

# Thursday Afternoon, October 31, 2013

## Thin Film

Room: 102 C - Session TF-ThA

## Energetic Thin Films

Moderator: D.P. Adams, Sandia National Laboratories

2:00pm **TF-ThA1 Reactive Foil Ignition Threshold Dependence on Laser and Foil Properties**, *R.D. Murphy*, Sandia National Laboratories, *J.P. McDonald*, Dow Corning Corporation, *D.P. Adams*, Sandia National Laboratories

It has been shown that forced mixing of reactive layers (foils) leads to an exothermic release of energy after initiation of mixing by forced impact or pulsed laser irradiation. In this work, in order to understand the ignition of foils initiated by laser irradiation, we present laser ignition thresholds of Al/Pt multilayer reactive foils prepared by sputter deposition. It will be shown that the single-pulse ignition threshold is dependent on both the length of the laser pulse and properties of the foil such as bilayer thickness. The laser pulse length is varied from 100 fs to 100 ms and the bilayer thickness is varied from 20 nm to 200 nm. Models will be presented to account for the dependence of the ignition thresholds on diffusion and laser pulse - foil interaction mechanisms such as melting and ablation. Sandia is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:20pm **TF-ThA2 Direct Visualization of Atomic Diffusion Distances after Self-Propagating Reactions in Zr/Al Multilayers**, *D.P. Adams*, *R.V. Reeves*, *P.G. Koula*, Sandia National Laboratories

It is generally assumed that the diffusion distance for heterogeneous reactive materials is defined simply as half of the characteristic dimension of the constituent materials. In a powder system, this assumption results in the diffusion distance being equivalent to the particle radius, and, in a lamellar system, the diffusion distance would be half of the thickness of a single layer of material. This assumption is important as it is used to estimate overall reaction times and heat release rates. In this study, the validity of this assumption was investigated in sputter deposited multilayers of Zr/2Al composition with a single Zr layer replaced by a Hf marker layer. Hafnium was selected as the marker material because Zr and Hf have similar chemical behavior. This is due to lanthanide contraction, which causes Hf and Zr to have very nearly identical electronegativities and atomic radii. Hafnium and zirconium also react with Al to form intermetallic compounds with similar structures, including di-aluminide line compounds. These similarities between Zr and Hf allow the reaction to progress with little detrimental effect from the Hf inclusion. Multilayers containing a single marker layer were converted to product phases (nominally  $ZrAl_3/HfAl_3$ ) in the self-propagating reaction mode. Both unreacted and reacted foils were then cross-sectioned and imaged in an aberration-corrected transmission electron microscope. Energy dispersive spectroscopy (EDS) was performed to quantitatively identify the elemental distribution in both reacted and unreacted multilayers. EDS results clearly showed that the Hf atoms spread to over ten times the assumed diffusion distance. The results are in strong disagreement with the general assumption of diffusion distance and indicate that the atoms can remain mobile, even after complete mixing has occurred.

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2:40pm **TF-ThA3 Analysis and Modeling of Self-Propagating Reactions in Ni/Al and Ru/Al Nanoscale Thin Film Multilayers**, *C. Rebholz*, University of Cyprus, *I.E. Gunduz*, Northeastern University, *K. Fadenberger*, University of Cyprus, *K. Woll*, Johns Hopkins University, *C.C. Doumanidis*, University of Cyprus

Reactive nanoscale multilayer films/foils represent a relatively new class of materials which have recently received considerable attention for use in joining applications. However, due to the fast reaction rates in these foils (between 1 and ~ 20 m/s for the Ni/Al system) much of the understanding of the reactions is derived from comparing before and after states of the samples.

In this work, reaction characteristics of nanoscale multilayer foils of Nickel (Ni) and Aluminum (Al) and Ruthenium (Ru) and Al were investigated using a numerical model based on sequential diffusion limited growth with diffusivity values obtained from previous diffusion experiments. The model

makes use of percentages of each phase that can exist at each grid point, which simplifies the enthalpy calculations and incorporation of phase changes. Obtained results show excellent agreement with measured velocity values, observed *in-situ* morphology of the thermal fronts and temperatures for both Ni/Al and Ru/Al multilayer foils, obtained using high-speed optical camera and infrared thermometry in combination with fast high resolution *in-situ* XRD.

