure 1) made from scanning electron microscopy (SEM) are shown in Figure 4. The two measurements compare quite favorably, and when coupled with the qualitative similarities between the transverse reaction bands and the final reacted foil morphology it is clear that the transverse reaction bands are the source for the primary periodic morphology. The presence of the transverse reaction fronts has not been previously observed in reactions of Co/Al foils due to limited spatial resolution and insufficient frame rates to capture local reaction dynamics [6].

New transverse bands are created and then propagate the net reaction. New transverse reaction bands originate at the edges of the foils (for both the 66.4 nm and 250 nm bilayer thickness foils), and at the point of collision of two transverse reaction fronts (for the 250 nm bilayer thickness foil). Once formed, the new transverse reaction fronts propagate along the outer edge of the previous transverse reaction front. It is proposed that the width of the transverse reaction fronts is related to pre-heating of unreacted material via thermal diffusion, although the specific details are not yet fully understood. Modeling efforts are underway to better understand the origins and physical characteristics of the transverse reactions bands.

Still frames collected from high-speed movies with greater magnification are shown in Figure 5. From these images it is apparent that the secondary periodicity forms during the passage of the primary reaction front for both foils with 66.4 nm and 200 nm bilayer thickness. As with the primary periodicity, the physical mechanisms underlying the formation of the secondary periodicity are not yet fully understood.

Transverse reaction waves have been observed during combustion reaction propagation in other material systems in cylindrical geometries [10-12]. In these works the unsteady reaction behavior was called *spin* or *spiral* combustion due to the manner in which the combustion front propagated in a spiral around the outside surface (and presumably interior) of a cylinder compact of energetic material. Here, we borrow the expression and refer to the reactions we observe as *spin-like*, with the idea that if the outer surface of a cylinder were spread into a plane that a spin reaction would look similar to what is apparent in the high speed movies we have collected.

While spin-like reactions have been proposed to exist in planar multilayer reactive foils (based on post-reaction surface morphologies [13]), we present the first direct evidence for such behavior.

CONCLUSIONS

In summary, exothermic reactions in Co/Al multilayer reactive foils are studied with high-speed digital photography. The results of this study indicate that the net reaction of a foil is achieved through subsequent transverse reaction bands, which are the source of primary periodic surface morphologies observed after the foil has reacted and cooled to room temperature.

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