3:00pm **TF-ThA4 Combustion Characterization of Blade Cast Magnesium and Manganese Dioxide**, *K. Meeks*, *M.L. Pantoya*, Texas Tech University, *C.A. Applett*, Sandia National Laboratories

There is a current need for low cost heat sources for a variety of applications, from local joining and welding, to providing local heat for power sources. In this work, powders of magnesium and manganese oxide were mixed with a fluoropolymer or paraffin binder and blade cast onto a stainless steel foil substrate. The three binder-solvent systems investigated were Methyl Pyrrolidone (NMP) and Polyvinylidene Fluoride (PVDF), Acet one and Viton A, as well as Paraffin and Xylene. Films were prepared by mixing the energetic composites with the binder and solvent to create a 40% solids content suspension, and then casting onto stainless steel foil to a 200um wet film thickness. In this study, binder content and type was varied, and calorific output and open flame propagation speed was investigated for each mixture ratio. It was found that calorific output increased with increasing binder content, to a maximum observed value of 954 calories per gram, indicating participation of the binder in the exothermic reaction. Flame speed was shown to decrease with increasing binder content, with a maximum recorded value of 0.14 m/s for unconfined tests. This may reflect the lower heat transfer of the binder, or some mechanism that blocks propagation with increasing binder content. Confined tests were also conducted for the PVDF/NMP system, with a maximum recorded flame speed of 3.46 m/s. High speed video of the flame propagation shows significant gas generation ahead of the flame front, which may explain the observed difference between confined and open burn speeds, as the ejecta plume preheats the material in advance of the flame front.

3:40pm **TF-ThA6 Reactive Nano Laminates with Tailored Yield**, *J.-P. Maria*, *E.J. Mily*, *H. Akyildiz*, North Carolina State University **INVITED**

In this presentation we report on a series of reactive oxygen exchange nanolaminates between an oxygen source, CuO, and a reactive metal oxygen sink where the propensity for energy release is tailored by material selection and by multilayer geometry. These results suggest it is possible to create a class of energetic materials whose yield can be tailored for specific applications.

We demonstrate that by considering anion transport in the terminal oxide, we can produce multilayers that are unstable at room temperature, or those which require substantial thermal energy to ignite. We first explored this terminal phase hypothesis by comparing CuO-metal laminates with the reactive metals: Mg, Zr, and Al. Zr-CuO laminates were the least stable, owing to the fast oxygen transport through the  $ZrO_2$  terminal oxide, while CuO-Al laminates were the most stable, owing to the excellent diffusion barrier properties associated with  $Al_2O_3$ . A second demonstration is made for laminates of CuO and  $Al_{1-x}Ti_x$  where x is varied systematically between the pure end members. We identify a composition of ~ 35% Ti, above which the laminates react at room temperature and below which thermal energy in the range of 300 °C and above is required to initiate oxygen exchange. Calorimetry analysis is used to measure effective activation energies for each material combination in order to better understand the material property / energy release relationships.

In addition, we report the use of *in situ* XPS analysis to explore, with nm resolution, the interface chemistry of as deposited nanolaminates precursors to identify the limitations of interface abruptness in the as-prepared state. We find that in all cases CuO/reactive metal interfaces have an unavoidable minimum oxide thickness but this thickness depends on a number of factors including thermodynamic driving force for oxygen exchange, wetting, and oxygen diffusivity.

4:20pm **TF-ThA8 A Novel Method of Managing Joint Stress, in a Metallic Bond Made Using Reactive Multilayer Foils, at a User Selected Temperature**, *G.J. Matteau*, Indium Corporation

Previously we have presented a joining method whereby materials of widely differing CTE were successfully bonded with no deformation at room temperature using reactive multilayer foils as the local heat source. This is unique in as far as creating a metallic bond with any other technique results in significant deformation upon cooling back to room temperature. For many large area applications this deformation results in having to use mechanical methods to flatten these surfaces to their original shape, which

is highly undesirable as such techniques are unpredictable and do cause yield loss when used. When reactive multilayer foils are used in the bonding process, no such deformation of materials occurs resulting in assemblies that can be effectively used as soon as they are bonded.

Critical to the use of parts at higher temperature is the need to minimize/manage joint stress in assemblies at a particular application temperature. This paper will demonstrate how this can be done effectively, with the use of a reactive multilayer foil in creating the bond.

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